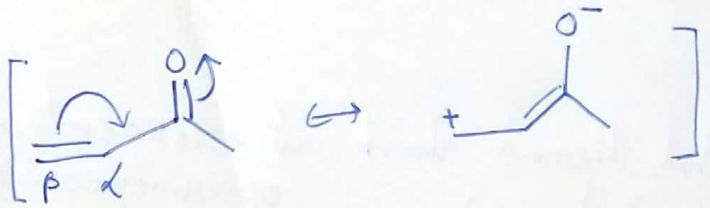
IR - Spectroscopy
(Vibrational spectroscopy)

Conjugation Effect:

on introduction of C=C double bond or aromatic ring extending conjugation, ~~decrease~~ $\nu_{C=O}$ (str.) and $\nu_{C=C}$ (str.) will decrease.

This is due to resonance.



Due to resonance bond order of C=O & C=C will decrease and hence force constant will also decrease which will result in to the absorption at lower frequency.

conjugation lowers $\bar{\nu}_{C=C}$ (str.) by approx. 10 cm^{-1} – 50 cm^{-1}

$>C=C<$

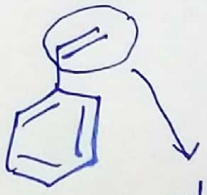
$\bar{\nu}_{C=C(str.)} \sim 1650\ cm^{-1}$

$>C=C-C=C<$

$\bar{\nu}_{C=C(str.)} \sim 1600\ cm^{-1}$

$>C=C<$

$\bar{\nu}_{C=C(str.)} \sim 1650\ cm^{-1}$



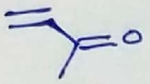
$\bar{\nu}_{C=C(str.)} \sim 1630\ cm^{-1}$

α, β conjugation (double bond) lowers $\bar{\nu}_{C=O}$ (str.) by 25 – 45 cm^{-1}

Further γ, δ conjugation (double bond) lowers $\bar{\nu}_{C=O}$ (str.) by ~15 cm^{-1} only

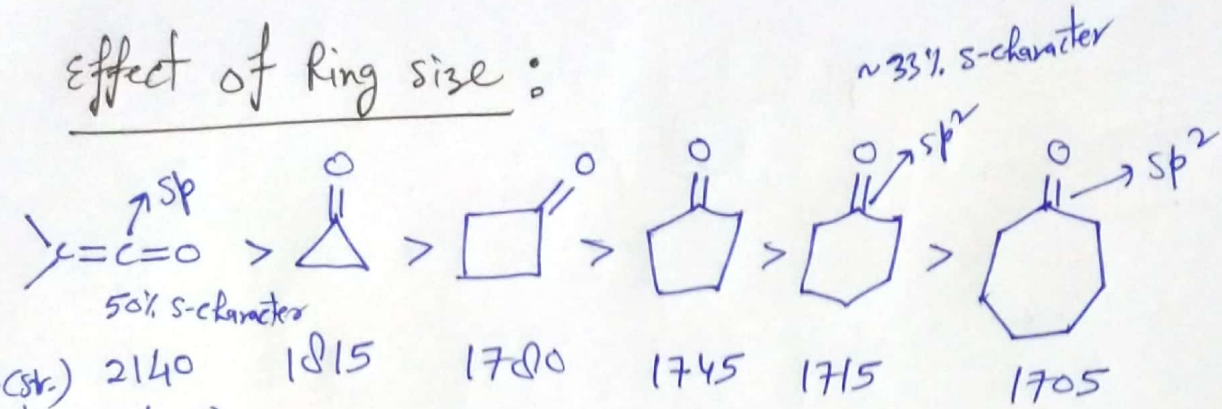
$>C=O$

$\bar{\nu}_{C=O(str.)} \sim 1715\ cm^{-1}$



$\bar{\nu}_{C=O(str.)} \sim 1690\ cm^{-1}$

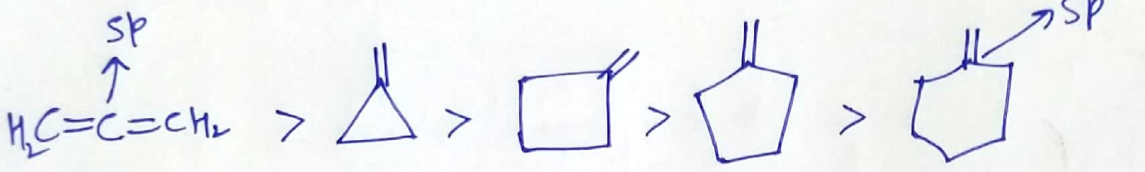
Effect of Ring size :



$\nu_{C=O}$ (str.) (cm^{-1})	2140 (Ketene)	1815	1780	1745	1715	1705

←

s-character in carbonyl carbon is increasing as we decrease the ring size (Ring strain is increasing)
So the force contt is increasing (due to small bond length) and hence the $\bar{\nu}_{C=O}$



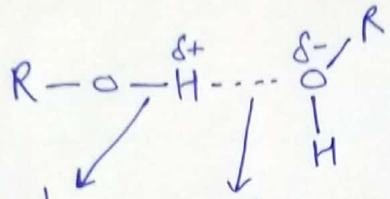
$\nu_{C=C}$ (str.) (cm^{-1})	1940	1780	1678	1657	1651

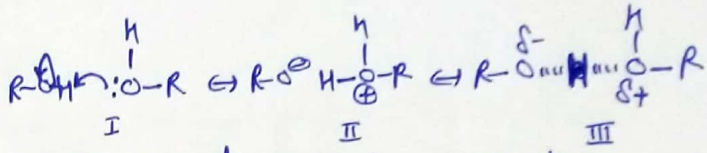
←

on moving towards left s-character is increasing as the ring size is decreasing.
So the force constant as well as frequency of absorption i.e. $\bar{\nu}_{C=C}$ is increasing

Effect of Hydrogen bonding :

Hydrogen bonding decreases stretching frequencies ($\bar{\nu}$) of both the groups involved in it due to decrease in force constant of those bonds.





Lengthening of O-H bond in H-bonding

Alcohols and Phenols (intermolecular H-bonding)

→ Due to H-bonding, we get broad and highly intense band for O-H str. at ~ 3300 – 3400 cm^{-1} (Neat Liquid)

→ Without H-bonding (in very dilute solution in nonpolar solvent), O-H str. absorption appears at ~3600cm^{-1}

→ In dilute solution both (i.e. H-bonded and without H-bonded) O-H str. absorption appear at ~3300–3400 cm^{-1} and ~3600cm^{-1} respectively.

Alcohols

Neat Liquid

$\bar{\nu}_{O-H\,(str)}$ ~3300–3400cm^{-1} H-bonded (broad) & intense

Dilute Solution (in non-polar solvent) e.g. CCl_4, CS_2, $CHCl_3$

$\bar{\nu}_{O-H\,(str)}$ ~3300–3400cm^{-1} H-bonded (broad) & intense

$\bar{\nu}_{O-H\,(str)}$ ~3600cm^{-1} free (sharp) & Less intense

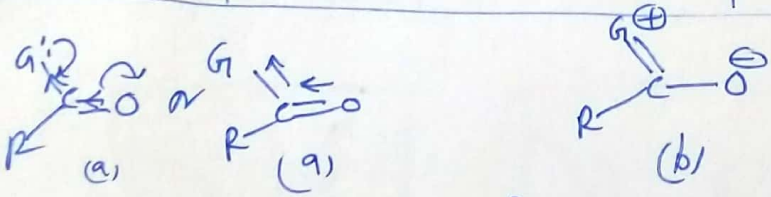
Very dilute solution (in nonpolar solvent)

$\bar{\nu}_{O-H\,(str)}$ ~3600cm^{-1} free (sharp) & Less intense

P.T.O.

Stretching frequencies in H-bonding

X–H···Y Strength	Intermolecular frequency Reduction (cm^{-1}) ν_{OH}	$\nu_{C=O}$	Compound class	Intramolecular frequency red^{n} (cm^{-1}) ν_{OH}	$\nu_{C=O}$	
weak	300	15	Alcohols, Phenols & intermolecular Hydroxyl to carbonyl bonding	<100	10	1,2-Diols, α & most β-hydroxy ketones, o-chloro & o-alkoxy phenols
Medium				3503 100–300	50	1,3-Diols, some β-hydroxy ketones, β-hydroxy amino compounds, β-hydroxy Nitro compounds
Strong	7500	50	R–COOH dimers	7300	100	o-Hydroxy aryl ketones, o-hydroxy aryl acids, o-hydroxy aryl esters, β-diKetones & Tropolones



$\bar{\nu}_{C=O}$ in $R-\overset{O}{\overset{\|}{C}}-G$.

G Effect predominantly Inductive

G	$\bar{\nu}_{C=O}$ (cm^{-1})
Cl	1815–1785
F	~1869
Br	1812
OH (monomer)	1760
OR	1750–1735

G Effect Predominantly Resonance

G.	$\bar{\nu}_{C=O}$ (cm^{-1})
$-NH_2$	1695–1650
$-SR$	1720–1690

Alcohols

O–H (free) 3650–3600 cm^{-1} sharp

O–H (H-bonded) 3400–3300 cm^{-1} (ν 3350 cm^{-1}) (s), (br)

C–O–H Bending 1440–1220 cm^{-1} (w) often overlap with C–H bending.

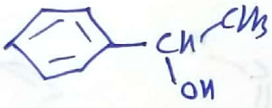
C–O str. vib. 1260–1000 cm^{-1}

Compound	C–O str (cm^{-1})	O–H str (cm^{-1})
Phenols	1220	3610
3° Alcohols (saturated)	1150	3620
2° Alcohols (H)	1100	3630
1° " (")	1050	3640

(2°)

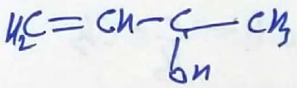
1100 → 1070 cm^{-1}

(2°)



(2°)

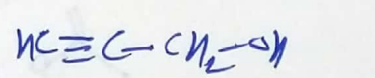
1100 → 1070 cm^{-1}



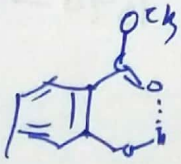
1100 → 1060 cm^{-1}

(1°)

1050 — 1017 cm^{-1}



1050 — 1030 cm^{-1}



methyl salicylate

O–H centered at 3200 cm^{-1} (wide 3400–2400)

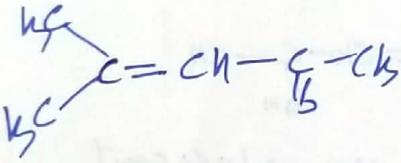
Ethers :

C–O (str) 1300 – 1000 cm⁻¹ (absence of C=O & O–H (ester) (alcohol)

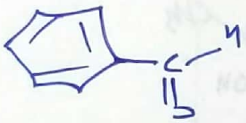
Phenyl alkyl ethers give two strong bands at ~1250 & 1040 cm⁻¹ while aliphatic ethers give one strong band at ~1120 cm⁻¹

$CH_2=CH-OR$ ⟶ 1220 cm⁻¹

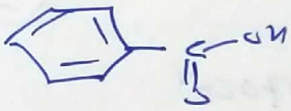
R–O–R 1120 cm⁻¹



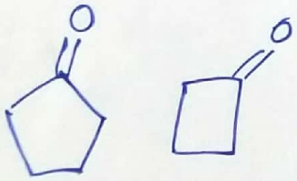
1715 → 1690 cm⁻¹



1725 → 1700

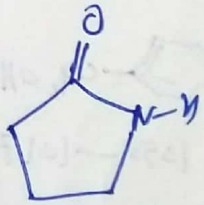


1710 – 1680

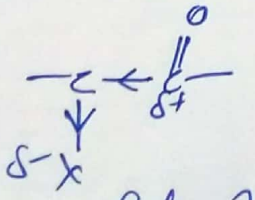


1715 → 1745 1715 → 1780

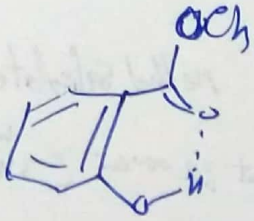
1735 → 1770 cm⁻¹



cyclic 1690 – 1705 cm⁻¹

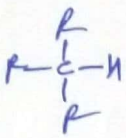


higher D

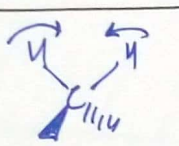


1680 cm⁻¹

(A) ⇒ C–H str. vibrations for sp^3 hybridized C–H bonds.

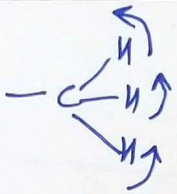
Gp	$\bar{\nu}_{C-H}$ Str. vib. (cm^{-1}) Asymmetric	Symmetric
Methyl R–CH_3	2962 (s)	2872 (s)
methylene R–CH_2–R	2926 (s)	2853 (s)
methine 	2890 cm^{-1} (very weak)	

(B) C–H Bending vibrations for methyl & Methylene Gps :



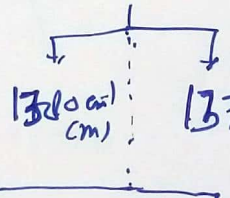
Scissoring
~ 1465 cm^{-1} (m)

Asym. bending
~ 1450 cm^{-1} (m)

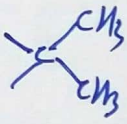


Sym. bending
~ 1375 cm^{-1} (m)

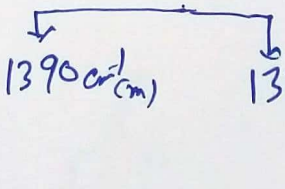
–CH_3 lone methyl gp



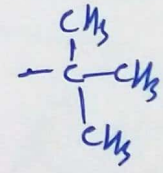
1380 cm^{-1} (m) 1370 cm^{-1} (m)



gem-dimethyl split into two bands



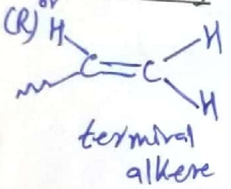
1390 cm^{-1} (m) 1370 cm^{-1} (m)



t-butyl, two bands, wider split

C–H Bending Vibrations for Alkenes:

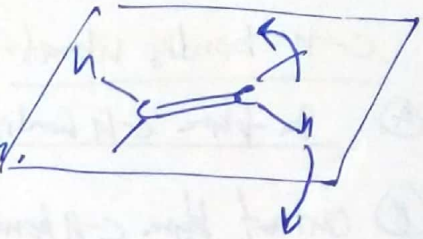
In plane bending:



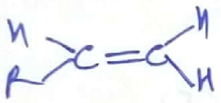
scissoring in plane ~1415 cm⁻¹ (m–w) for monosubstituted & 1,1-disubstituted
(in plane bending)

out of plane bending (1000 – 650 cm⁻¹)

→ These bands are frequently the strongest peaks in the spectrum.



① **Monosubstituted double bonds (vinyl)**



~990 cm⁻¹ (~1000 cm⁻¹) (s) & ~910 cm⁻¹ (~900 cm⁻¹) (s) (two strong bands)

→ an overtone of ~910 cm⁻¹ band usually appears at 1820 cm⁻¹ which and helps in confirmation of the vinyl gp.

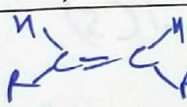
→ The 910 cm⁻¹ band is shifted to a lower frequency as low as 810 cm⁻¹, when a gp attached to the double bond can release e⁻ by resonance effect (eg. –Cl, F, OR etc).

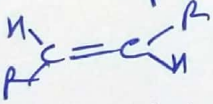
→ The 910 cm⁻¹ band is shifted to a higher frequency, as high as 960 cm⁻¹, when the group withdraws e⁻ by a resonance effect (C=O, C≡N).

→ The use of the out of plane vibration to confirm the mono substituted str. is considered very reliable.

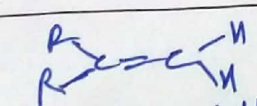
→ The Absence of these bands means absence of vinyl gp.

② **cis & trans-1,2-Disubstituted double bonds:**

cis-1,2  ~700 cm⁻¹ (s)

trans 1,2  ~970 cm⁻¹ (~1000 cm⁻¹) (s)

③ **1,1-disubstituted double bond:**

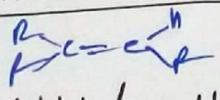


(gem dialkyl substituted double bond)

~890 cm⁻¹ (~900 cm⁻¹) (s)

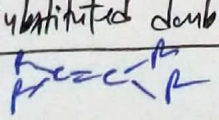
e⁻ releasing gp decreases the freq.
e⁻ withdrawing gp increased the ν

④ **Trisubstituted double bonds:**



~815 cm⁻¹ (~800 cm⁻¹) (m)

⑤ **Tetra substituted double bonds:** → don't give any absorption (H atom is absent)



→ In addition, the C=C str. vibration is very weak or absent at about 1670 cm⁻¹.

Aromatic Rings

=C–H str. (3050–3010 cm⁻¹) ~ 3100 cm⁻¹

=C–H oop bending 900–690 cm⁻¹

C=C Ring stretch absorption often occur in pairs at 1600 cm⁻¹ & 1475 cm⁻¹ b/w (1600 & 1450 cm⁻¹)

overtone/combination bands b/w 2000 and 1667 cm⁻¹ (w)

C–H bending vibrations:

(A) In-plane C–H bending: b/w 1300 & 1000 cm⁻¹ (rarely useful)

(B) out of plane C–H bending vib.: b/w 900 & 690 cm⁻¹ (for mono useful)

Mono substituted: ~ 690 cm⁻¹ (s) (~ 720 cm⁻¹) (s) & ~ 750 cm⁻¹ (s)

o-di substituted: ~ 750 cm⁻¹ (s)

m-di Substituted: ~ 690 cm⁻¹ (~ 700 cm⁻¹) (s), ~ 780 cm⁻¹ (~ 800 cm⁻¹) (s) & ~ 880 cm⁻¹ (900 cm⁻¹) (m)

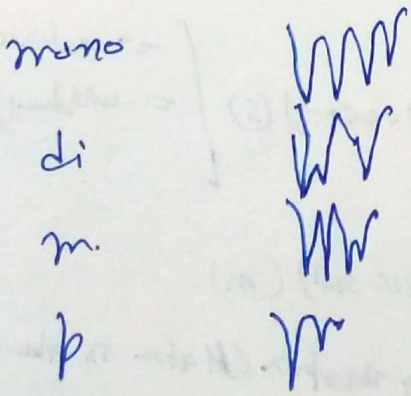
p-disubstituted: ~ 800–850 cm⁻¹ (~ 850 cm⁻¹) (s)

1,2,4 → two ~ 800 cm⁻¹ (s) ~ 900 cm⁻¹ (m)

1,2,3 → two ~ 720 cm⁻¹ (m) & ~ 750 cm⁻¹ (s)

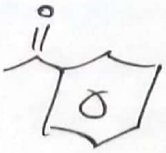
1,3,5 → two ~ 700 cm⁻¹ (m) & ~ 900 cm⁻¹ (s)

for 2000 1667 cm⁻¹ (overtones & combinations)



Conjugation lowers frequency of C=C & C=O

$\bar{\nu}_{C=O}$ 1780 cm^{-1} 1700 cm^{-1}

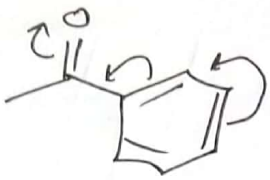


1700 cm^{-1}

$\bar{\nu}_{C=C}$ 1650 cm^{-1}

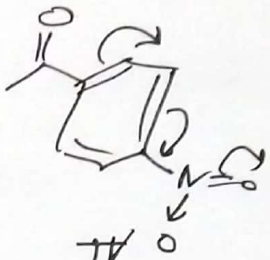
1610 cm^{-1}

I

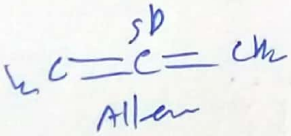


II (+M)

III

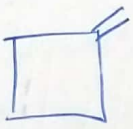


IV



1940

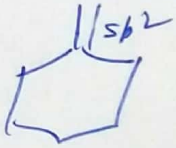
1780



1678

1657

1655



1651

	Asym	Sym
$-CH_3$	2962	2872
$-CH_2-$	2926	2853
$-\overset{|}{C}-H$	~2890	very weak

Hydrocarbons: Alkanes, Alkenes, and Alkynes

(A) Alkanes: (Even few peaks)

sp^3 C–H.

C–H str. ~ 3000 cm^{-1} i.e. < 3000 cm^{-1} (3000–2840 cm^{-1})
(Except ring strained compounds

CH_2 bending ~ 1465 cm^{-1}

CH_3 " ~ 1375 cm^{-1}

CH_2 bending (rocking) four or more CH_2 group in an open chain, ~ 720 cm^{-1} (long chain band)

C–C Not useful (many weak peaks)

(B) Alkenes:

=C–H str. for sp^2 C–H. > 3000 cm^{-1} (3100–3010 cm^{-1})

=C–H out-of-plane (oop) bending 1000–650 cm^{-1}

C=C str 1660–1600 cm^{-1} (Conjugation moves C=C str. to lower frequencies & increase the intensity)

Symmetrically substituted bonds (e.g. 2,3-dimethyl-2-butene) do not absorb in the Infrared (no dipole change)

Symmetrically disubstituted (trans) double bonds are often Remarkably weak in absorption; cis are stronger

---

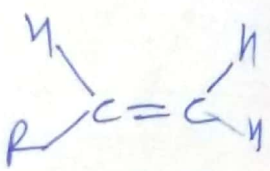
(C) Alkynes

≡C–H str. sp C–H ~ 3300 cm^{-1}

C≡C str. ~ 2150 cm^{-1} (Conjugation moves str. towards lower frequency. Disubstituted or symmetrically substituted give either no absorption or weak absorption.

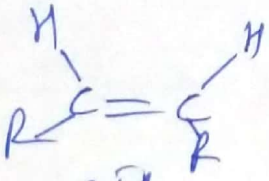
≡C–H bendy ~~700 cm⁻¹~~ ~630 cm^{-1}

Alkene



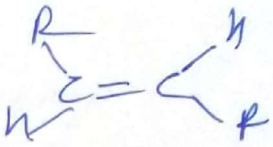
vinyl

1648–1638 cm^{-1} (~1643)
995–985 cm^{-1} (S) (~990)
915–905 cm^{-1} (S) (~910) → overtone (1820)



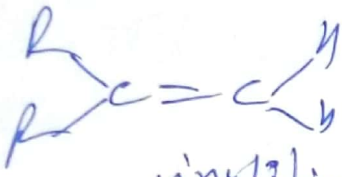
cis

1662–1626 cm^{-1} (V) (~1640)
730–665 cm^{-1} (S)
(~720)



Trans (~1673)

1678–1668 cm^{-1} (V)
980–960 cm^{-1} (S)
(~970)

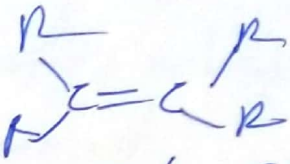


vinylidine

(~1653)
1658–1648 cm^{-1} (m)
895–885 cm^{-1} (S)
(890 cm^{-1})

Tri-substituted (~1670)

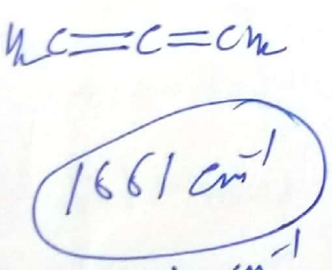
1675–1665 cm^{-1} (W)
840–790 cm^{-1} (m)
(~815)



(~1670) Tetra-sub.

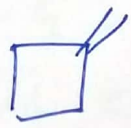
1675–1665 cm^{-1} (very weak or absent)

C–H bend absent

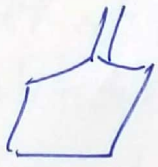


1661 cm^{-1}
1940 cm^{-1}

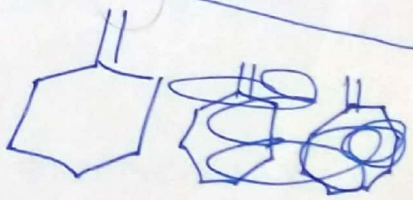
1780



1678



1657



1651

Effect of H-bonding O–H & N–H.

O–H str (free) ~ 3650 cm⁻¹ (Neat liquid)

O–H Bonded band str) (H bonded) ~ 3350 cm⁻¹

3500 cm⁻¹ (dilute soln with non polar solvent)

---

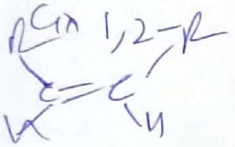
oop bending

Mono (Vinyl gp) 990 cm⁻¹ (S) & 910 cm⁻¹ (S)

upto 810 cm⁻¹ (R = Cl, F, OR etc)

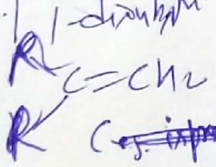
upto 960 cm⁻¹ (C=O, C≡N gp)

(overtone of 910 cm⁻¹ at 1820 cm⁻¹ confirm vinyl group)

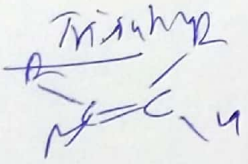


~ 700 cm⁻¹ (S)

Trans ~ 970 cm⁻¹ (S)



1,1-disubstituted ~ 890 cm⁻¹ (S)



Trisubstituted ~ 815 cm⁻¹ (m)

Tetra No band (No C–H bond)

C–H bending in Alkenes.

In-plane vibration for terminal alkene (scissoring) ~ 1415 cm⁻¹ (m → w)

(for both mono & 1,1-disubstituted alkene)

Out of plane bending 1000 – 650 cm⁻¹ (strongest bands)

Very weak band at 1675 cm⁻¹ due to C=C str.

C–H oop bendings

Mono, 690 cm⁻¹ (S) 750 cm⁻¹ (S) ← if absent (NO Mono substitution)

o-di 750 cm⁻¹ (S)

m-di 690 cm⁻¹ (S) 780 cm⁻¹ (m-s) 880 cm⁻¹ (m)

p- 800 – 850 cm⁻¹ (S)

Aromatic C–H in plane (1000 – 1300 cm⁻¹ (W))

Amides

$\nu_{C=O}$ str. ~ 1680–1630 cm^{-1}

N–H str. in pri amides (–NH_2) give two band ~ 3350 cm^{-1} + 3150 cm^{-1}

sec. amides give one band ~ 3300 cm^{-1}

N–H bending ~ 1650–1550 cm^{-1} for pri + sec- amides

C–N str band for pri amides ~ 1400 cm^{-1}

Amines

N–H str ~ 3500–3300 cm^{-1} (pri- two bands)

sec + tre one band (w) ali/phatic

(s) for aromatic

N–H bends (broad) ~ 1650–1550 cm^{-1} (pri)

~ 1500 cm^{-1} (sec-)

C–N str. ~ 1350–1000 cm^{-1})

S–H stretching vibrations (Mercaptans and thiophenols)

ν_{S-H} (cm^{-1}) = 2600 – 2550 cm^{-1} (w)

→ It may be undetected in the spectra of dilute soln or thin films.

→ Since very few other grps show absorption in this region, so it is useful in detecting S–H grp.

→ The band due to S–H str. may be obscured by strong ~~C~~ –OH absorption in the same region. (O–H - Hydrogen bonded dimer)

→ H-bonding is much weaker for S–H grp than for –OH & N–H grp

→ S–H grp of thiol acids absorbs in the same region as mercaptans & thiophenols

⇒ C–S and C=S stretching vib. (sulphides)

C–S 700 – 600 cm^{-1} (w)

⇒ disulphide → S–S str. 500 – 400 cm^{-1} (very w)

⇒ Thiocarbonyl grp: –C=S

C=S is less polar than C=O

C=S 1250 – 1020 cm^{-1}

Thiophenone & its derivatives — 1224 – 1207.

Note (also C–O & C–N in same region)

Amides

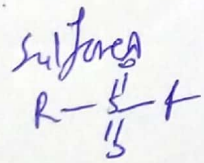
~1660

~1705 cm^{-1}

~1745 cm^{-1}

R–SH S–H str. (w) ~2550 cm^{-1}

Sulfoxide S=O str. ~1050 cm^{-1} (s)



Sulfone S=O str. 1300 cm^{-1} (s) Asym. 1150 cm^{-1} (s) Sym.

C=O 1850 – 1630 cm^{-1} (sharp, strong)

C=C 1680 – 1620 cm^{-1} weak.

O–H — 3650 – 3200 (broad peak)

N–H — 3500 – 3300 sharp medium

Base values

O–H — 3400 cm^{-1}

N–H — 3400 cm^{-1}

C–H — 3000 cm^{-1}

C≡N — 2250 cm^{-1}

C≡C — 2150 cm^{-1}

C=O — 1715

C=C — 1650

C–O — 1150

Aldehyde

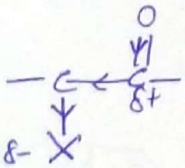
C–H 2900 – 2800 cm^{-1}

2800 – 2700 cm^{-1}

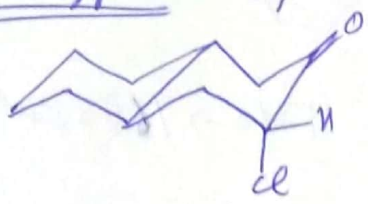
↓

overtone of C–H bending at 1390

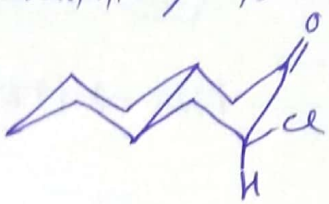
∠- Substitution effect



Field effect → (space interaction) / (electrostatic / steric)

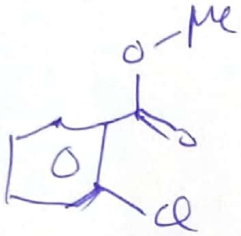


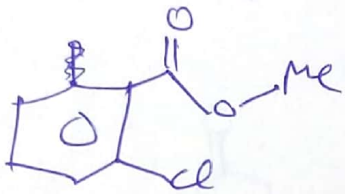
axial chlorine
~1725 cm⁻¹



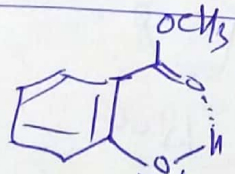
equatorial chlorine
~1750 cm⁻¹

Repulsion b/w non bonding e⁻ of oxygen and chlorine due to close together, which results in a change in the hybridization state of oxygen and therefore shift in C=O str. frequency

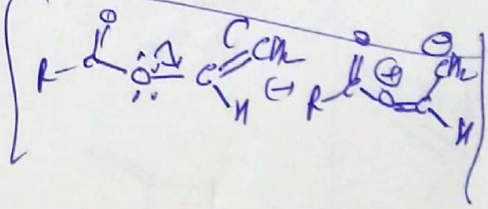


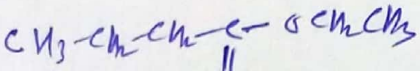


π-bonding

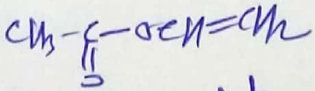


methyl salicylate
1680 cm⁻¹

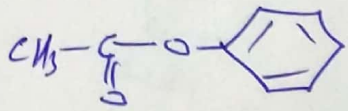




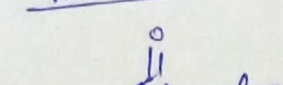
Ethyl butyrate
1738 cm⁻¹
Normal



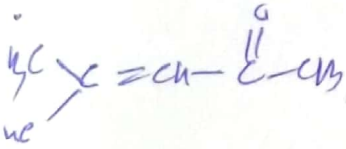
vinyl acetate
1762 cm⁻¹



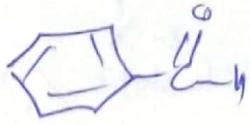
Phenyl acetate
1765 cm⁻¹



∠β or aryl conjugation
1725 cm⁻¹



1715 → 1690 cm⁻¹



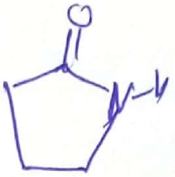
1725 → 1700 cm⁻¹

1710 → 1680 cm⁻¹

* Conjugation doesn't reduce the C=O frequency in amides.

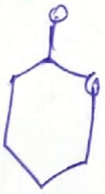
lactone

1735 → 1770 cm⁻¹



Lactam

1690 – 1705 cm⁻¹.

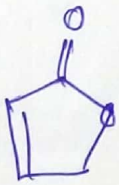


1735

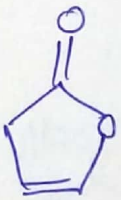
1725

1760

1770

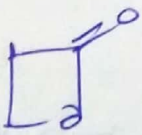


1750

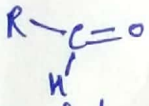


1800

Ring size

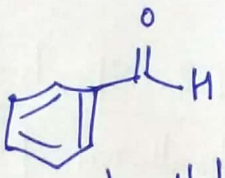


1820



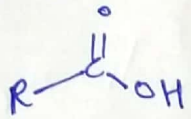
aldehyde

$\bar{\nu}_{C=O\,(Str.)} \sim 1725\,cm^{-1}$



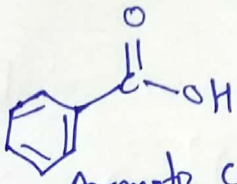
Aromatic aldehyde

$\bar{\nu}_{C=O\,(Str.)} \sim 1700\,cm^{-1}$



carboxylic acid

$\bar{\nu}_{C=O\,(Str.)} \sim 1710\,cm^{-1}$ (dimer form)



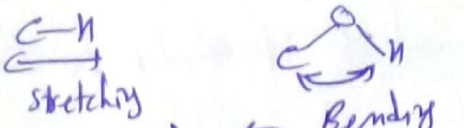
Aromatic carboxylic acid

$\bar{\nu}_{C=O\,(Str.)} \sim 1680\,cm^{-1}$

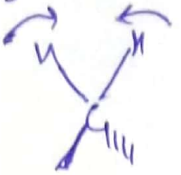
→ Asymmetric conjugated dienes absorb at $\sim 1650\,cm^{-1}$ and $\sim 1600\,cm^{-1}$ (for eg. 1,3-pentadiene) $H_2C=CH-CH=CH-CH_3$

→ Symmetric conjugated dienes absorb at only $\sim 1600\,cm^{-1}$ (for eg. 1,3-butadiene) $H_2C=CH-CH=CH_2$

Modes of stretching and Bending :



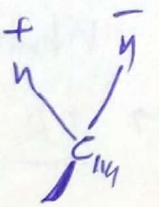
Symmetric stretching
(~2853 cm⁻¹)



Scissoring
(~1450 cm⁻¹)

Rocking
(~720 cm⁻¹)

Wagging
(~1250 cm⁻¹)



Twisting
(~1250 cm⁻¹)

In-plane

out-of-plane

Asymmetric stretching
(~2926 cm⁻¹)

Stretching vibrations

Bending vibrations (deformation

$-CH_2-$

Methyl

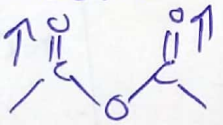
2900
Symmetric stretching

~2872 cm⁻¹

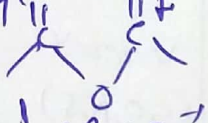
3000
Asymmetric stretching

~2962 cm⁻¹

Anhydride



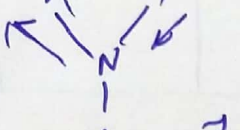
~1760 cm⁻¹



~1810 cm⁻¹

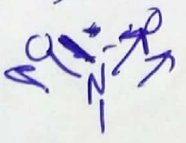
Amine

~3300 cm⁻¹



~3400 cm⁻¹

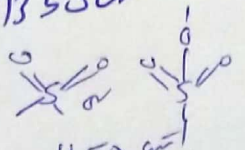
Nitro



~1350 cm⁻¹

~1550 cm⁻¹

Sulphoxide + Sulphonic acid

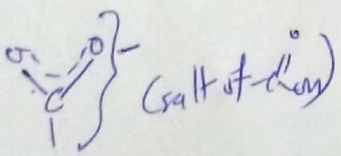


1150 cm⁻¹

1400

1350 cm⁻¹

1600 cm⁻¹

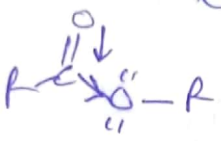


(salt of them)

1850–1650 cm^{-1}

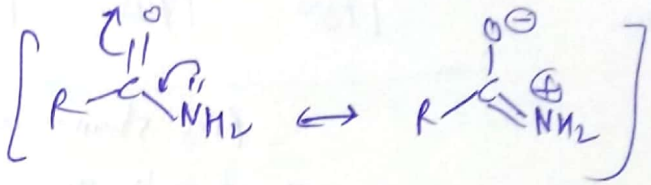
cm^{-1} ⟵ ⟶

1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1) (Asym)	Acid chloride	Anhydride (band 2) (Sym)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide



Ester

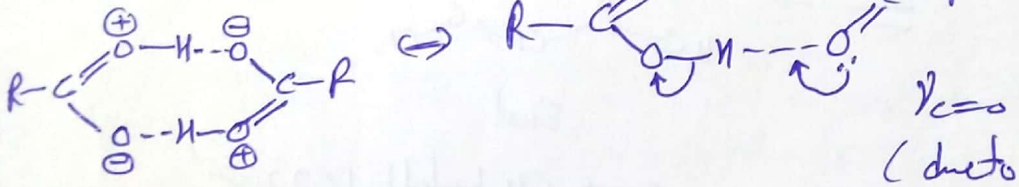
-I Effect raises $\nu_{C=O}$.



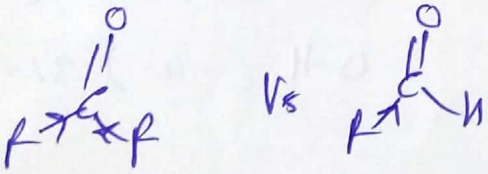
Resonance effect lowers C=O frequency

→ Carboxylic acid exists in monomeric form only in very dilute soln. & absorb at ~1760 cm^{-1} due to -I effect

→ In conc. soln i.e. neat (liquid or in the solid (KBr pellet or Nujol)) → dimerized via H-bonding



Ionic - resonance structure (Strong H-bonding)

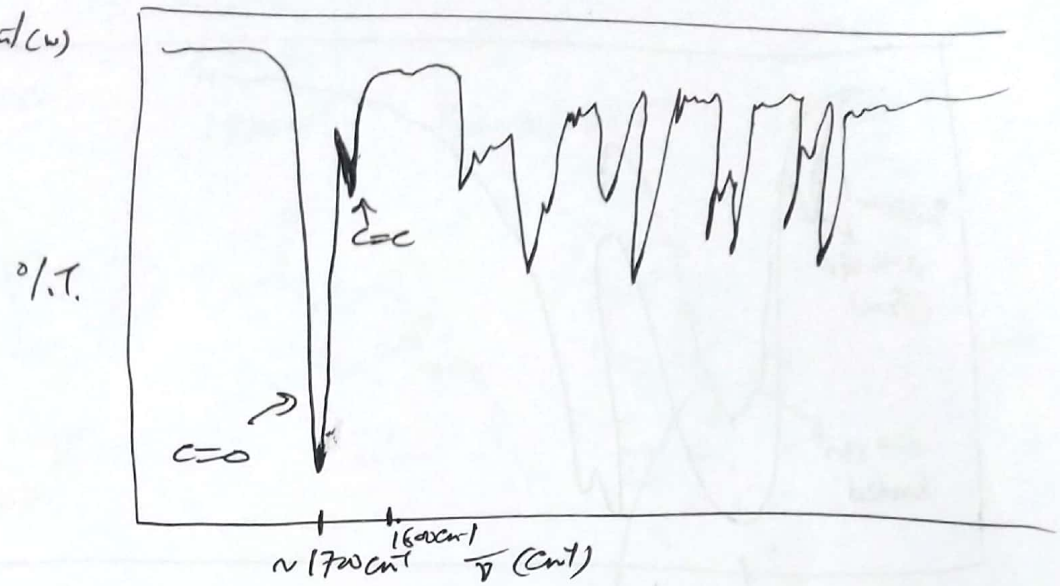


$\nu_{C=O}$ ~ 1710 cm^{-1} (due to lowering of K) due to H-bonding

Shape and intensity :

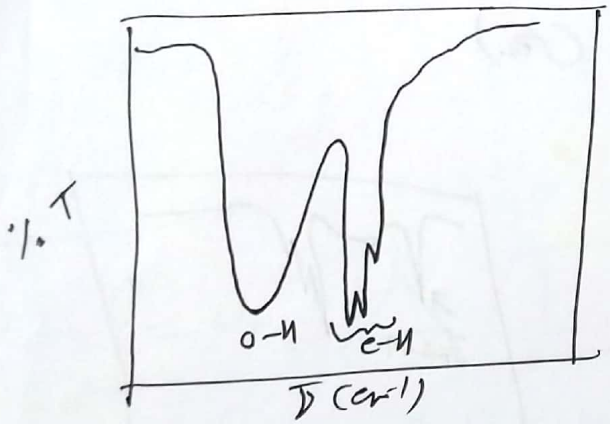
(1) C=O 1850-1630 cm^{-1} (S)

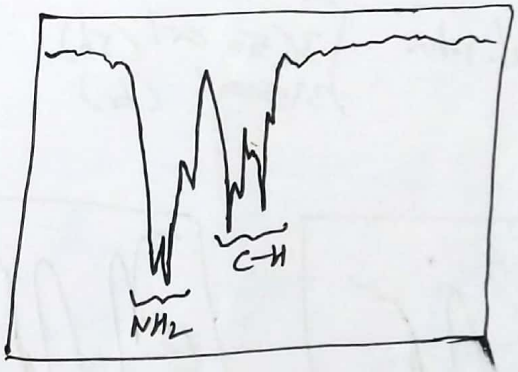
C=C 1680-1620 cm^{-1} (w)



(2) O-H 3650-3200 cm^{-1} (br, s)

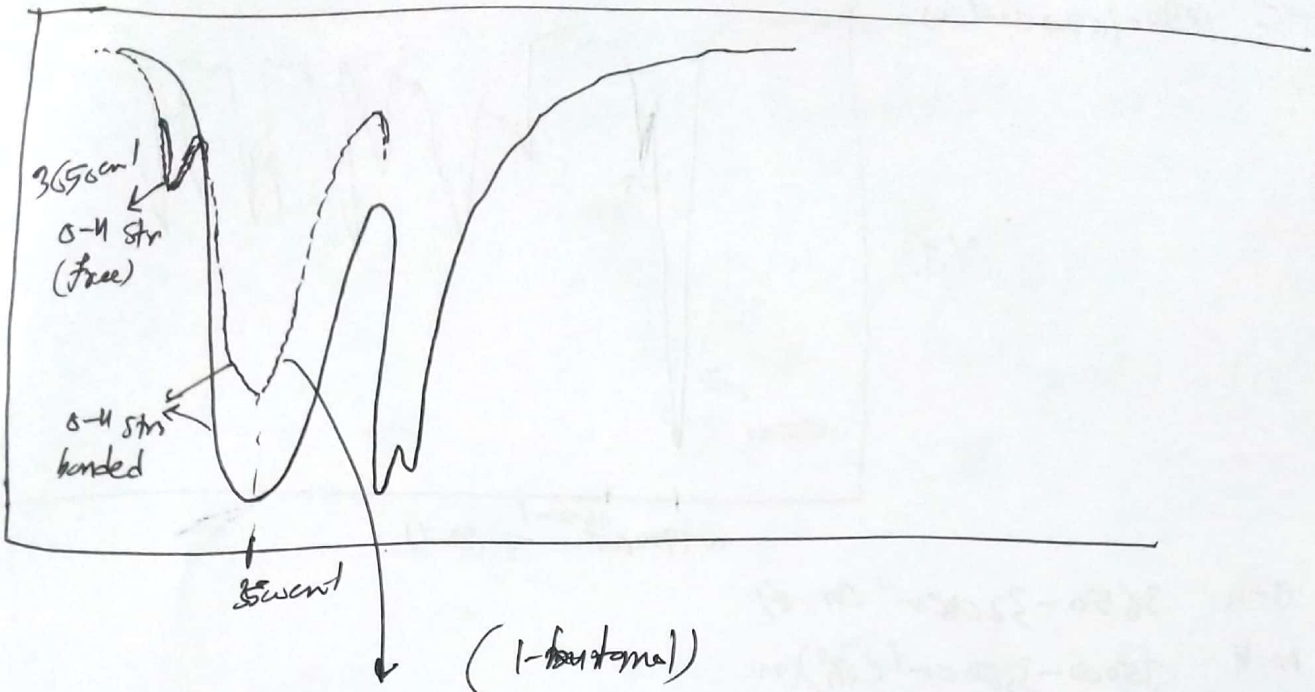
N-H 3500-3300 cm^{-1} (sh) (m)





Bond values for absorptions of bonds :

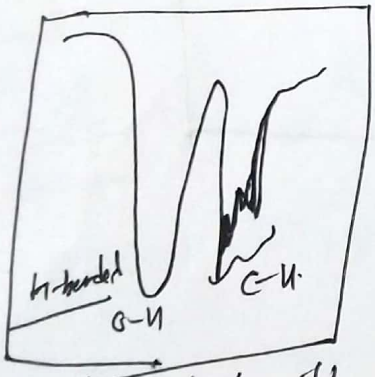
O-H	~3400 cm^{-1}
N-H	~3400 cm^{-1}
C-H	~3050 cm^{-1}
C≡N	~2250 cm^{-1}
C≡C	~2150 cm^{-1}
C=O	~1715 cm^{-1}
C=C	~1650 cm^{-1}
C-O	~1100 cm^{-1}



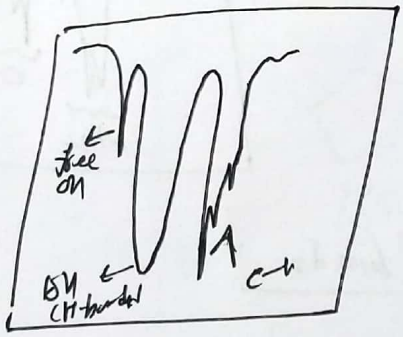
(Intermolecular)

dil. soln. in CCl₄ (~ 1%)

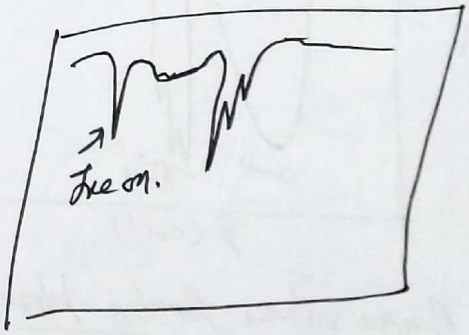
dil. soln. { 3650 cm⁻¹ (sh) O–H str (free)
3350 cm⁻¹ (br)



(neat Liquid)
H-bonded



dil. soln.
free & H-bonded



very dil. soln.
free O–H

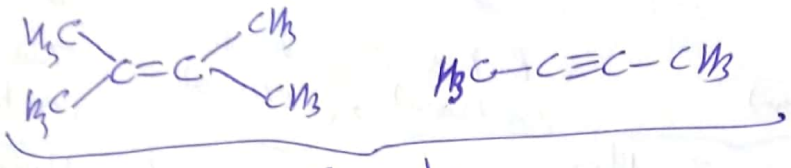
O–H (free) 3650–3600 cm⁻¹ (sh)

O–H (H-bonded) ~ 3400–3300 cm⁻¹ (br.)

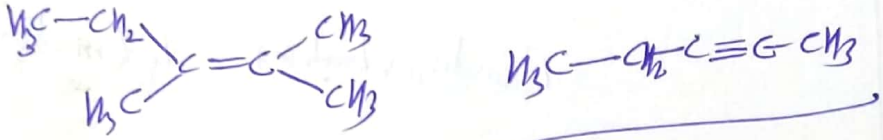
IR Spectroscopy

→ Bond should possess a dipole moment & it should be changed during vibrations.

→ IR inactive → H_2 Cl_2

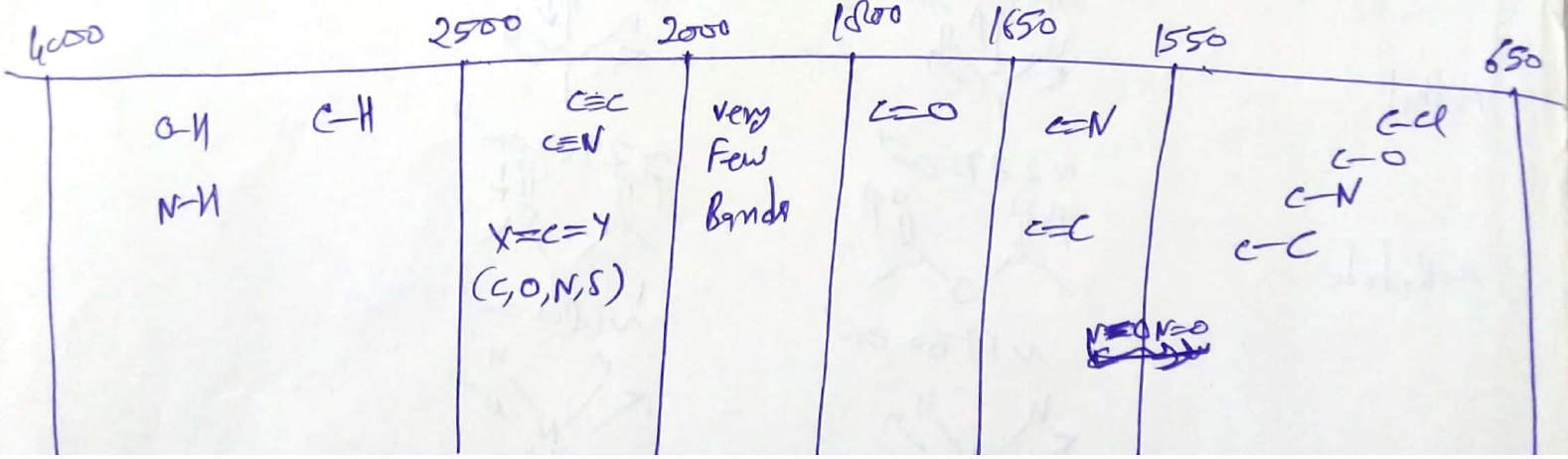


Symmetric



Pseudosymmetric

Frequency (wave number $\bar{\nu}$ (cm^{-1}))



How to approach the analysis of an IR spectrum (or what you can tell at a glance)

(C=O, O–H, N–H, C–O, C=C, C≡C, C≡N & NO_2 peaks are most conspicuous and give immediate str. information if they are present)

→ Do not try to make a detailed analysis of C–H absorptions near 3000 cm^{-1}; almost all compounds have these absorptions.

① If a carbonyl gp present? → >C=O gp gives rise to a strong absorption in the region 1820–1660 cm^{-1}.
→ The peak is often strongest in the spectrum and of medium width.

② If >C=O is present, check the following types (If it is absent, goto step 3)

→ Acids (–C(=O)–O–H): Is O–H also present?
→ Broad absorption near 3400–2400 cm^{-1} (usually overlaps C–H)

→ Amides (–C(=O)–NH_2): Is N–H also present?
→ Medium absorption near 3400 cm^{-1}; sometimes a double peak with equivalent halves.

→ Esters (–C(=O)–O–R): Is C–O present?
→ Strong-intensity absorption near 1300–1000 cm^{-1}

→ Anhydrides (–C(=O)–O–C(=O)–): Two C=O absorptions near 1810 & 1760 cm^{-1}

→ Aldehydes (–C(=O)–H): Is aldehyde C–H present?
→ Two weak absorptions near 2850 & 2750 cm^{-1} on right side of the aliphatic C–H absorptions.

→ Ketones (–C(=O)–): ~~The~~ If above five gps are absent.

③ If C=O is absent:

→ Alcohols & Phenols (R-OH & Ar-OH): check for O-H
→ Broad absorption near 3400–3300 cm⁻¹
→ Confirm this by finding C-O near 1300–1000 cm⁻¹

→ Amines (–NH₂): check for N-H
→ Medium absorption(s) near 3400 cm⁻¹

→ Ethers (R–O–R): check for C-O near 1300–1000 cm⁻¹
(and absence of O-H near 3400 cm⁻¹)

④ Double bonds and/or aromatic rings:

→ C=C is a weak absorption near 1650 cm⁻¹
→ Medium to strong absorptions in the region 1600–1450 cm⁻¹ these often imply an aromatic ring.
→ Confirm the double bond or aromatic ring by consulting the C-H region;
Aromatic and vinyl C-H occur to the left of 3000 cm⁻¹
(aliphatic C-H occurs to the right of this value)

⑤ Triple bonds:

→ C≡N is a medium, sharp absorption near 2250 cm⁻¹
→ C≡C is a weak, sharp absorption near 2150 cm⁻¹
→ Check also for acetylenic C-H near 3300 cm⁻¹

⑥ Nitro groups (–N(=O)=O): → Two strong absorptions at 1600–1530 cm⁻¹ & 1390–1300 cm⁻¹

⑦ Hydrocarbons:

→ If none of the above found.
→ Major absorptions are in C-H region near 3000 cm⁻¹
→ Very simple spectrum; the only other absorptions appear near 1460 & 1375 cm⁻¹ (–CH₂– & –CH₃ bending)

Fingerprint region:

App? of IR Spectroscopy – Identity by fingerprinting

→ Fingerprint region: (1400 – 900 cm^{-1})

→ IR spectra contain many absorptions associated with the complex interacting vibrating systems in the molecule, and this pattern of vibrations, since it is uniquely characteristic of each molecule, give rise to a uniquely characteristic set of absorption bands in the spectrum.

This band pattern serves as a fingerprint of the molecule; the region that contains a particularly large number of unassigned vibrations (and is most valuable in this respect) is roughly from 900 cm^{-1} to 1400 cm^{-1}, and this general area is often called the fingerprint region.

→ To identify an unknown compound, one need only compare its IR spectrum with a set of standard spectra recorded under identical conditions.

→ Substances that give the same IR spectra are identical.

→ This proof of identity is far more characteristic than the comparison of any other physical property.

→ Having stated the principle, a few cautionary words should be added. For two spectra to be really identical would involve recording the spectra on the same machine under identical conditions of sampling, scan speed, slit width, etc. Where this condition doesn't apply, some discretion must be allowed, but, in general, the greater the number of peaks in the fingerprint region the more reliable the proof of identity.

Q.1. A compound with molecular formula C_7H_8O gives the following IR spectral data.
Deduce the structure of the compound and assign each band.

IR bands (cm^{-1}): ~3300 (s), ~3040 (m), 2800–2950 (w), 1606 (m), 1582 (m), 1500 (m), 1450 (w), 1380 (w), 1185 (s), 780 (s) and 692 (s).