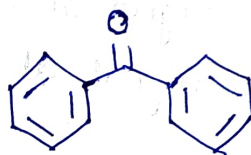


Structure-Spectrum Relationship

Factors affecting the values of absorption frequency

1. Resonance
2. Inductive effect
3. H-Bonding
4. Steric
5. Electronegativity

example:



$\bar{\nu}_{\text{C}=\text{O}}$
(cm^{-1})

1717

1710

1700

1669

acetophenone

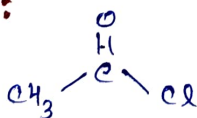
benzophenone



single bond character

becoz of +R effect the $\text{C}=\text{O}$ get some ~~no~~ character therefor reducing the frequency

example:

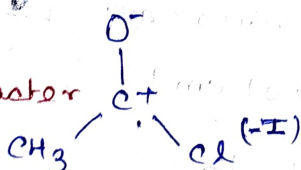


1795 cm^{-1}

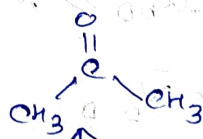
considerable

double bond

character

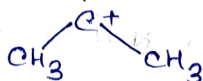


-I effect of Cl destabilizes the polar structure



1720 cm^{-1}

has some single bond character

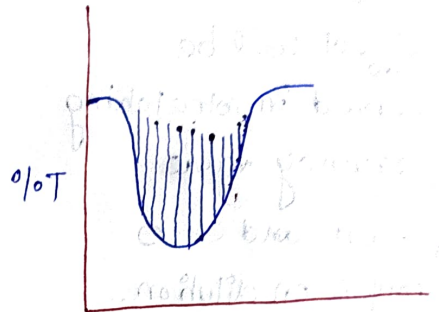
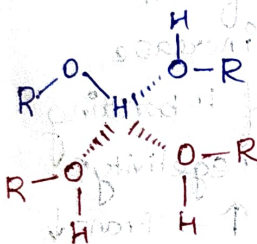
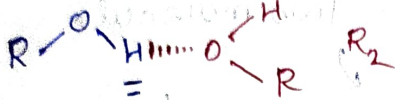
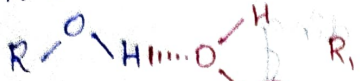


+I effect stabilizes the polar structure.

$R_{\text{acetone}} < R_{\text{CH}_3\text{COCl}}$

Hook's Law \rightarrow Ye phle likhna hai ans mai to obtain full marks!

Example: (H-Bonding effect)



Group having H-Bonding effect exhibit strong and broad peak in I-R Spectrum.

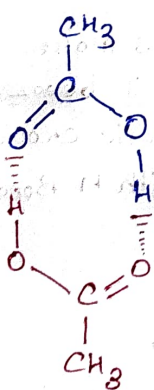
polar bond \rightarrow interact more
 \rightarrow Trans \downarrow \rightarrow absorb \uparrow

Carboxylic acid, $\bar{\nu}_{O-H} \approx 2500 \text{ cm}^{-1}$

due to H-Bonding electron of O transfer to H that's why electronegativity of O decreases \rightarrow less absorption \rightarrow less $\bar{\nu}_{O-H}$

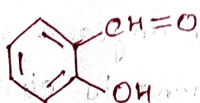
Higher extent H-bonding in carboxylic acid compare to normal alcohols.

$\bar{\nu}_{O-H}$ of carboxylic acid $<$ $\bar{\nu}_{O-H}$ of alcohol

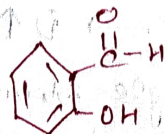


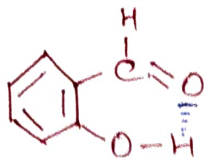
$R_{O-H}(\text{COOH}) < R_{O-H}(\text{alcohol})$

problem: How to differentiate between



and





Intramolecular

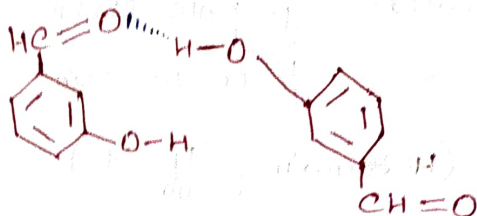
H-Bonding



no effect on dilution



no effect will be observed in stretching frequency value of $-OH$ and $CH=O$ groups on dilution.



Intermolecular

H-bonding

depending on distance

btw the two molecule

depends on conc/dilution

on dilution the stretching frequency values of $-OH$ and $CH=O$ will increase

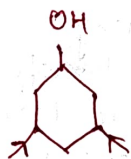
(why?) \Rightarrow extent of H-bonding

H Bonding $\downarrow \rightarrow$ O electronegativity \uparrow

$\rightarrow (-) \uparrow \rightarrow$ absorbed $\uparrow \rightarrow$ Trans \downarrow

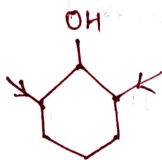
$\rightarrow \bar{\nu} \uparrow$

example: (steric effect)



I

$\bar{\nu}_I$



II

$\bar{\nu}_{II}$

H Bonding

$I > II$

H-Bonding effect is more prominent in I becoz in comp II steric crowding increased with H-Bonding

problem:



1717



1717



1745



1780



1828

cm^{-1}

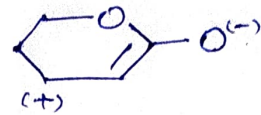
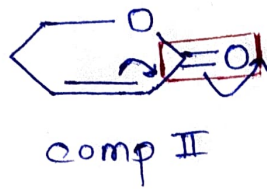
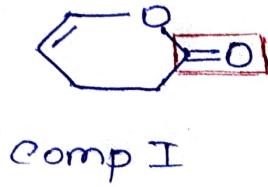
external angle increase \rightarrow bond strength \uparrow
 \rightarrow absorption $\uparrow \rightarrow \bar{\nu} \uparrow \rightarrow s$ character \uparrow

becoz of internal angle strain exocyclic angle around

$C=O$ group increases from cyclohexanone to cyclopropanone

as a result $C=O$ bond strength also increases from cyclohexanone to cyclopropanone leading to highest $\bar{\nu}_{C=O}$ in Cpro

Problem \Rightarrow Is it possible to distinguish the following compounds by I-R spectroscopy.



considerable amount
of single bond
character

$$\bar{\nu}_{C=O}(\text{COOR}) \approx 1740$$

$$\bar{\nu}_{C=O}(\text{ketone}) \approx 1720$$

$$\bar{\nu}_{C=O}(\text{Comp I}) > \bar{\nu}_{C=O}(\text{Comp II})$$

no resonance happens in comp I \rightarrow becoz it's $\bar{\nu}_C = 1740$
that means it is not showing any resonance. It will show
only when some attacking group is present.