Chapter - 8

Spectroscopy :

Referred Books:-

① Donald Pavia - Spectroscopy

② Y. R. Sharma

③ P. S. Kalsi

④ Questions are from

- → Organic Chemistry (7th Ed) by [redacted] Mcmurry
- → Organic chemistry by Hornback
- → Organic Chemistry by Carey
- → Organic chemistry by Hoffmann
- → Organic chemistry by P. Y. Bruice
- → Organic Chemistry by S. H. Pine
- → Schaum Series - Organic Chemistry
- →

⑤ Read spectroscopy related chapters of clayden

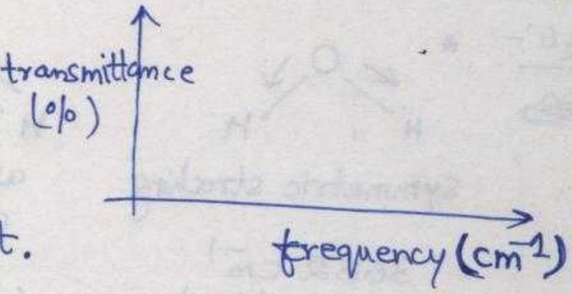
⑥ Do spectroscopy related problems from Morrison & Boyed.

write questions frm Kemp, Silverstein, Pavia ①

Infra red Spectroscopy:→

- Infra red region is beth 4000 − 650 cm^{-1}.
- functional groups in organic compounds have absorptions which are characteristic not only in position but also in intensity.
- In an infra red spectrometer, infrared radiation of successively increasing wavelength is passed through the sample of the compound and percent transmittance measured.

→ A 100% transmittance means no absorption and if all the radiation is absorbed the transmittance is 0 percent.

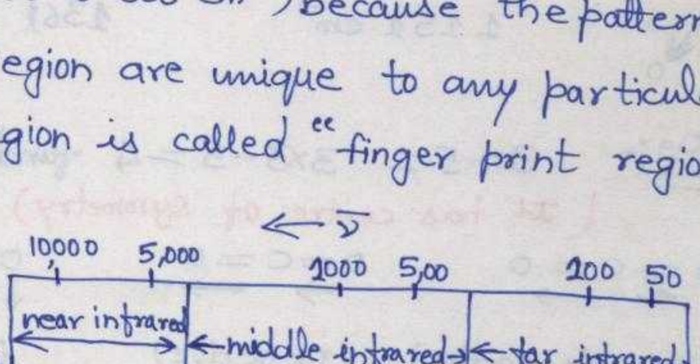


* It is impossible for any two different compounds (except enatiomers) to have precisely the same infrared spectrum.

* Finger print region:- (1500 to 600 cm^{-1}) because the pattern of absorption in this region are unique to any particular compound, so this region is called "finger print region".

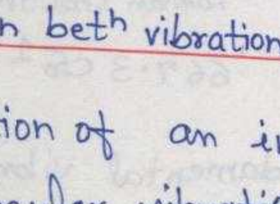
* Infrared regions:-

→ radiations in middle infrared regions corresponds to transition beth vibrational states.

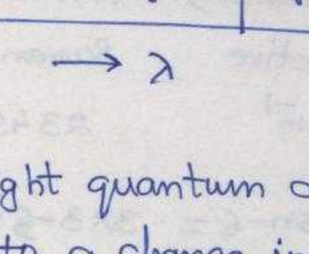


* The absorption of an infrared light quantum can occur only if the molecular vibrations lead to a change in the dipole moment of the molecule. Otherwise, they are said to be infrared inactive.

→ For ex:-



(I.R active)



(I.R inactive) becoz $\mu=0$

for c=c, vibration

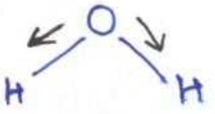
* Fundamental Vibrations :-

→ A non-linear molecule with n atoms generally has 3n−6 fundamental vibrational modes

→ A linear molecule has 3n−5 vibrational modes.

→ many of these vibrations occur at the same frequency and are therefore "degenerate" so all the possible peaks are not seen as independent absorptions.

i) H_2O :-

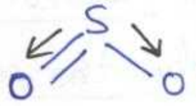

symmetric streching
$3652\ cm^{-1}$
(I.R active)

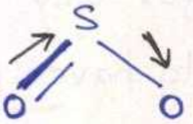

asymmetric stretching
$3756\ cm^{-1}$
(I.R active)


bending (scissoring)
$1596\ cm^{-1}$
(I.R active)

ii) SO_2 :→

no centre of symmetry

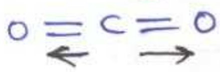

(I.R active)
Raman active
$1151\ cm^{-1}$

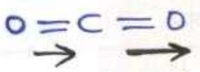

(I.R active)
Raman active
$1361\ cm^{-1}$

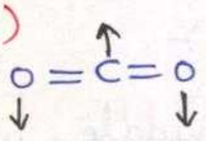

(I.R active)
Raman active
$519\ cm^{-1}$

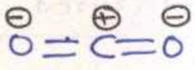
iii) CO_2 :- $3n-5 = 3\times3-5 = 4$ fundamental vibrational modes

(It has centre of symmetry)


(I.R inactive)
Raman active
$1330\ cm^{-1}$


(I.R active)
Raman inactive
$2349\ cm^{-1}$

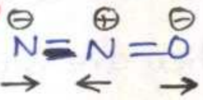

(I.R active)
Raman Inactive
$667.3\ cm^{-1}$

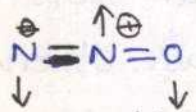

(I.R active)
Raman inactive
$667.3\ cm^{-1}$

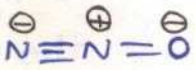
iv) N_2O :- $3n-6 = 3\times3-5 = 4$ fundamental vibrations

(No centre of symmetry)

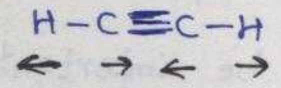

(I.R. active)
Raman active
$1285\ cm^{-1}$


(I.R active)
Raman active
$2224\ cm^{-1}$

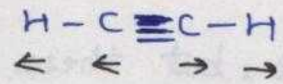

(I.R active)
Raman inactive
$589\ cm^{-1}$


(I.R active)
Raman inactive
$589\ cm^{-1}$

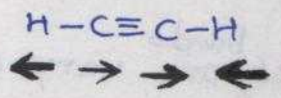
V.) Acetylene:- (C_2H_2) $3\times4-5=7$ fundamental vibrations



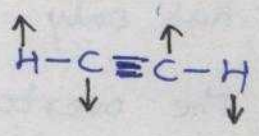
(I.R. inactive)
(Raman active)
3374 cm^{-1}



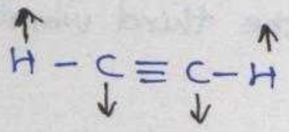
(I.R inactive)
(Raman active)
1974 cm^{-1}



(I.R. active)
(Raman inactive)
3287 cm^{-1}

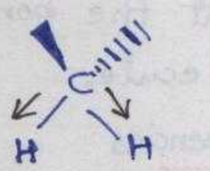


(I.R inactive)
(Raman active)
doubly degenerate
612 cm^{-1}

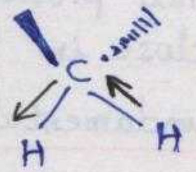


(I.R active)
(Raman inactive)
doubly degenerate
(729 cm^{-1})

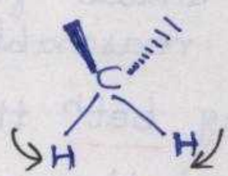
VI) Methylene Group:- $>CH_2$



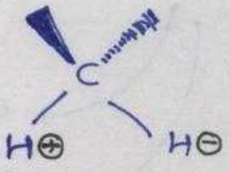
Symmetric stretching



asymmetric stretching



Scissoring



twisting

- Because of its high symmetry Buckminsterfullerene (C_{60}) has only four absorption bands in its I.R spectrum.
- The overtones bands are very weak, but these can be important for characterisation of certain class of compounds, particularily benzene derivatives.

overtones may arise → when molecule in lowest or first vib. state is excited to the third vibrational level

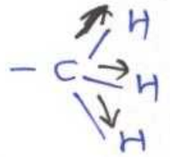
→ "Combination band" occurs when a single photon has precisely the correct energy to excite two vibrations at once.

- Coupled vibrations:- → takes place bet^{h} two bonds vibrating with similar frequency provided that the bonds are reasonably close in the molecule.

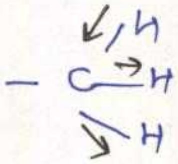
→ coupling bet^{h} the fundamental frequencies

→ Coupling bet^{h} the fundamental vibration and the overtone of some other vibration (This is called Fermi Resonance)

ex:- methyl group



$\nu_{C-H\,sym} = 2872\ cm^{-1}$



$\nu_{C-H\,asym} = 2962\ cm^{-1}$

→ other compds showing coupling; $-CH_2$ group, nitro($-NO_2$); amino groups ($-NH_2$).

→ Generally anti-symmetric streching frequency is of higher frequency

→ In CO_2, $O\underset{\rightarrow}{=}C\underset{\rightarrow}{=}O$ ($\nu_{C=O\,asym} = 2350\ cm^{-1}$) is due to coupling beth two C=O vibrations

** → Coupling is useful for the detection of → primary amines and primary amides via two

| nitro compds | carboxylic anhydrides

* Secondary amides → Amine III Band:-

→ interaction of C-H stretching vibration with NH bending mode, in case of secondary amides. These are known as amide II and amide III bands.

→ Amide II band (N-H bending) at 1550-1510 cm^{-1}

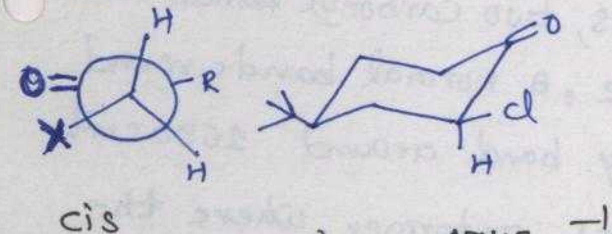
→ Amide III band (C-N stretching) weak band near 1250 cm^{-1}

* Fermi Resonance:-
- Since there is sharing of intensity, the overtone can come out to be a strong band.
- Coupling betn fundamental vibration with an overtone or combination.

ex:-
i) In benzoyl chloride, two bands at 1790 cm^{-1} and 1745 cm^{-1} due to coupling of C-H bending mode at 875 cm^{-1} and C=O strectching fundamental.
ii) The C-H str region of an aldehydic group
iii) spectrum of cyclopentamone (near C=O str)

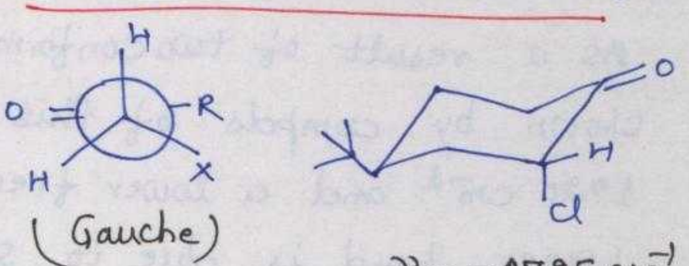
* Conformational Isomerism:-

Ex) Two C=O str bands are observed in α-haloketones.



cis
(eclipsed)

$\nu_{C=O} = 1745\ cm^{-1}$



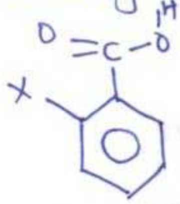
(Gauche)

$\nu_{CO} = 1725\ cm^{-1}$

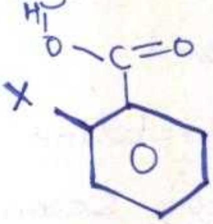
→ It is due to eclipsed interaction betn halogen atom and C=O group in cis configuration, cis isomer has higher frequency than trans isomer.

→ In cyclohexanols, the equitorial C-OH str. is 1050-1030 cm^{-1} while the axial C-OH str is lowered by 30-10 cm^{-1}.

→ Ortho halogenated benzoic acid

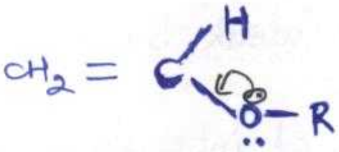


(cis)

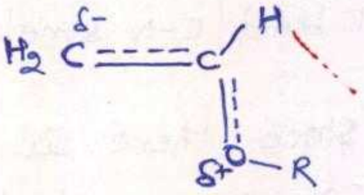


(trans)

→ Vinyl ethers:-



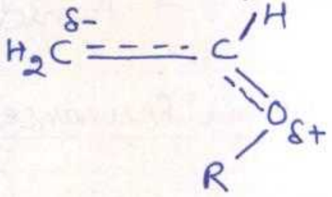
(Vinyl ether)



(trans) ~1620 cm^{-1}

(R & CH_2 trans here)

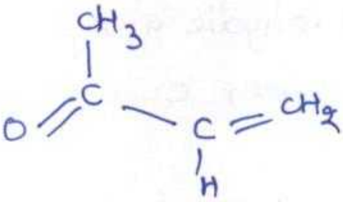
R & CH_2 are cis here

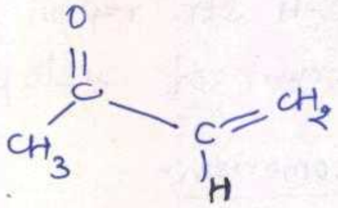


cis ~1640 cm^{-1}

Due to coplanarity in the trans isomer (max^m resonance) the double bond character of the alkene linkage is reduced. Steric hinderance reduces resonance in the cis isomer.

→ α, β -unsaturated Ketone :-





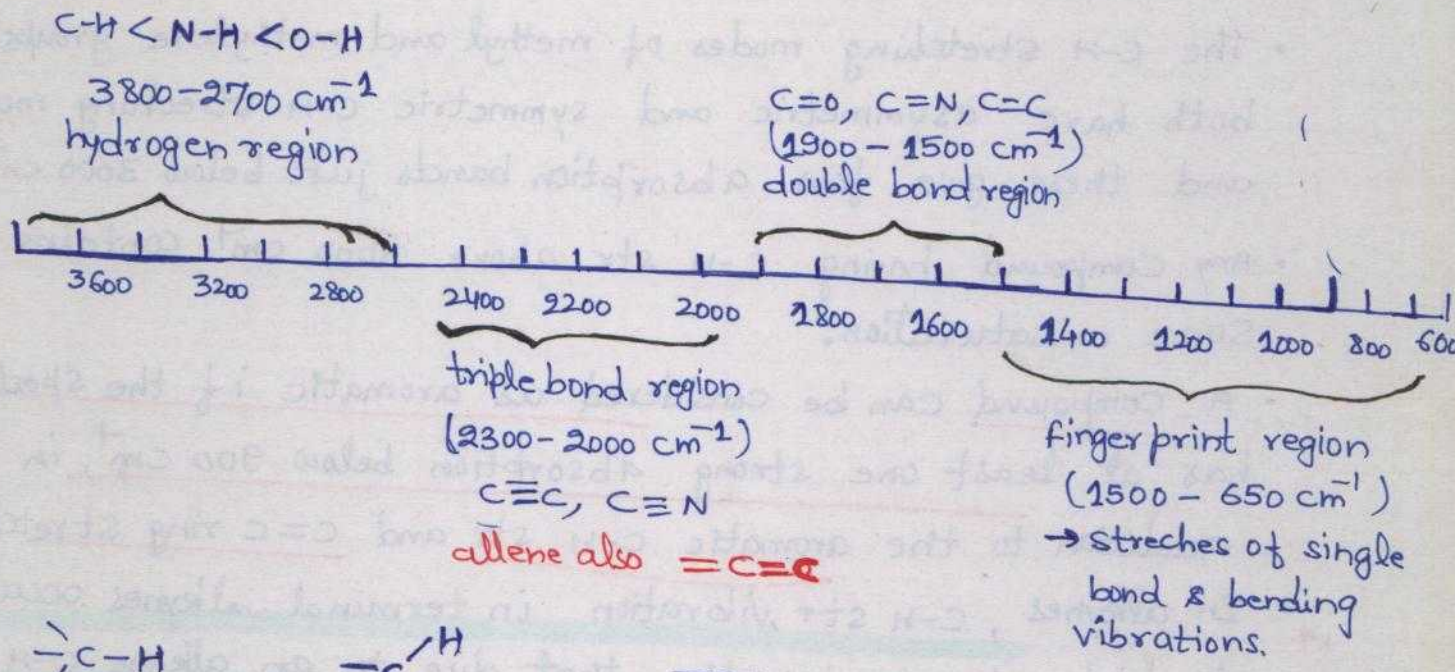
$\nu_{C=O}$: (S-trans) < (S-cis)

As a result of two conformations, two carbonyl bands are shown by compds of this type, a normal band around 1720 cm^{-1} and a lower frequency band around 1690 cm^{-1}. Lower band is due to S-trans conformer, where the electron delocalization is more effective.

* $$\boxed{\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}}$$

bond dissociation energy of
C-H bond is 104 kcal/mole
C-C bond is 88 kcal/mole

I.R spectrum



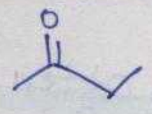
* $-\overset{\backslash}{\underset{/}{C}}-H$ $\quad =C\langle^{H}_{H}$ $\quad \equiv C-H$

$H-C_{sp^3} < H-C_{sp^2} < H-C_{sp}$

$\nu_{C-H} = 3000 \quad 3080 \quad 3300\ cm^{-1}$

→ as hybridization increases, % s character ↑ ⇒ C-H bond strength increases so the C-H str frequency increases.

* Conjugation lowers the absorption frequencies of each conjugated group (due to a lowering of the bond order) because of the contributions of resonance forms with lower bond orders.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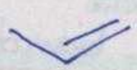
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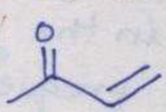


$\nu_{C=O} : 1715 cm^{-1}$ $\quad \nu_{C=C} : 1647 cm^{-1}$ $\quad \nu_{C=O}\ 1685\ cm^{-1}$

$\nu_{C=C}\ 1623\ cm^{-1}$

* I.R absorption bands for Alkynes

$RC\equiv CH$	3300 cm^{-1}	strong	$\equiv C-H$ str
	2100-2140 cm^{-1}	medium	$C\equiv C$ str
	600-700 cm^{-1}	strong	$\equiv C-H$ bend
$RC\equiv C-R$	2190-2260 cm^{-1}	very weak	$C\equiv C$

*Identification of Alkane residue:-

- strong absorption band centred around 2925 cm^{-1} represents C-H str.
- The C-H stretching modes of methyl and methylene groups both have asymmetric and symmetric C-H streching modes and these give four absorption bands just below 3000 cm^{-1}.
- Any compound having C-H str above 3000 cm^{-1} contains some unsaturation.
- A compound can be considered as aromatic if the spectrum has at least one strong absorption below 900 cm^{-1}, in addition to the aromatic C-H str and C=C ring stretch
- ** In alkynes, C-H str vibration in terminal alkynes occurs at higher frequencies than that due to an alkane C-H str.

→ The C≡N stretch displays itself around 2200 cm^{-1} which is of variable intensity. On conjugation as in aryl nitriles the frequency gets lowered and the band becomes stronger. The presence of nitriles can be detected from this band.

* The alcohol or Phenols can be recognised from its infrared spectrum from the O—H str in the region 3200–3600 cm^{-1}.

→ Alcohols also give a strong & broad band due to C–O stretching in the 1000–1200 cm^{-1} region.

** → The exact frequency of this band (C–O) is often used to distinguish bet^{n} primary, secondary and tertiary alcohols.

* Ethers:- Ethers can be recognized by their strong **C–O** stretching bands at 1060–1275 cm^{-1} which falls in the fingerprint region

→ In case of highly unsymmetrical ethers e.g alkyl aryl ethers the two C–O bonds couple and thus show anti-symmetric and symmetric C–O stretching i.e two bands.

→ In case of dialkyl or diaryl ethers the symmetric C–O stretch is infraredinactive and only the anti-symmetric C–O

* Similarities in O-H & N-H stretching bands:-

→ Phenols & alcohols are very easy to recognise from O-H str absorption (in region 3650-3200 cm^{-1})

→ The str of N-H bonds of amines ~~also~~ and amides also give absorption is same region

→ Since oxygen is more electronegative than nitrogen, O-H str results in a greater change in bond moment, than the N-H str so O-H stretching is stronger than the N-H str band.

→ In dilute solutions, O-H str is sharp & is at 3600 cm^{-1}
But in dilute sol^{n}s N-H str never goes as high as the free O-H range around 3600 cm^{-1}.

→ In O-H str, in concentrated solutions, the peak broadens and shifts its position to lower frequency (3200-3500 cm^{-1}).

* N-H str in amines

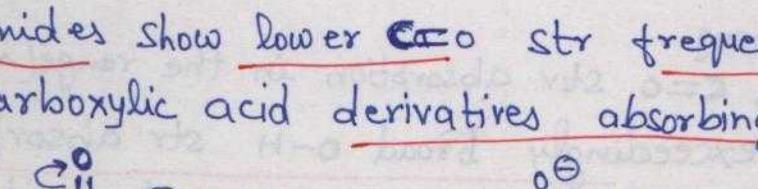
- secondary amines:- It consists of one band near 3200 cm^{-1}
- ** primary amines - It displays two bands (due to vibrational coupling) around 3200 and 3500 cm^{-1}.
- tertiary amines - Since there is no N-H, there is no absorption in the region.

* I.R spectra of amides:-

In amides the N-H stretching give absorptions (3140-3500) cm^{-1}.

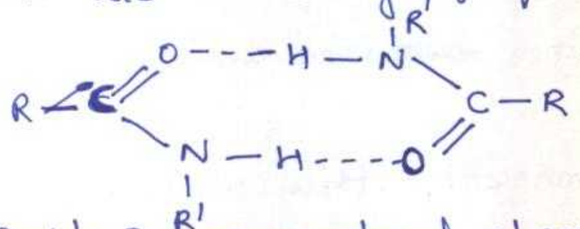
primary amides → shows double band in the region (N-H str)
Secondary amides → only one N-H bond show one band.
tertiary amines → no N-H bond show absorption

→ ** amides show lower $C=O$ str frequencies than the other carboxylic acid derivatives absorbing at 1650 to 1690 cm^{-1}.



→ If the amide is conjugated then $C=O$ str frequency is lowered still further.

→ When a Carbonyl of amide is involved in hydrogen bonding then its stretching frequency is again lowered.



→ Amide I:- The carbonyl absorption of amides is known as Amide-I.

- On dilution of the sample with a solvent, extent of H-bonding decreases and $C=O$ absorption is shifted to higher frequency around 1690 cm^{-1}.

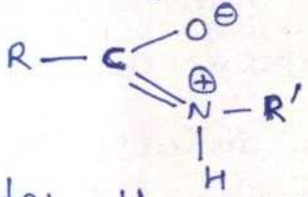
- The carbonyl freq of tertiary amides is however, independent of its physical state as H-bonding with another tertiary group is not possible.

→ Amide II:- The amide-II band of primary appears ($1640-1600\ cm^{-1}$) due to N-H bending

→ tertiary amide does not show this band.

→ Secondary amides in solid state show the amide II band in the region $1570-1515\ cm^{-1}$.

- secondary amides, exist mainly in the trans conformation, the free NH stretching vibration in dilute solutions is near 3430 cm^{-1}.



✓ • In secondary amides, the C-N str vibration couples with N-H bending to give two bands → one N-H bending (amide-II)

→ one is C-N stretching at lower frequency near 1750 cm^{-1}.

* Carboxylic acids:→ • strong $C=O$ str absorption in the range (~1710 cm^{-1})

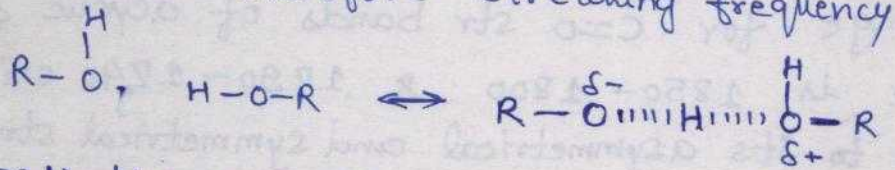
- exceedingly broad O-H str absorption.
- free O-H can be detected only if the infrared spectrum of carboxylic acid is scanned in very dilute sol^n in non-polar solvents or in vapour phase.

⇒ COOH is recognised from the broad O-H stretching of the dimer together with the strong C=O str band at 1715 cm^{-1}.

* Effect of H-bonding :→

- In case of intermuclear hydrogen bonding some OH groups are bonded, some are not and thus both peaks may show
- ** Sharp non hydrogen bonded O-H absorption band around Note 3600 cm^{-1} can be observed in the vapour phase, in dilute solution or if steric hinderance prevents hydrogen bonding.

→ The reason that bonded O-H stretch appear at lower frequency than free O-H stretch is assigned to lengthening of the original O-H bond on hydrogen bonding as shown; as a result the bond is weakened, its force constant is reduced therefore stretching frequency is lowered.

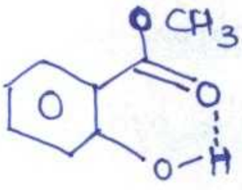


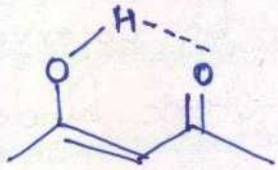
$$R-\overset{H}{\overset{|}{O}},\quad H-O-R \longleftrightarrow R-\overset{\delta-}{O}\cdots H\cdots \underset{\delta+}{\overset{H}{\overset{|}{O}}}-R$$

→ **Distinction bet^n inter- and intra molecular hydrogen bonding :-**

- In very dilute solution, formation of intermolecular hydrogen bonds does not take place.
- ↑ the concentration causes ⇒ broad & lower frequency band.
- Plot of spectra of t-butyl alcohol as the pure liquid & its solutions in CCl_4.
  - → In pure liquid ⇒ only a strong bonded O-H str around 3360 cm^{-1}.
  - → In CCl_4 → 3300 cm^{-1} O-H absorption is accompanied by a sharp band at 3620 cm^{-1}.
  - ↑ the CCl_4 → 3620 cm^{-1} band becomes more intense relative to the 3360 cm^{-1} band. These two bands are both due to O-H str.
- ✓ Intra molecular H-bonding remains unaffected with effect of dilution

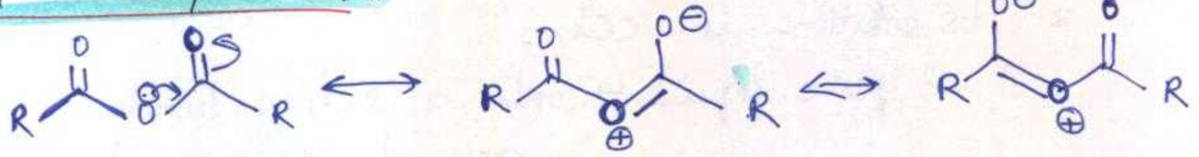
- Internuclear hydrogen bonds are however, broken on dilution and as a result there is a decrease in the bonded O-H absorption and an increase in or the appearance of free O-H absorption.
- H-bonding in enols & Chelates is very strong (O-H str may be as low as 2800 cm^{-1}) since these are not easily broken on dilution by an inert solvent, free O-H str may not be seen at low concentrations.





* Fermi Resonance & Coupling

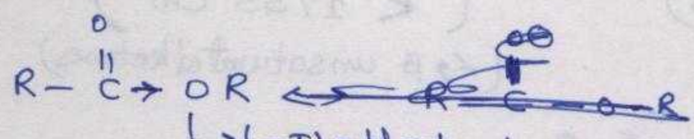
- In carboxylic acid anhydrides coupling betn two carbonyl groups occur (which are indirectly linked via O)
- The general range for C=O str bands of acyclic saturated acid anhydride is 1850 – 1800 & 1790 – 1740 cm^{-1} which are due to its asymmetrical and symmetrical stretchings.
- ** The higher frequency band is more intense in acyclic anhydrides, while the lower frequency band is more intense in cyclic anhydrides. (This feature can be gainfully used to distinguish between acyclic and cyclic anhydrides).



→ Conjugated anhydrides show a decrease in C=O stretching due to resonance.

→ Under usual conditions, spectrum of cyclopentanone displays, as expected a single carbonyl stretching absorption. When adequate resolution is employed, its spectrum shows two carbonyl absorptions in C=O str region (1745 cm^{-1} and 1730 cm^{-1}), due to Fermi Resonance with an overtone of an α-methylene group.

* Esters (ethyl acetate) have two characteristic ~~system~~ absorptions due to C=O str around 1735 cm^{-1} and C–O str around 1200 cm^{-1}.

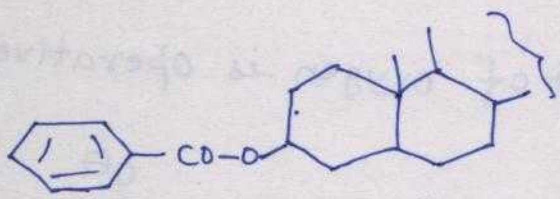
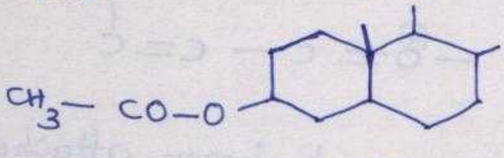
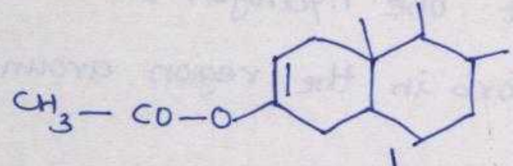
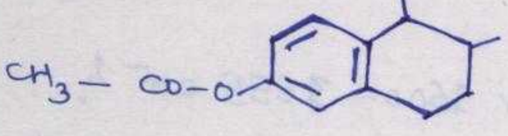


$R-\overset{O}{\overset{\|}{C}}\rightarrow OR \longleftrightarrow$ ~~$R-\overset{O^{\ominus}}{\overset{|}{C}}=O-R$~~

↳(–I) effect of oxygen.

** The differentiation betn an ester and ketone is possible by C=O str which is a strong band and easily distinguishable from C–C str.

ex.1: –

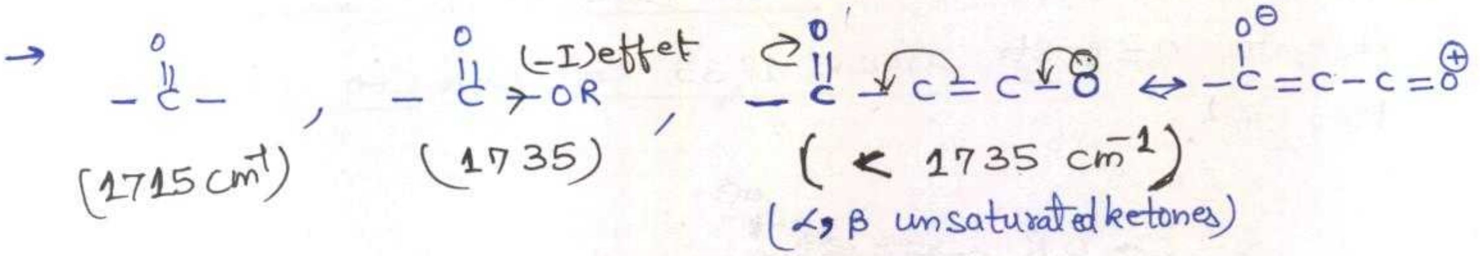
		C=O str	C–O str
i)		1720	1270
ii)		1735	1239
iii)		1755	1217
iv)		1766	1204

→ In (i) since conjugation with benzene reduces C=O str. The introduction of unsaturation into the alcohol moiety of the ester, as in the enol acetate (iii) or the phenolic acetate (iv) induces a C=O frequency displacement in negative dir

$R-\overset{O}{\overset{\|}{C}}-O-C=C \longleftrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{O}=C-\overset{\ominus}{C}$

* In acid chlorides, (–I) effect of a halogen dominates over +M and as a result, unconjugated acid chlorides show their C=O str in 1815 - 1785 cm^{-1} region.

→ Aroyl chlorides can be identified by the Fermi resonance band near 1750 - 1735 cm^{-1}, between C=O band and the overtone of the longer wavelength band near 875 cm^{-1}.

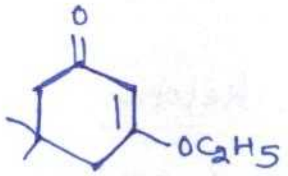


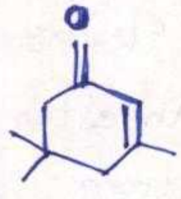
→ $-\overset{O}{\overset{\|}{C}}-$, $-\overset{O}{\overset{\|}{C}}\rightarrow OR$ (–I)effet , $-\overset{O}{\overset{\|}{C}}-C=C-\ddot{O} \leftrightarrow -\overset{O^{\ominus}}{\overset{|}{C}}=C-C=\overset{\oplus}{O}$

(1715 cm^{-1}) (1735) (< 1735 cm^{-1})

(α, β unsaturated ketones)

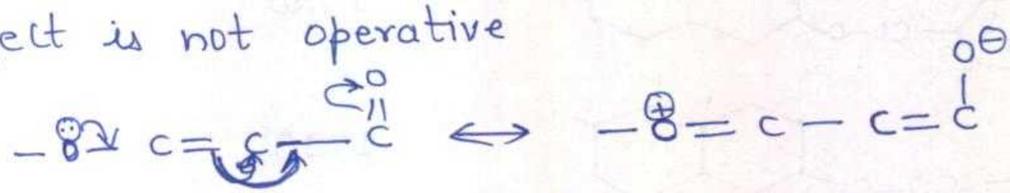
→ Ex.)





C=O str vibrations 1640 cm^{-1} 1680 cm^{-1}

It is due to (+ M) effect of oxygen is operative and (– I) effect is not operative



$-\ddot{O}-C=C-\overset{O}{\overset{\|}{C}} \longleftrightarrow -\overset{\oplus}{O}=C-C=\overset{O^{\ominus}}{\overset{|}{C}}$

* Alkenes which have at least one hydrogen attached to the double bond normally absorb in the region around 3020-3140 cm^{-1}.

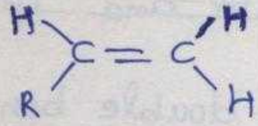
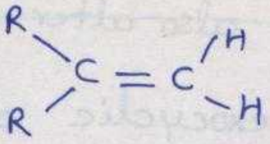
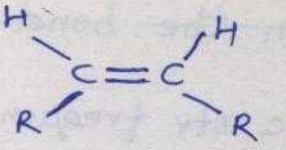
C=C str in alkenes:- near 1600 – 1655 cm^{-1}.

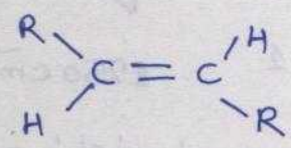
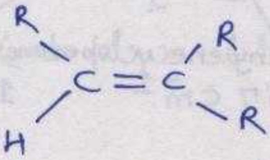
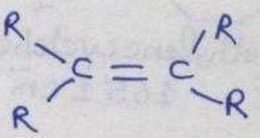
→ This is most intense in case of methylenic (vinylidine) and vinyl double bonds.

→ As more alkyl groups are added, the intensity of absorption decreases since the vibration now results in a smaller change of dipole moment.

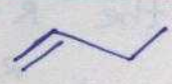
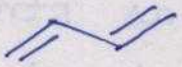
→ It is difficult to detect & often of low intensity in case of tri ~~substitted~~ substituted, tetrasubstituted and relatively symmetrical di-substituted alkenes.

→

			 (cis)
C=C str	1648–1638 (med^m)	1658–1648 (med^m)	1662–1626 (weak)
=C–H bend	995–985 (strong) 915–905 (strong)	895–885 (strong)	730–665 (med^m)

	 (trans)		
C=C str	1678–1668 absent	1675–1665 (weak)	absent
=C–H bend	980–960 strong	840–790 (med^m)	absent

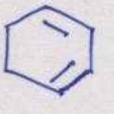
* The conjugation of an olefinic double bond with α,β-unsaturation, a C=O or an aromatic ring not only lowers the C=C stretching by about 30 cm^{-1} but also enhances the intensity of this band

C=C str ~ 1650 cm^{-1} 1610 cm^{-1}

NOTE → (Conjugation of an olefinic double bond) C=C str is lowered, the intensity of absorption is increased

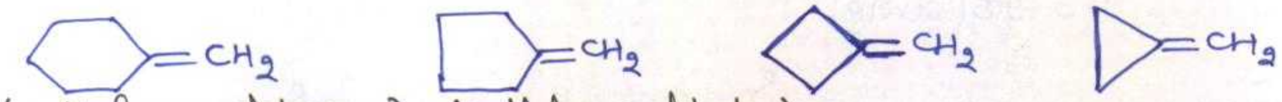
→ Resonance results in partial π-bond character bet^n the two double bonds, with decreased electron density and decreased stifness in the double bonds themselves. Conjugated double bonds therefore vibrates at lower frequencies than similar isolated double bonds


C=C str 1645 cm^{-1} 1620 cm^{-1} 1600 cm^{-1}

~~* Change in the bond angles also alter C=C str and thus~~

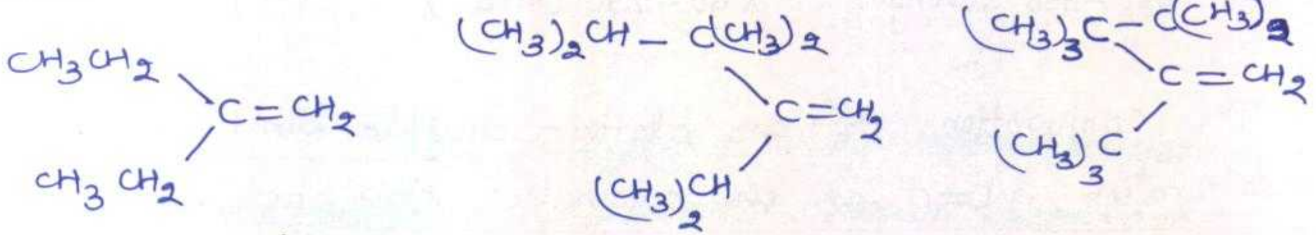
* The C=C str frequency of exocyclic olefinic double bond (Vinylidene double bond) is known to increase with a decrease in the ring size.



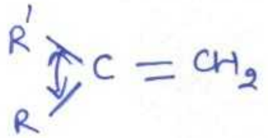
(methylenecyclohexane) (methylenecyclopentane)

C=C str 1651 cm^{-1} 1657 cm^{-1} 1690 cm^{-1} 1750 cm^{-1}

* Change in the bond angles also alter C=C stretching, thus spreading of the angle due to the size of R groups lowers the C=C str of vinylidene double bond in the compound shown



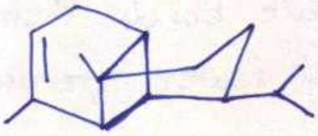
C=C str (1652 cm^{-1}) (1639 cm^{-1}) (1621 cm^{-1})



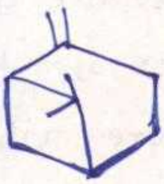
as strain increase the $R-\underset{R}{C}$ bond angle spreads and C=C str freq. decreases.

The ring strain has also a marked influence on the olefini C-H bending vibrations, the frequency of absorption gets lowered.

(α-pinene)



Copaene



(β-pinene)

=C-H bending 788 cm^{-1} 875 cm^{-1}

* Cumulated double bonds ($X=Y=Z$) display unusually high double bond frequencies.

→ The allenes $>C=C=CH_2$ absorb around $1950\ cm^{-1}$ due to asymmetric $C=C=C$ stretching.

* The benzene confirmation frequency:-

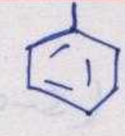
→ two bands near 1600 and $1500\ cm^{-1}$

→ Once these bands are detected, the band around $3030\ cm^{-1}$ (aromatic C-H str) serves to confirm the presence of this group.

→ The substitution pattern in an aromatic is identified by looking at the C-H out of the plane bending bands.

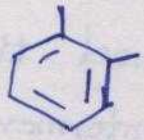
• The position of absorption of the out-of-plane bending bands depends on the no. of adjacent hydrogen atoms on the ring.

case-i) A monosubstituted benzene displays two very strong bands, betn 690 and $710\ cm^{-1}$ and between 730 and $770\ cm^{-1}$.



{ out of the plane C-H bending 690-710, 730-770 }

ii) ortho-substituted benzenes show only a strong band betn 735 and $770\ cm^{-1}$.

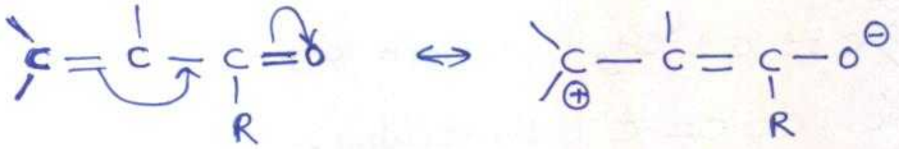


{ out of the plane C-H bending 735-770 }

iii) meta-substituted benzenes show ~~only~~ two bands, but at different positions and the intensity of one band is stronger than the other i.e. one band is betn 680 and $725\ cm^{-1}$ and one very strong band between 750 and $810\ cm^{-1}$.

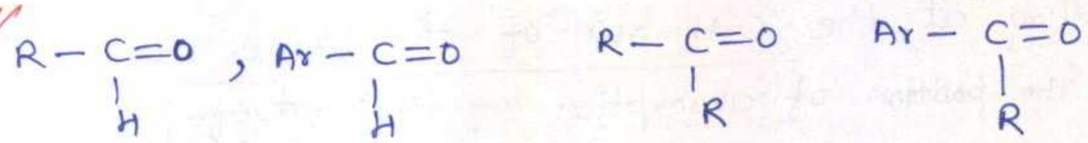
iv) Para-substituted benzenes give a single strong band, however, this is at higher frequencies ($790-850\ cm^{-1}$) than the ortho-disubstituted benzenes.

* C=O frequency is affected by several factors → conjugation
→ hydrogen bonding
→ ring strain



→ conjugation of C=O with a C=C or an aryl group leads to the delocalization of the π-electrons of both the unsaturated groups. i.e. (C=C) and (C=O) The double bond character e.g in the C=O group is reduced and therefore, the C=O stretching in a conjugated ketone occurs at lower frequencies. (~ 30-40 cm^{-1}).

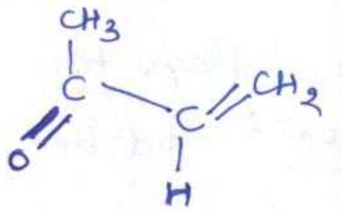
→ *



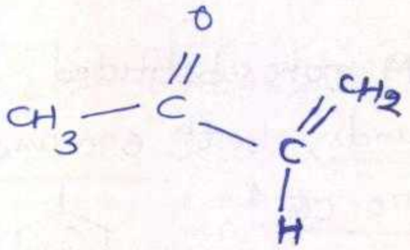
$R-\underset{H}{C}=O$, $Ar-\underset{H}{C}=O$ $R-\underset{R}{C}=O$ $Ar-\underset{R}{C}=O$

C=O str 1725 1700 1710 1690 cm^{-1}

→



(s-trans)

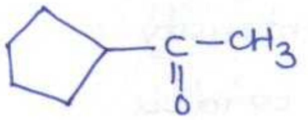


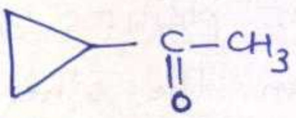
(s-cis)

C=O str 1690 1720

- It is assumed that the lower frequency band is due to s-trans conformer, where the electron delocalization is more effective.

→ **



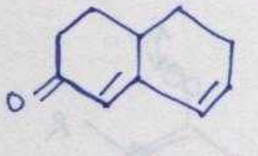


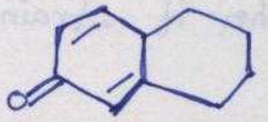
C=O str 1710 cm^{-1} 1700 cm^{-1}

- The cyclopropyl ring behaves much like a π-system, in conjugation with the carbonyl π-bond. Thus C=O str frequency of a ketone which has cyclopropyl conjugation is thus decreased.

* Extension of a conjugated system by additional double bonds has generally much less effect on the C=O str frequencies than the first double bond.

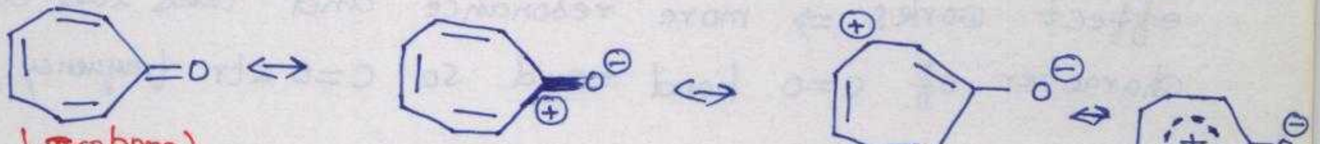
for ex:-





C=O str 1665 cm⁻¹ 1666 cm⁻¹

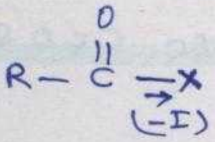
* Tropone shows C=O str at 1638 cm⁻¹. The lowering is due to strong resonance → stabilized electron delocalization



(Tropone)

Tropone represents a series of dipolar structures which constitute the aromatic tropylium system.

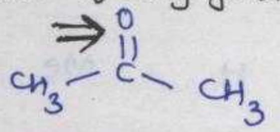
* When X is an electron-attracting group (e.g. Cl) the C=O str frequency increases



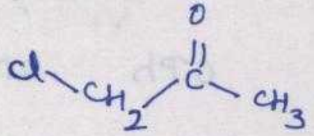
$$\mathrm{R-\overset{\overset{O}{\|}}{C}-\underset{(-I)}{\overrightarrow{X}}}$$

Lower if conjugated, higher if strained

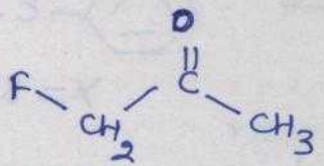
ex.)



$$\mathrm{\Rightarrow\ CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$



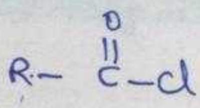
$$\mathrm{Cl-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$



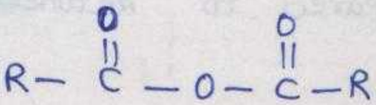
$$\mathrm{F-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}$$

C=O str (1720 cm⁻¹) (1750 cm⁻¹) (1770 cm⁻¹)

→ This increase is further increased when the electron withdrawing substituent is directly attached to the carbonyl carbon as in an acid chloride.



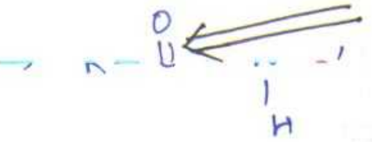
$$\mathrm{R-\overset{\overset{O}{\|}}{C}-Cl}$$



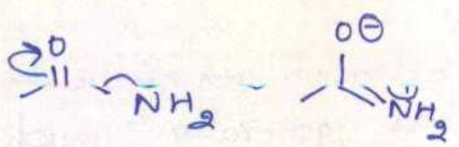
$$\mathrm{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R}$$

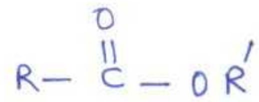
C=O str. (1800 cm⁻¹)

C=O str. = 1800 and 1750 cm⁻¹
(two peaks)



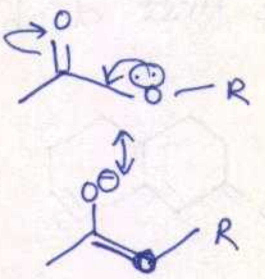
C=O ; 1650 - 1680 cm^{-1}
lower if conjugated,
higher if strained

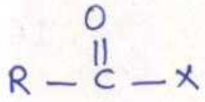


→ 

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

C=O str 1735 cm^{-1}
lower if conjugated,
higher if strained



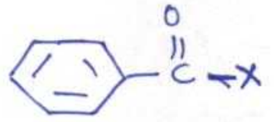
* Mesomeric Effects :- 

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

→ When X is a carbon-carbon unsaturated bond then the inductive effects are virtually absent and only mesomeric effect works ⇒ more resonance and thus less double bond character of C=O bond and so C=O str frequency decreases.

→ When X is ~~either~~ $-NH_2$ ~~or -OR~~, the mesomeric effect of the nitrogen lone pair is more important than the inductive effect of the nitrogen, and this leads to a decrease in C=O str.

→ When X is −OR, then (−I) effect is more than (+M) becoz oxygen is more electronegative so C=O str increases.

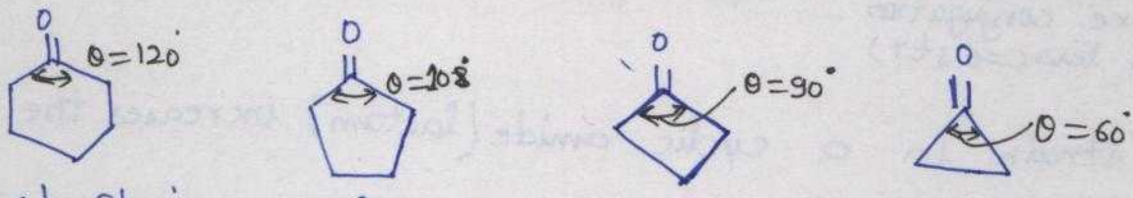
→ Ex.) 

	X = Br	OPh	OMe	H	Me	NMe_2
C=O str in hexane (cm^{-1})	1760	1750	1735	1714	1697	1660
	(−I)	(−I)>(+M)	(−I)>(+M)			(+M)>(−I)

- In phenyl esters ie. $Ph-\overset{O}{\overset{\|}{C}}-OPh$ there is some delocalization of electrons into the phenyl ring and thus C=O str is more as compared to ketones. In esters in fact (−I)>(+M).

* Effect of ring strain:-

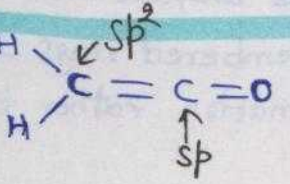
→ ↑ in ring strain causes C=O str to increase.



	0° of strain	12° of strain	30° of strain	60° of strain
C=O str	1715 cm⁻¹	1745 cm⁻¹	1780 cm⁻¹	1813 cm⁻¹

increased s-character →

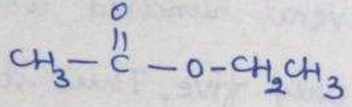
- here the C-CO-C bond angle is reduced below the normal 120° in strained rings. This leads to an increase in the s-character in the C=O bond, which is, therefore, strengthened and consequently C=O stretching frequency is increased.
- Branching at the α-carbon atoms leads to an increase in the C-CO-C bond angle leading to a decrease in frequency of absorption from the normal value of 1720 cm⁻¹ to, for ex. 1698 cm⁻¹ in di-t-butylketone.
- Ketenes have very strong carbonyl group as the inner carbon is sp hybridised and is not the usual sp². The more s-character in a bond, the stronger it is, therefore ketene absorb in the I.R at very high frequency (~2150 cm⁻¹)



$H_2C=C=O$

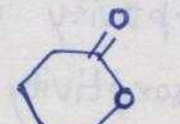
C=O str ≃ 2150 cm⁻¹

- In cyclic esters (lactones), the carbonyl stretching frequency increases with increase in the ring strain.

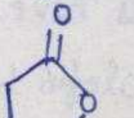


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

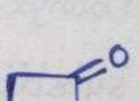
ethyl acetate
(1735 cm⁻¹)
(no strain)



δ-Valerolactone
(1735 cm⁻¹)

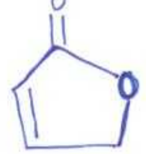


γ-butyrolactone
(1770 cm⁻¹)



highly strained.

β-propiolactone
(1800 cm⁻¹)



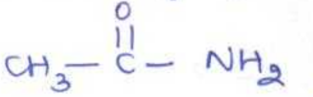
C=O str $1750\ cm^{-1}$ (more conjugation so less C=O str)

$1800\ cm^{-1}$

here the C=O str depends on the location of the double bonds.

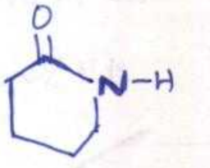
~~Ring~~

- Ring strain in a cyclic amide (lactam) increases the carbonyl stretching frequency.

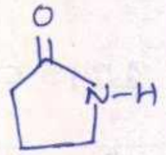


$CH_3-\overset{\overset{O}{||}}{C}-NH_2$,

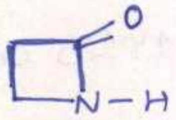
acetamide ($1680\ cm^{-1}$) (no strain)



δ-Valerolactam $1670\ cm^{-1}$ (no strain)

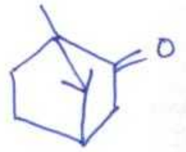


γ-butyrolactam $1700\ cm^{-1}$ (moderate strain)

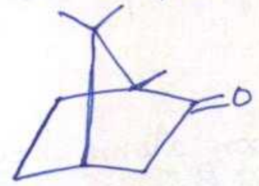


β-propiolactam $1745\ cm^{-1}$ (highly strained)

→ Effect of ring strain in bicyclic systems:-

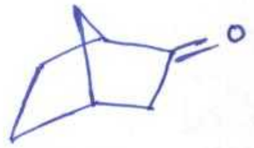


≡

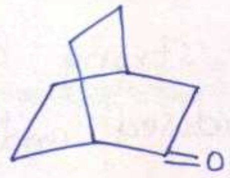


C=O str. $1740\ cm^{-1}$

The C=O group of camphor which is part of a five-membered ring displays its stretching frequency at $1740\ cm^{-1}$ and C=O str is not according to six membered ring.



(norborane) $1750\ cm^{-1}$



C=O str = $1731\ cm^{-1}$

A carful examination of the structure of this bicyclic ketone shows, that its six-membered rings is in a boat conformation rather than a chair.

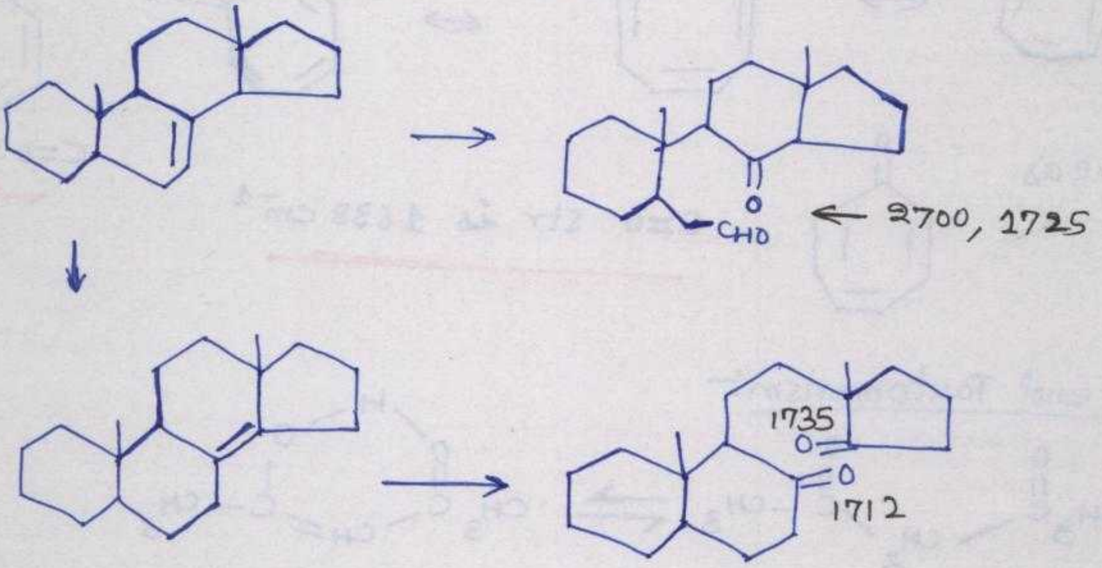
* Detection of double bonds via conversion to carbonyl compds:-

Carbonyl compds have absorptivity of several hundred whereas a tri substituted olefin has absorptivity of only five. Thus it is possible that the expected absorption of a double bond may not be detectable where as the carbonyl group in the same molecule gives a very strong absorption.

→ A trisubstituted double bond $(-\overset{|}{C}=\overset{H}{\overset{|}{C}}-)$ is difficult to detect from its I.R. becoz its C=C str is very weak.

→ A tetra substituted double bond being symmetrical gives no C=C str and also no C-H bending bands.

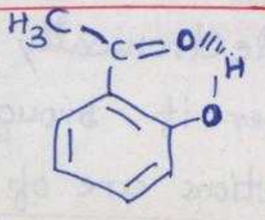
→ The position of isolated tri- or tetra substituted double bond may be located by refluxing the compound with Osmium tetra oxide in ether and by subsequent reduction of osmate ester with $LiAlH_4$ and cleaving diols with $Pb(OAc)_4$. The resulting compound is often scanned in reliable carbonyl region.



- Effect of hydrogen bonding and enols:→

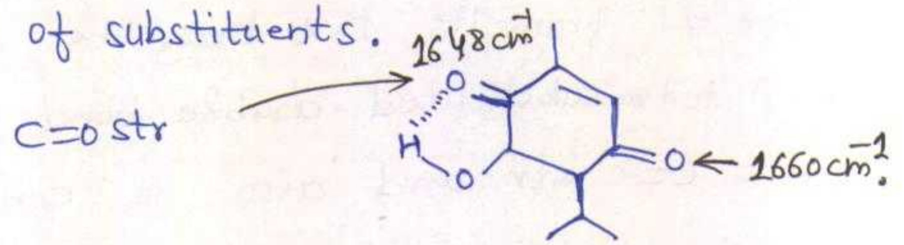
→ When a carbonyl group is involved in hydrogen bonding its C=O str freq is lowered. As a result of intermolecular hydrogen bonding betn a ketone and a hydroxylic solvent.

→ Intra-molecular H-bonding lowers C=O str by about 50 cm⁻¹. This lowering, is however dependent on the strength of the hydrogen bond.

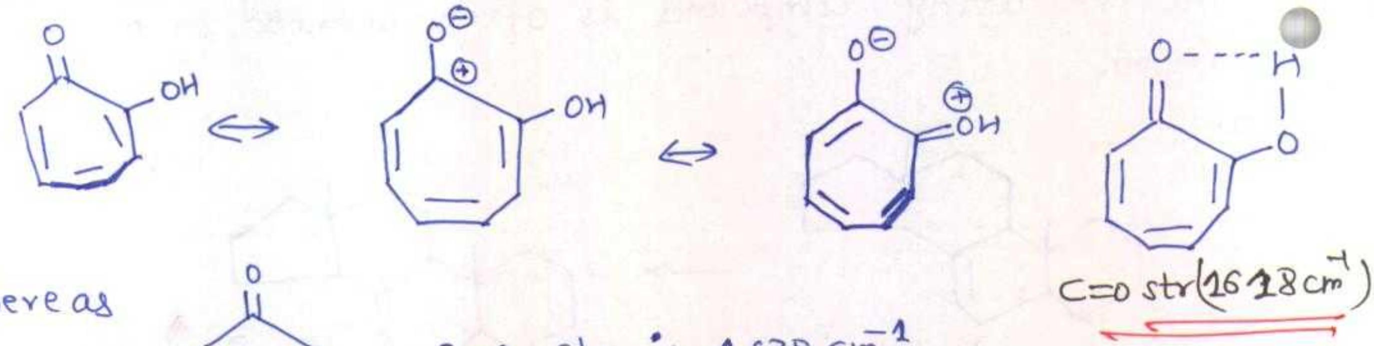


C=O str = 1634 cm⁻¹

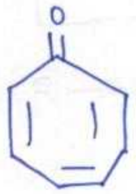
→ A 1,4 or 1,2-quinone shows a band around 1675 cm^{-1}. The position of this band gets lowered considerably by the electrical effects of substituents.



→ The comparatively lower C=O frequency in tropolone as compared with tropone is again due to strong intra molecular hydrogen bond betⁿ the carbonyl oxygen and the hydroxylic proton.



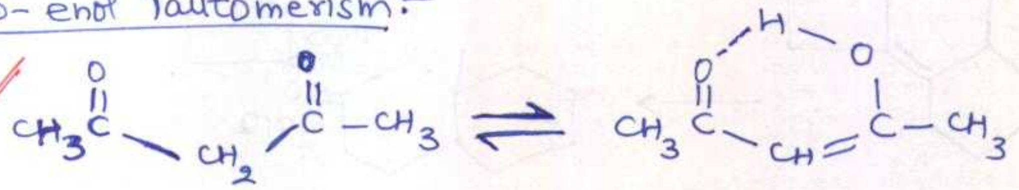
whereas



C=O str is 1638 cm^{-1}

* Keto-enol Tautomerism:-

Note



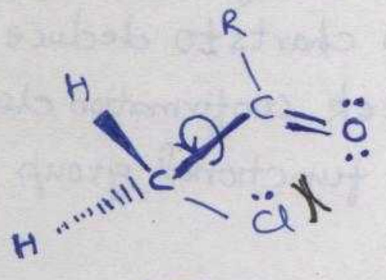
two C=O groups so two peaks near 1700 cm^{-1}

only one C=O group and its stretching is lowered by 100-80 cm^{-1} due to hydrogen bonding and conjugation. It also gives one C=C str

* Field Effects:-

→ Two or more polar groupings situated in the same molecule but insulated electronically from each other by single bonds, influence one another if brought close together. These dipolar, non-bonded interactions are of electrostatic origin.

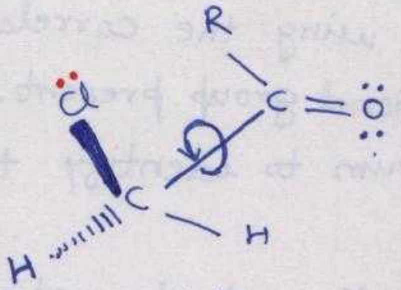
- A simple acyclic α-haloketone, $RCOCH_2X$ is normally free to adopt several conformations,



(cis)

non bonded repulsion

C=O str, X=Br 1740 cm^{-1}



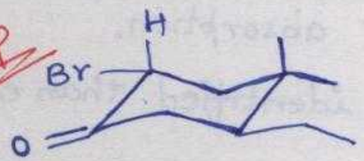
(trans)

normal C=O str

X=Br, 1720 cm^{-1}

The coplanar, opposed conformer (cis) is found to have a higher carbonyl frequency. However, two carbonyl frequencies are displayed proving that both roational isomers are present

- gmp



raised C=O str (1733 cm^{-1})

When Br is near the oxygen, its negative field repels the non-bonding electrons of the oxygen atoms, as a consequence the force constant of the C=O bond is increased.

* Unsaturated Nitrogen compounds → they absorb in the 2300-2000 cm^{-1} region of the spectrum.

→ stretching of the C≡N bond in aliphatic nitriles shows a band at $\boxed{2260-2240}$ cm^{-1}, which is shifted to lower freq. with a double bond or aromatic ring. Conjugation also tends to increase the intensity of the band which is very strong in, for ex, benzonitrile.

→ Any substituent which tends to decrease the dipole moment of the bond would be expected to produce a decrease in the intensity and vice-versa.

→ Isocyanates display a very intense absorption band near 2275-2240 cm^{-1}.

* Axial and equitorial chlorine, and also bromine, in cyclohexanes and steroids, can be differentiated since the equitorial C-X bond absorbs at a higher frequency.

* Structural diagnosis:-

→ Pick out the strong bands, particularily in the functional group region (4000 - 1500 cm^{-1}) using the correlation charts to deduce which are the functional group present. Seek confirmation else where in the spectrum to identify the functional group correctly.

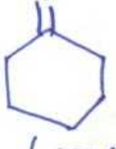
- Confirm this with other spectroscopic and chemical data.

→ A functional group which display many characteristic absorptions can usually be identified more definately than a function that gives rise to only one characteristic absorption.
Thus ketones (C=O str) are less easily identified than esters [C=O str and C-O str];
esters are less easily identified than amides [C=O str, N-H stretching, N-H bending and so on]

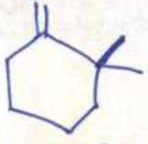
→ Similar compounds no doubt have similar spectra but exact correspondence is only possible if samples are identical.

- The individual (+) or (−) optical isomers of an enatiomeric pair always give identical spectra.
- The racemic mixture however, may show differences in the solid state which, of course, dissappear in solution.
- The comparison by infrared method therefore, excludes the tedious resolution of the racemic mixture e.g., at the end of a synthesis and provides an excellent method of comparison of an optically active natural product with the racemic product.

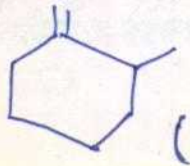
→ Many cyclohexanones show their C=O str frequencies in the range where medium ring size ketones absorb (~ 1705 cm^{-1}) and in all such cases the α- carbons are highly alkylated.



C=O str. (1714 cm^{-1})

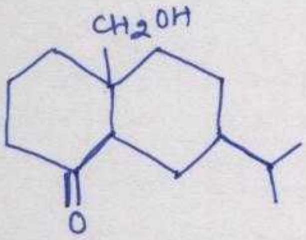


(1702 cm^{-1})



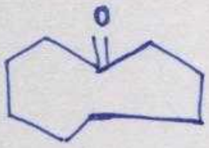
(1715 cm^{-1})

Ex.) Hydroxy - Valeranone is a typical 2,2-alkyl substituted cyclohexanone and shows its stretching frequency at 1692 cm^{-1}

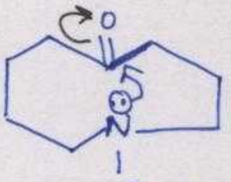


C=O str 1692 cm^{-1}

→ Abnormal C=O str frequencies have been shown by several medium - sized rings which contain a nitrogen atom as in the figure given below. This is due to transannular electron donation from the hetero atom to the carbonyl group.



C=O str. (1705 cm^{-1})



(1670 cm^{-1})