

INFRARED SPECTROSCOPY

SEM-4, CC-8
PART-5, PPT-11

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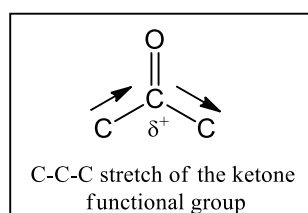
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INFRARED SPECTROSCOPY (PART-5, PPT-11)

Absorptions of Ketones ($RR^1C=O$)

C=O Stretching Vibrations: The C=O stretch appears at 1715 cm^{-1} and, for saturated ketones, in general, this vibration occurs at $1715\pm 10\text{ cm}^{-1}$.

C-C-C Stretching Vibration: Saturated ketones show moderate absorption in the $1230\text{-}1100\text{ cm}^{-1}$ region as a result of C-C-C stretching in the C-CO-C group. This stretch involves the asymmetric stretching of the two alpha carbon C-C bonds.



For the acetone molecule, this vibration involves one methyl group moving toward the carbonyl carbon while the second methyl group moves away. In hydrocarbons, C-C stretching vibrations are weak because of the small (or non-existent) dipole moment of these bonds. However, the carbonyl carbon has a partial positive charge on it, and any C-C bond that includes the carbonyl carbon will have a significant dipole moment. The C-C-C stretch in the spectrum of acetone is seen at 1222 cm^{-1} . Aromatic ketones absorb at the higher frequency. The C-C-C stretch of benzophenone appears at 1264 cm^{-1} .

Absorptions of Aryl Ketones ($RCOAr$)

An aryl ketone can be distinguished from a saturated ketone based on the position of the C=O and C-C-C stretches. In the spectrum of an aryl ketone, e.g., acetophenone, the C=O stretching wavenumber is lowered by conjugation with the benzene ring and appears at 1684 cm^{-1} . For mixed ketones, the C=O stretch appears in the $1700\text{-}1670\text{ cm}^{-1}$ region.

The C-C-C stretch of acetophenone is at 1266 cm^{-1} , and generally appears for mixed ketones in the $1300\text{-}1230\text{ cm}^{-1}$ region.

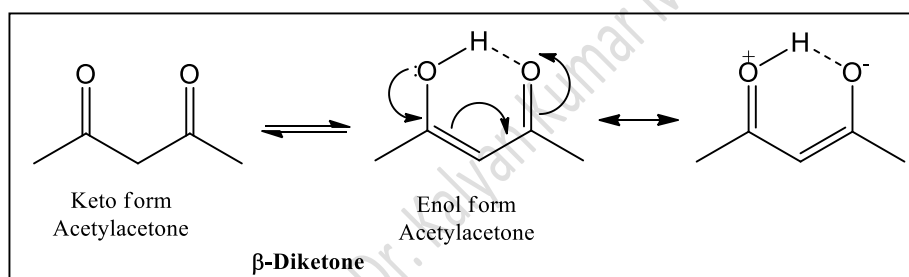
For a diaryl ketone, conjugation has an even greater impact on the position of the C=O stretch than in a mixed ketone. The C=O stretch of diphenylketone (benzophenone) occurs at 1652 cm^{-1} . For most diaryl ketones, this band appears in the $1680\text{ and }1600\text{ cm}^{-1}$ region. The C-C-C stretch of benzophenone appears at 1264 cm^{-1} and, for diaryl ketones, is generally found in the $1300\text{-}1230\text{ cm}^{-1}$ region.

Absorption of Diketones

α -Diketones (RCOCOR^1): α -Diketones, in which carbonyl groups exist in formal conjugation, show a single absorption band near the frequency observed for the corresponding mono-ketone. Biacetyl ($\text{CH}_3\text{COCOCH}_3$) absorbs at 1718 cm^{-1} . If the two carbonyl groups are conjugated with aromatic rings, the absorption is shifted to a lower frequency. Benzil (PhCOCOPh) absorbs at 1681 cm^{-1} . Conjugation is ineffective for α -diketones and the $\text{C}=\text{O}$ groups of these diketones do not couple as do the corresponding groups in acid anhydrides.

β -Diketones ($\text{RCOCH}_2\text{COR}^1$): β -Diketones usually exist as mixtures of tautomeric keto and enol forms. The enolic form does not show the normal absorption of conjugated ketones. Instead, a broad band appears in the $1640\text{-}1580\text{ cm}^{-1}$ region, many times more intense than normal carbonyl absorption. The intense and displaced absorption results from intramolecular hydrogen bonding, the bonded structure being stabilized by resonance.

Absorption of β -Diketones



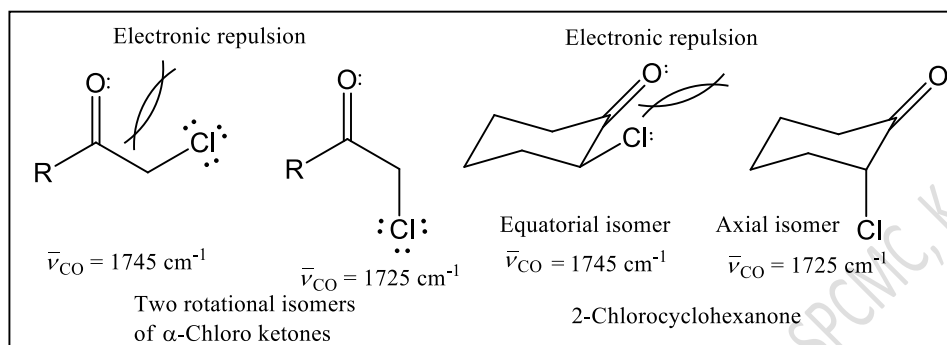
Acetylacetone as a liquid at 40°C exists to the extent of 64% in the enolic form that absorbs at 1613 cm^{-1} . The keto form and a small amount of unbonded enolic form may be responsible for two bands centering near 1725 cm^{-1} . Interaction between two carbonyl groups in the keto form splits the absorption band into a doublet. The enolic O-H stretching absorption is seen as a broad shallow band at $3000\text{-}2700\text{ cm}^{-1}$.

Absorption of α -Chloro Ketones (RCOCH_2Cl)

Acyclic α -chloro ketones absorb at two frequencies due to rotational isomerism. When the chlorine atom is near the oxygen, its negative field repels the non-bonding electrons of the oxygen atom, thus increasing the force constant of the $\text{C}=\text{O}$ bond. This conformation absorbs at a higher frequency (1745 cm^{-1}) than that in which the carbonyl oxygen and chlorine atom are widely separated (1725 cm^{-1}).

Six-membered cyclic α -chloro ketones, such as 2-chlorocyclohexanone exists in two conformers. In the equatorial orientation, the chlorine atom is near the carbonyl group and the "field effect" causes an increase in the $\text{C}=\text{O}$ stretching frequency. In the axial orientation, the chlorine atom is distant from the $\text{C}=\text{O}$, no shift is observed.

Absorptions of Ketones



The Group wavenumbers of Ketones (all numbers in cm^{-1})

Vibration	Wavenumber Range
Saturated C=O stretch	1725-1705
Aromatic C=O stretch	1700-1640
Saturated C-C-C stretch	1230-1100
Aryl/Alkyl and Diaryl C-C-C stretch	1300-1230

Absorptions of Aldehydes (R-CH=O)

C=O Stretching Vibrations: The C=O groups of aldehydes absorb strongly at slightly higher frequencies than that of the corresponding methyl ketones. Aliphatic aldehydes absorb near $1740\text{-}1720 \text{ cm}^{-1}$. Aldehydes C=O absorption responds to structural changes in the same manner as ketones. Electronegative substitution on the α carbon increases the frequency of C=O absorption. Acetaldehyde absorbs at 1730 cm^{-1} , whereas trichloroacetaldehyde absorbs at 1768 cm^{-1} .

Conjugation of C=O with the C=C bond, as in α,β -unsaturated aldehydes and aromatic aldehydes, reduces the frequency of C=O absorption. C=O stretch of these aldehydes shows up in the $1710\text{-}1685 \text{ cm}^{-1}$ region. Intramolecular hydrogen bonding, such as occurs in salicylaldehyde, shifts the absorption (1666 cm^{-1} for salicylaldehyde) to lower wavenumbers.

Glyoxal (O=CH-CH=O), like the α -diketones (RCOCOR), shows only one carbonyl absorption peak with no shift from the normal absorption position of mono-aldehyde absorption.

C-H Stretching Vibrations: One of the most important group wavenumbers for aldehydes is the C-H stretching vibration of the aldehydic hydrogen. The aldehydic C-H stretch occurs in the 2850-2700 cm^{-1} region as a pair of bands which is lower than most other C-H stretches.

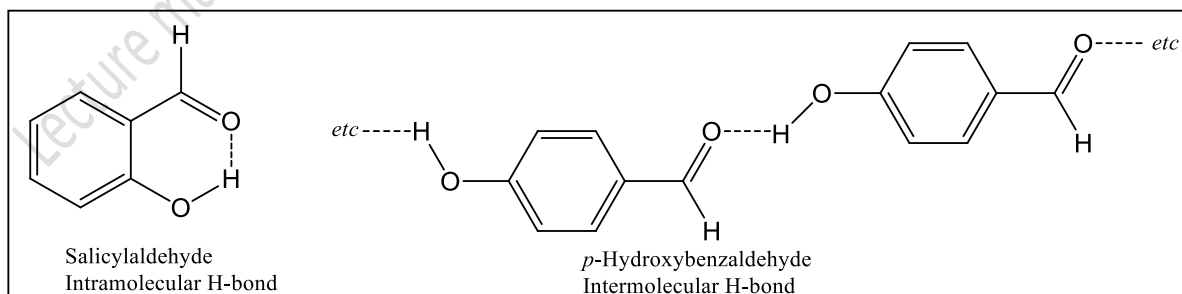
The appearance of two bands (at ~ 2820 and ~ 2720 cm^{-1}) with almost equal intensity for aldehydic C-H stretch is attributed to Fermi resonance between the fundamental aldehydic C-H stretch and the first overtone of the aldehydic C-H bending vibration (which appears near 1390 cm^{-1}).

C-H Bending Vibration: C-H bending vibration appears at 1400-1380 cm^{-1} with medium to weak intensity. The carbonyl group and the two substituents in an aldehyde all lie in the same plane. Thus, this C-H bending vibration is an *in-plane* vibration.

C-C Stretching Vibrations (-C-CO): The large dipole moment of the carbonyl group causes the C-C bond in an aldehyde to have an appreciable dipole moment. The stretching of this bond gives rise medium intensity bands in the 1400-1100 cm^{-1} . For aromatic aldehydes, the stretching of the C-C bond of the group -C-CO- gives a medium intensity band in the 1210-1160 cm^{-1} region.

The Group wavenumbers of Aldehydes (all numbers in cm^{-1})	
Vibration	Wavenumber Range
Saturated C=O stretch	1740-1720
Aromatic C=O stretch	1710-1685
C-H Bend	1400-1380
Aldehydic C-H stretch	2850-2700, 2 bands
C-C stretch	1400-1100

Salicylaldehyde versus *p*-Hydroxybenzaldehyde



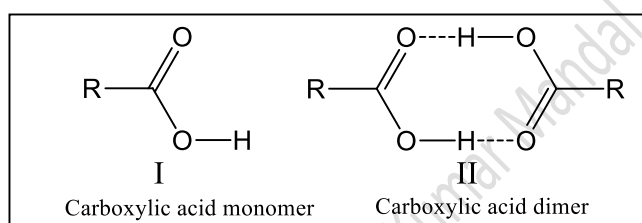
- Lower $\bar{\nu}_{\text{O-H}}$ and $\bar{\nu}_{\text{C=O}}$ for salicylaldehyde compared to *p*-hydroxybenzaldehyde
- Formation of intramolecular H-bonding in salicylaldehyde, whereas intermolecular H-bonding in *p*-hydroxybenzaldehyde

- **Effect of dilution:** No change in frequency of $\bar{\nu}_{\text{O-H}}$ and $\bar{\nu}_{\text{C=O}}$ absorptions for salicylaldehyde but $\bar{\nu}_{\text{O-H}}$ and $\bar{\nu}_{\text{C=O}}$ absorption frequencies of *p*-hydroxybenzaldehyde increase on dilution.

Carboxylic Acids (RCO-OH)

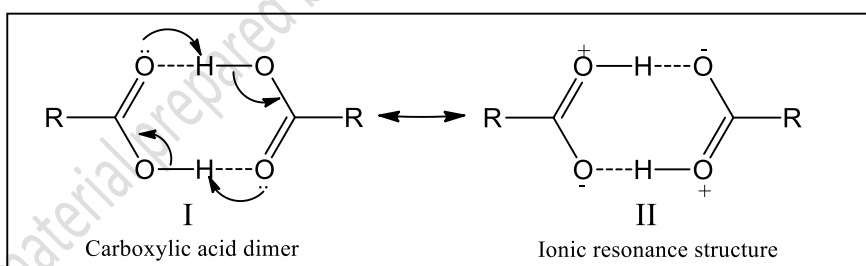
Carboxylic acids are partly similar to alcohols in one hand and partly carbonyl on the other in that they all contain the O-H and C=O groups. This structural unit is responsible for hydrogen bonding. The hydrogen bonds in carboxylic acids are so strong that the acid molecules are bound together in dimers (II) when in the solid and liquid state. The -OH group of one molecule hydrogen bonds to the C=O of a second molecule, and vice versa.

Carboxylic acids are found only in monomeric (I) form in the vapour phase and in dilute solution of a non-polar solvent.



Absorptions of Carboxylic acids (RCO-OH)

O-H Stretching Vibrations: In the liquid or solid state, and in CCl₄ solution at concentrations much over 0.01 (*M*), carboxylic acids exist as dimer (I) due to strong hydrogen bonding.



The exceptional strength of the hydrogen bond is explained on the basis of the large contribution of the ionic resonance structure (II). Because of this strong bonding, a free O-H stretching vibration (near 3520 cm⁻¹) is observed only in a very dilute solution in non-polar solvents or in the vapour phase. Carboxylic acid dimers (I) display very broad, intense O-H stretching absorption in the region of 3300-2500 cm⁻¹ (centres near 3000 cm⁻¹).

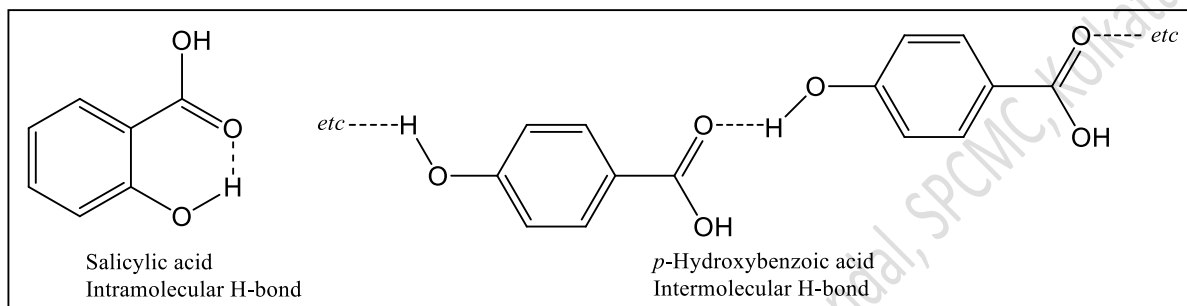
Absorptions of Carboxylic acids (RCO-OH)

C=O Stretching Vibrations: The monomers of saturated aliphatic acids absorb near 1760 cm⁻¹ which is more intense than ketonic C=O stretching bands. The carboxylic acid dimer has a centre of symmetry; only the asymmetrical C=O stretching mode absorbs in the IR. Hydrogen bonding and resonance weaken the C=O bond, resulting in absorption at a lower

frequency than the monomer. The C=O group in dimerized saturated aliphatic acids absorb in the region of 1720-1705 cm^{-1} .

Intramolecular hydrogen bonding reduces the frequency of the carbonyl stretching absorption to a greater degree than does intermolecular hydrogen bonding. For example, salicylic acid absorbs at 1665 cm^{-1} , whereas *p*-hydroxybenzoic acid absorbs at 1680 cm^{-1} .

Absorptions of Aromatic Carboxylic acids

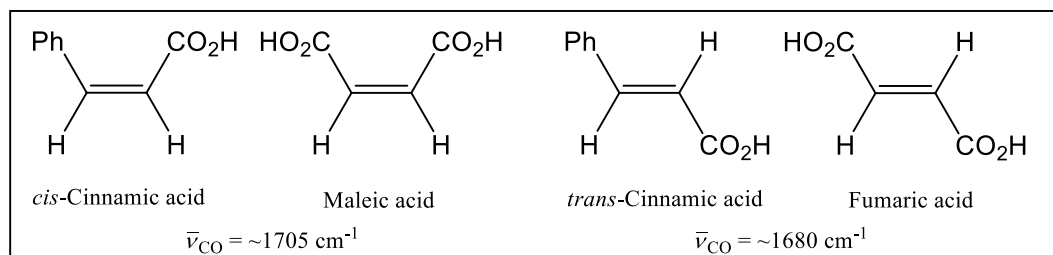


Unsaturation in conjugation with the carboxyl group (presence of $-\text{C}=\text{C}-\text{COOH}$ unit) decreases the frequency of C=O absorption of both the monomer, and the dimer forms only slightly. In general, α,β -unsaturated and aryl conjugated acids show absorption for the dimer in the 1710-1680 cm^{-1} region.

IR Spectra of *cis/trans* Isomers

In *cis-trans* isomers of an acid, small differences in C=O absorptions are usually observed. But in case of *cis/trans* cinnamic acid, maleic acid/fumaric acid etc., C=O absorption frequencies differ to a greater extent.

C=O Stretching vibration of *cis*-cinnamic acid absorbs at a higher wavenumber than that of the corresponding *trans* isomer. It is due to the steric effect caused by the bulky groups on the same side of the double bond. Due to repulsive interactions, the C=O part of $-\text{COOH}$ group goes out of the plane of the C=C bond. Thus, conjugation diminishes and hence C=O absorption occurs at a higher wavenumber. Similar explanation can be given to the C=O absorptions of maleic acid and fumaric acid.



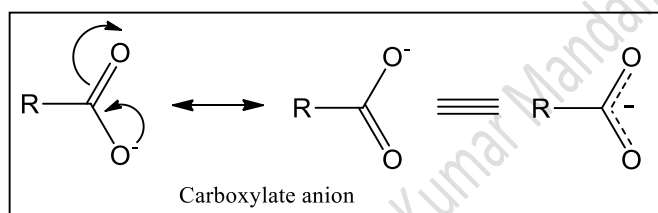
Absorptions of Carboxylic acids (R-CO-OH)

C-O Stretching and O-H Bending Vibrations: Two bands arising from C-O stretching and O-H bending appear in the spectra of carboxylic acids near 1320-1210 and 1440-1395 cm^{-1} , respectively. Both of these bands involve some interaction between C-O stretching and in-plane C-O-H bending. The more intense band, near 1315-1280 cm^{-1} for dimers, is generally referred to as the C-O stretching band.

The C-O-H bending band near 1440-1395 cm^{-1} is of moderate intensity and occurs in the same region as the CH_2 scissoring vibration of the CH_2 group adjacent to the carbonyl.

Absorptions of Carboxylate Anion (R-CO-O⁻)

The carboxylate anion has two strongly coupled bonds with bond strengths intermediate between C=O and C-O.



The carboxylate ion gives rise to two bands: a strong asymmetrical stretching band near 1650-1550 cm^{-1} and a weaker, symmetrical stretching band near 1400 cm^{-1} . The conversion of a carboxylic acid to a salt can serve as confirmation of the acid structure. The O-H stretching band, of course, disappears.

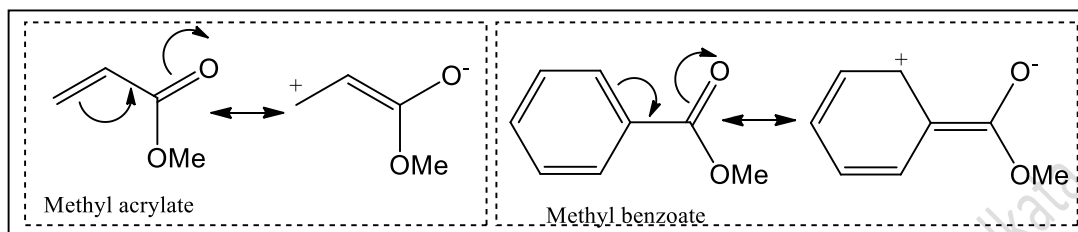
Absorptions of Esters (R-CO-OR¹) and Lactones

Esters and lactones have two characteristically strong absorption bands arising from C=O and C-O stretching. The intense C=O stretching vibration occurs at higher frequencies than that of normal ketones. The force constant of the carbonyl bond is increased by the electron-attracting nature of the adjacent oxygen atom (inductive effect). The frequency of the ester carbonyl responds to environmental changes in the vicinity of the carbonyl group in much the same manner as ketones. A distinguishing feature of esters and lactones, however, is the strong C-O stretching band in the region where a weaker band occurs for ketones.

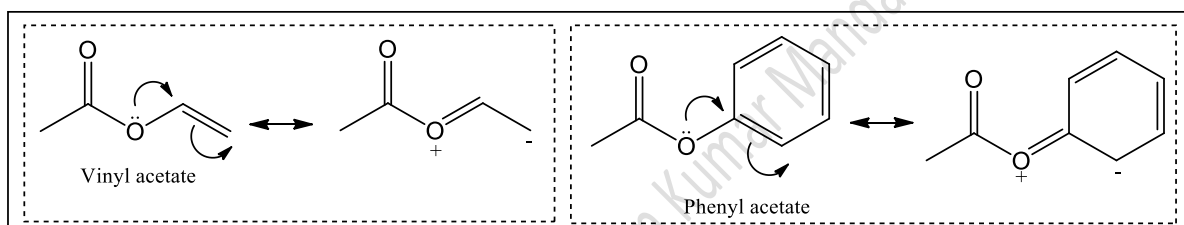
Absorptions of Esters (R-CO-OR¹)

C=O Stretching Vibrations: The C=O absorption band of saturated aliphatic esters (except formates) is in the 1750-1735 cm^{-1} region. The C=O absorption bands of formates, α,β -unsaturated and benzoate esters are in the region of 1730-1715 cm^{-1} . Further conjugation has little or no additional effect upon the frequency of the carbonyl absorption.

If the carbonyl group is in conjugation with a double bond or on aromatic ring (such as in the acrylates, $\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$, or in the benzoates, $\text{Ph}-\text{CO}-\text{O}-$), the $\text{C}=\text{O}$ absorption frequency is lowered to near 1720 cm^{-1} . $\text{C}=\text{O}$ acquires some single bond character due to conjugation, bond order decreases, $\bar{\nu}_{\text{CO}}$ is lowered.

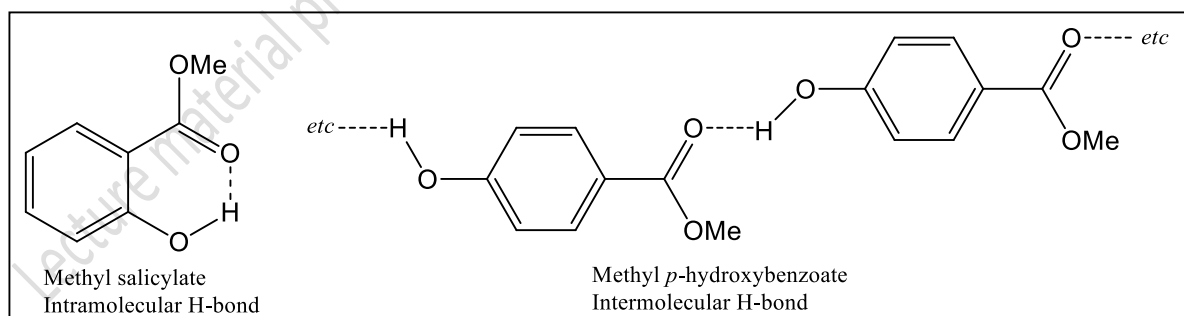


In contrast, for esters containing the groupings $-\text{CO}-\text{O}-\text{CH}=\text{CH}_2$ or $-\text{CO}-\text{O}-\text{Ar}$ (such as vinyl or phenyl esters), the $\text{C}=\text{O}$ stretching band appears at much higher frequency, near 1770 cm^{-1} . In contrast, for esters containing the groupings $-\text{CO}-\text{O}-\text{CH}=\text{CH}_2$ or $-\text{CO}-\text{O}-\text{Ar}$ (such as vinyl or phenyl esters), the $\text{C}=\text{O}$ stretching band appears at much higher frequency, near 1770 cm^{-1} .



Absorptions of Esters

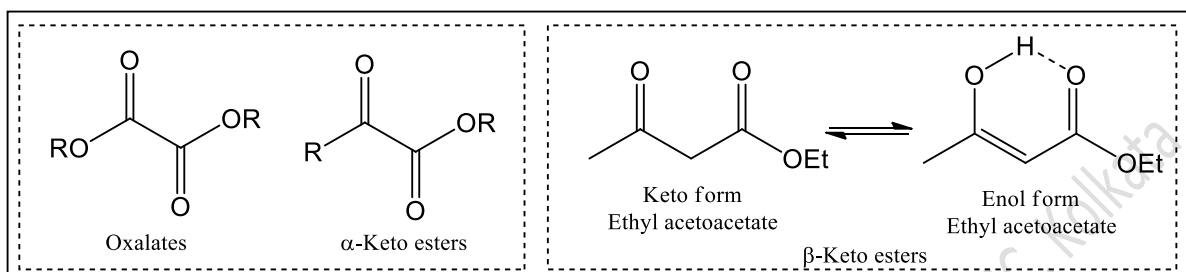
Besides conjugation, chelation of the $\text{C}=\text{O}$ group to a nearby $-\text{OH}$ group lengthens and weakens the $\text{C}=\text{O}$ bond even further and the $\text{C}=\text{O}$ stretching frequency moves to near 1680 cm^{-1} . The lower value of $\text{C}=\text{O}$ stretching vibration is due to the conjugation of $\text{C}=\text{O}$ with $\text{C}=\text{C}$ as well as formation of intramolecular hydrogen bond. Both the factors cause weakening of the $\text{C}=\text{O}$ bond strength.



Absorptions of Keto Esters

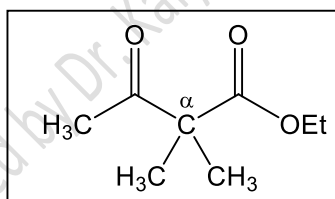
In oxalates and α -keto esters ($\text{R}-\text{CO}-\text{CO}_2\text{R}^1$), as in α -diketones, there appears to be little or no interaction between the two carbonyl groups so that normal absorption occurs in the region of $1755\text{--}1740\text{ cm}^{-1}$.

In the spectra of β -keto esters ($\mathbf{R-COCH_2CO_2R^1}$), however, where enolization can occur, a band is observed near 1650 cm^{-1} that results from bonding between the ester $\text{C}=\text{O}$ and the enolic hydroxyl group. The lower value of $\text{C}=\text{O}$ stretching vibration is due to the conjugation of $\text{C}=\text{O}$ with $\text{C}=\text{C}$ as well as formation of intramolecular hydrogen bond. Both the factors cause weakening of the $\text{C}=\text{O}$ bond strength.



Absorptions of β -Keto Esters

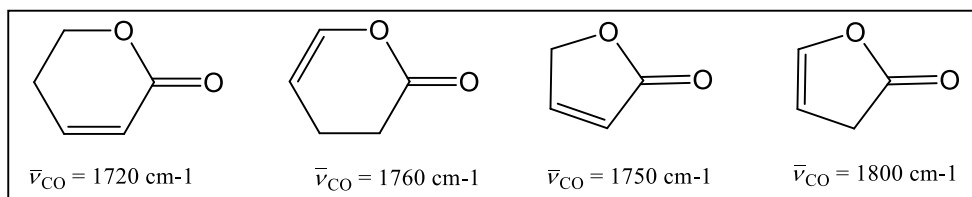
This type of enolization occurs for compounds having active methylene group (a $-\text{CH}_2-$ unit flanked between two $\text{C}=\text{O}$ groups). β -keto esters containing no active methylene group [such as $\text{CH}_3\text{COC}(\text{CH}_3)_2\text{CO}_2\text{Et}$] absorb separately for keto carbonyl and ester carbonyl at their normal regions (1715 cm^{-1} and 1740 cm^{-1} , respectively). This is because of the absence of the enolic structure.



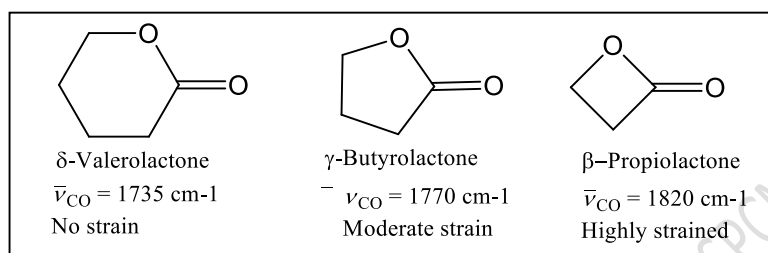
Absorptions of Lactones

The $\text{C}=\text{O}$ absorptions of saturated δ -lactones (six-membered ring) occurs in the same region as straight-chain, unconjugated esters. Unsaturation α to the $\text{C}=\text{O}$ reduces the $\text{C}=\text{O}$ absorption frequency. Unsaturation α to the $-\text{O}-$ group increases it. Saturated γ -lactones (five-membered ring) absorb at higher frequency than esters or δ -lactones: $1795\text{--}1760\text{ cm}^{-1}$; γ -valerolactone absorbs at 1770 cm^{-1} . Unsaturation in the γ -lactone molecule affects the $\text{C}=\text{O}$ absorption in the same manner as unsaturation in δ -lactones.

In unsaturated lactones, when the double bond is adjacent to the $-\text{O}-$, a strong $\text{C}=\text{C}$ absorption is observed in the $1685\text{--}1660\text{ cm}^{-1}$. As is the case with unsaturated acetates, in the case of lactones as well, their $\text{C}=\text{O}$ stretching depends on the location of the double bonds.



When the ring is strained, the interaction with C-C bond leads to an increase in the energy needed to produce C=O stretching and as a consequence C=O stretching frequency increases.



C-O stretching Vibrations of Esters (R-CO-OR¹) and Lactones

C-O Stretching Vibrations: The C-O stretching vibrations of esters actually consists of two asymmetric coupled vibrations: C-C(=O)-O and O-C-C, the former being more important. These bands occur in the region of 1300-1050 cm⁻¹.

The C-C(=O)-O band of saturated esters, except for acetates, shows strongly in the 1210-1163 cm⁻¹ region. It is often broader and stronger than the C=O stretch absorption. Acetates of saturated alcohols display this band at 1240 cm⁻¹. Vinyl and phenyl acetates absorb at somewhat lower frequency, 1190-1140 cm⁻¹. Esters of aromatic acids absorb strongly in the 1310-1250 cm⁻¹ region. The C-O stretch in lactones is observed in the 1250-1111 cm⁻¹.

The O-C-C band of esters of primary alcohols occurs at about 1064-1031 cm⁻¹ and that of esters of secondary alcohols at about 1100 cm⁻¹. Aromatic esters of primary alcohols show this absorption near 1111 cm⁻¹.

Absorptions of Anhydrides (R-CO-O-CO-R¹)

Anhydrides display two strong stretching bands at the higher frequency end of the C=O stretching region. The two bands result from symmetrical and asymmetrical mode. The doublet appears because of the coupled vibrations of two C=O groups. In saturated acyclic anhydride, the two bands appear in the 1850-1800 cm⁻¹ and 1790-1740 cm⁻¹.

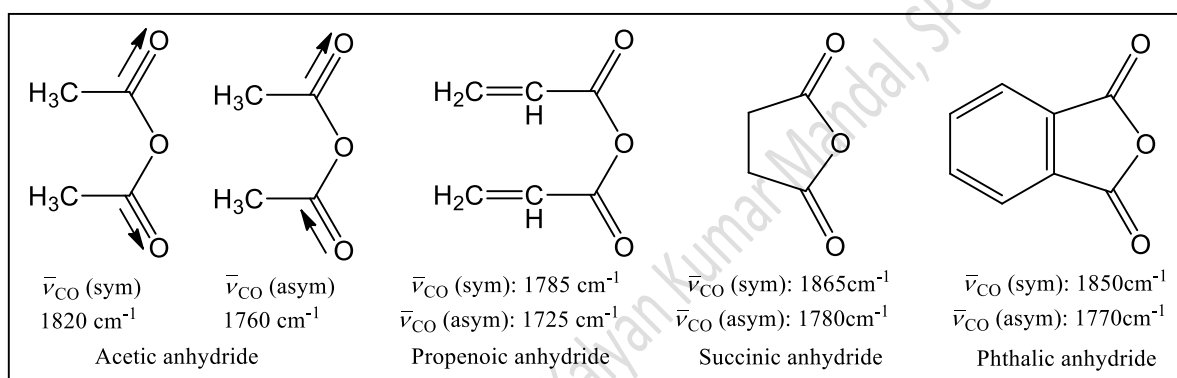
C=O Stretching Vibrations (Acyclic anhydride): The higher frequency band is due to the symmetric C=O stretching vibration, and in open chain anhydrides it is always of higher intensity than the lower frequency band arising from asymmetric vibrations.

Saturated acyclic anhydrides e.g., acetic anhydride, absorb near 1820 and 1760 cm⁻¹. Conjugated acyclic anhydrides show absorption near 1785 and 1725 cm⁻¹; the decrease in the

frequency of absorption is due to resonance. The higher frequency bands are the more intense in case of acyclic anhydrides.

C=O Stretching Vibrations (Cyclic anhydride): In cyclic anhydrides the high frequency band is always the weaker of the two and it diminishes in intensity with increasing ring strain, i.e., a five-membered ring anhydride exhibits a weaker high frequency absorption band than a six-membered ring anhydride.

Cyclic anhydrides with five-membered rings show absorption at higher frequencies than acyclic anhydrides because of ring strain; succinic anhydride absorbs at 1865 (sym) and 1780 cm^{-1} (asymm). The lower frequency C=O band is the stronger of the two carbonyl bands in five-membered ring cyclic anhydrides. This effect has been explained on the basis of a decreased dipole moment change in the symmetric vibrational mode when constrained in a cyclic system.



C-O Stretching Vibrations: Open chain and cyclic anhydrides show a strong band in the 1170-1050 cm^{-1} and 1300-1175 cm^{-1} regions respectively, arising from a C-O-C stretching vibration for the group -CO-O-CO-. Unconjugated straight chain anhydrides absorb near 1047 cm^{-1} . The C-O stretching band for acetic anhydride appears at 1125 cm^{-1} . Cyclic anhydrides display bands near 950-910 cm^{-1} and 1300-1175 cm^{-1} .

Coupling Interaction in Anhydrides

Coupling occurs between two carbonyl groups in anhydrides, which are directly linked through -O-; the interaction is encouraged because of the slight double-bond character in the carbon-oxygen bonds brought about by resonance, since this will keep the system coplanar.

