# Quadrant II – Transcript and Related Materials

**Programme: T.Y.B.Sc. (Chemistry)**

**Subject: Chemistry**

**Course Code: CHC 107 (Section A)**

**Course Title: Organic Chemistry**

**Unit: 03- Spectroscopic methods in Organic Chemistry**

**Module Name: Effect of H-bonding, conjugation, resonance, ring size on IR absorption. Problems based on IR spectroscopy (ketone, aldehyde, ester, acid and alcohol)**

**Module No: 20**

**Name of the Presenter: Ms. Anuja B. Naik**

## Notes

Transcript of the video

Hello students, I am Ms. Anuja Naik from Ganpat Parsekar College of Education, Harmal, Pernem Goa and I will be dealing with Effect of H-bonding, conjugation, resonance, ring size on IR absorption. Problems based on IR spectroscopy (ketone, aldehyde, ester, acid and alcohol).

The lecture deals with,

- ✓ Effect of H-bonding on IR absorption
- ✓ Effect of conjugation on IR absorption
- ✓ Effect of resonance on IR absorption
- ✓ Effect of ring size on IR absorption
- ✓ Problems based on IR spectroscopy (ketone, aldehyde, ester, acid and alcohol)

So, at the end of the lecture, the student will be able to:

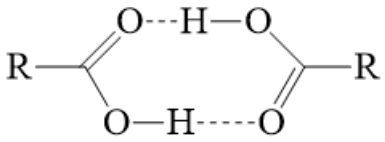
- ✓ Explain the effect of H-bonding on IR absorption

- ✓ Explain the effect of conjugation on IR absorption
- ✓ Explain the effect of resonance on IR absorption
- ✓ Explain the effect of ring size on IR absorption
- ✓ Solve the problems based on IR spectroscopy with respect to ketone, aldehyde, ester, acid and alcohol

**Effect of H-bonding on IR Absorption**

- ✓ Hydrogen bonding brings about changes in frequency shifts.
- ✓ Stronger the Hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value.
- ✓ For example, alcohol in the vapour state (isolated molecule) shows O-H str at about 3600 $cm^{-1}$ whereas that in the associated form gives a broad absorption band at 3200 $cm^{-1}$.
- ✓ Stronger the hydrogen bonding, more broadening of the band at much lower wave number.
- ✓ As Nitrogen is less electronegative than an Oxygen atom, hydrogen bonding in amines is weaker than that in alcohols and thus the frequency shifts in amines.
- ✓ Amines show N-H stretching at 3500 $cm^{-1}$ in dilute solutions while in condensed phase spectra, absorption occurs at 3300 $cm^{-1}$.
- ✓ In aliphatic alcohols, a sharp band appears at 3650 $cm^{-1}$ in dilute solutions due to free O-H group while a broad band is noticed at 3350 $cm^{-1}$ due to hydrogen bonded O-H group.
- ✓ Alcohols are strongly hydrogen bonded in condensed phases (dimers and polymers) which result in the broadening of bands at lower absorption frequencies.
- ✓ In vapour state or in inert solvents, molecules exist in free state and absorbs strongly at 3650 $cm^{-1}$.
- ✓ The band due to free O-H group is usually less intense while that due to bonded O-H group is broad and sharp.

- ✓ The carboxylic acid O-H stretch is extremely broad and often spans the region from 3400 to 2400 $cm^{-1.}$ This band arises from the strong hydrogen bonding present in the carboxylic acid dimer and is characteristic of carboxylic acids.




Hydrogen bonding in carboxylic acid

**Intermolecular hydrogen bonds**

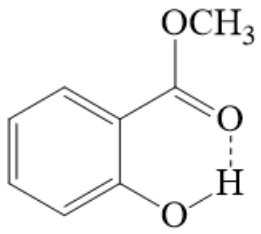
- ✓ Intermolecular hydrogen bonds give rise to broad bands.
- ✓ They are concentration dependent.
- ✓ On dilution, the intensities of such bands are independent of concentration.
- ✓ The bands generally disappear at low concentrations.
- ✓ The absorption frequency difference between free and associated molecule is higher than intramolecular association.

**Intermolecular hydrogen bonds**

- ✓ Bands arising from Intramolecular hydrogen bonds are sharp and well defined.
- ✓ Band persists at very low concentrations.
- ✓ The absorption frequency difference between free and associated molecule is smaller than intermolecular association.

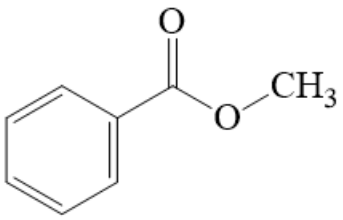
**Examples**

- Lowering of the ester C=O frequency in methyl salicylate caused by intramolecular hydrogen bonding.



Methyl salicylate

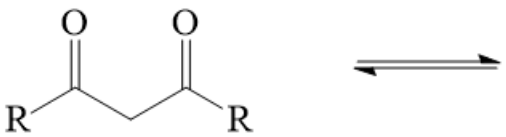
1680 $cm^{-1}$ (C=O stretch)



Methyl benzoate

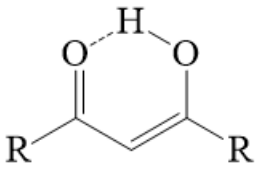
1730 $cm^{-1}$ (C=O stretch)

- The keto tautomer of β-Diketone absorbs at higher frequency whereas enolic β-Diketone absorbs at lower frequency due to intramolecular hydrogen bonding.



Keto tautomer of β-Diketone

1720 $cm^{-1}$ (C=O stretch)



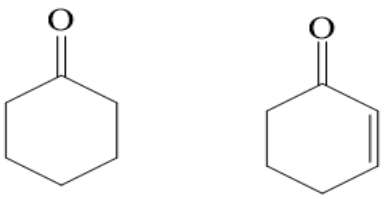
Enol tautomer of β-Diketone

1640 $cm^{-1}$ (C=O stretch)

**Effect of Conjugation on IR Absorption**

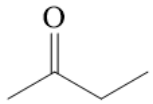
- ✓ Conjugation lowers the frequency of C=O str and C=C str, whether the conjugation is brought about by α-β unsaturation or by an aromatic ring.
- ✓ With conjugation the double bond character is reduced.
- ✓ On conjugation, the intensity of C=C stretch becomes stronger.

Example

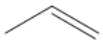


1715 $cm^{-1}$ 1690 $cm^{-1}$

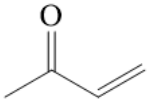
Example



1715 $cm^{-1}$ (C=O stretch)

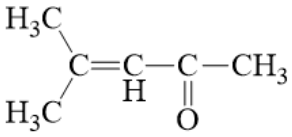


1640 $cm^{-1}$ (C=C stretch)



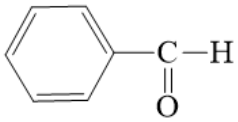
1690 $cm^{-1}$ (C=O stretch)
1620 $cm^{-1}$ (C=C stretch)

Example



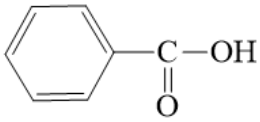
α, β - Unsaturated ketone

1725 ⟶ 1690 $cm^{-1}$



Aryl substituted aldehyde

1725 ⟶ 1700 $cm^{-1}$

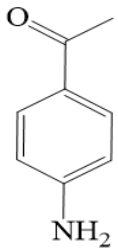


Aryl substituted acid

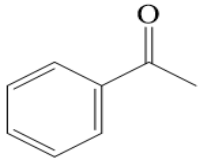
1710 ⟶ 1680 $cm^{-1}$

**Effect of resonance on IR absorption**

- ✓ Resonance causes lengthening or the weakening of a bond leading in the lowering of absorption frequency.
- ✓ The force constant or the bond strength changes and its absorption frequency shifts from the normal value.
- ✓ The presence of alkyl group causes +I effect which results in the lengthening or the weakening of the bond and hence the force constant is lowered and wave number of absorption decreases.



p-Aminoacetophenone
1677 $cm^{-1}$



Acetophenone
1693 $cm^{-1}$

✓ The introduction of an electronegative atom or group causes –I effect which results in the bond order to increase. Thus, the force constant increases and hence the wave number of absorption rises.

**Effect of ring size on IR absorption**

- **C=O stretching frequency**

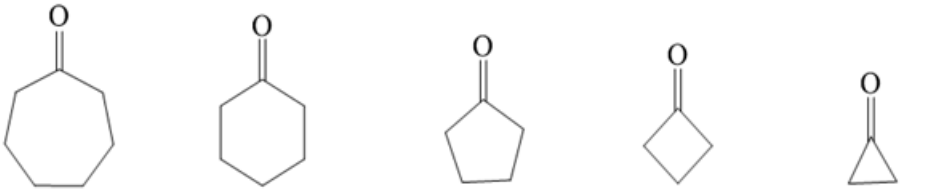
✓ Ring strain in cyclic compounds causes large shift of the C=O stretching to a higher frequency.

✓ Decreasing ring size causes an increase in wavenumber for the carbonyl stretching absorption.

✓ Six- ring ketones show the normal frequency found for the open chain compounds.

✓ The C-CO-C bond angle in strained rings is reduced below the normal (~$112^{O}$ in acyclic and six membered ring ketones which is close to the normal angle of $sp^2$ hybridization, $120^{O}$).

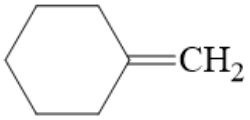
✓ This leads to an increase in the s character in the C=O bond, which is therefore strengthened and consequently C=O stretching frequency is increased.



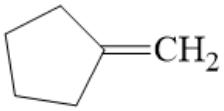

1702 $cm^{-1}$ 1715 $cm^{-1}$ 1745 $cm^{-1}$ 1780 $cm^{-1}$ 1850 $cm^{-1}$

- **C=C stretching frequency**

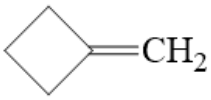
✓ The C=C stretching frequency of exocyclic olefinic double bond increases with decrease in the ring size but to a lesser extent than cyclic ketones.



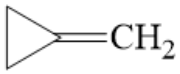
1651 $cm^{-1}$



1657 $cm^{-1}$



1690 $cm^{-1}$



1750 $cm^{-1}$

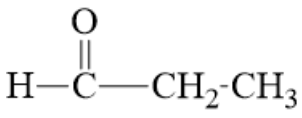
**Problems based on IR spectroscopy (ketone, aldehyde, ester, acid and alcohol)**

1) How will you distinguish between Propanal and acetone?

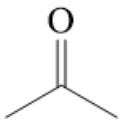
➢ Solution

In case of Propanal, in addition to C=O str at 1720 $cm^{-1}$, there will be a peak at C-H str at 2720 $cm^{-1}$

The peak at 2720 $cm^{-1}$ is missing in case of acetone.

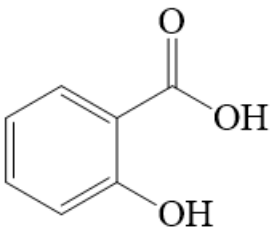


Propanal

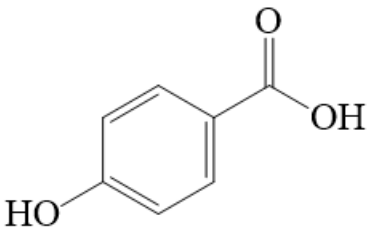


Acetone

2) How will you distinguish between o-Hydroxybenzoic acid and p-Hydroxybenzoic acid on the basis of IR spectroscopy?



*o*-Hydroxybenzoic acid



*p*-Hydroxybenzoic acid

➢ Solution

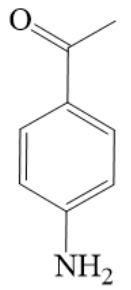
In o-Hydroxy benzoic acid (salicylic acid),there is intramolecular hydrogen bonding. The absorption band due to O-H str appears broad at nearly 3300 $cm^{-1}$ and is concentration independent. But in p-Hydroxy

benzoic acid, the association is due to intermolecular hydrogen bonding. In this, absorption occurs at about 3000 $cm^{-1}$.

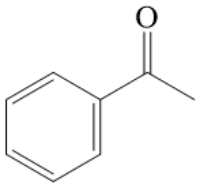
3) Arrange the following compounds in order of increasing wave number of carbonyl absorption in the IR spectrum:

   Acetophenone, p-Nitroacetophenone, p- Aminoacetophenone

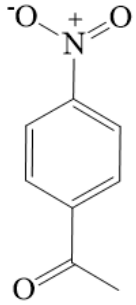
➢ Solution



p-Aminoacetophenone
1677 $cm^{-1}$



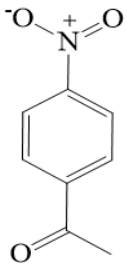
Acetophenone
1693 $cm^{-1}$



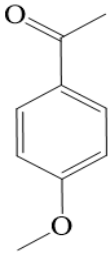
p-Nitroacetophenone
1700 $cm^{-1}$

Due to the electronegativity of Nitrogen atom, the lone pair of electrons participates more in conjugation in p-Aminoacetophenone. Thus in p-Aminoacetophenone C=O absorption occurs at lower wave number. In p-Nitroacetophenone, inductive effect dominates over mesomeric effect and hence absorption takes place at higher frequencies.

4) Which of the compounds (I and II) is expected to show a lower C=O stretching frequency?



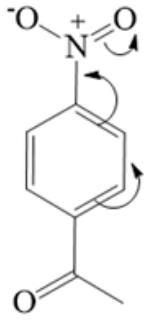
p-Nitro acetophenone
(I)



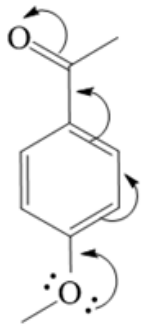
p-Methoxy acetophenone
(II)

- Solution

  The presence of *p*-OMe group in structure II assists the mesomeric shift to decrease the bond order of C=O bond leading to lower C=O stretching frequency. A *p*-$NO_2$ group tends to oppose these trends and thus in structure I the C=O stretching frequency is higher than structure II.



p-Nitro acetophenone



p-Methoxy acetophenone

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- ✓ The C=C stretching frequency of exocyclic olefinic double bond increases with decrease in the ring size but to a lesser extent than cyclic ketones.