

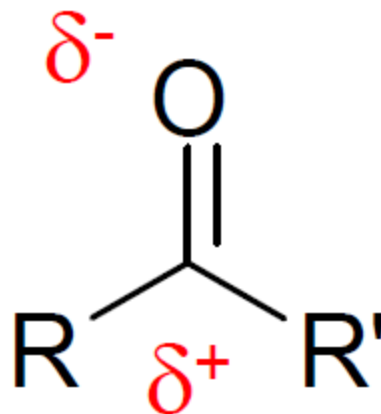
# **INFRARED (IR) SPECTROSCOPY**

# Factors Influencing Vibrational Frequencies

- 1) **The physical state** of measurement  
(solid, neat, dilute solution, conc. solution);
- 2) **Electronic effect** of substituents;
- 3) **Conjugation**;
- 4) **Hydrogen bonding**;
- 5) **Ring strain**.
- 6) **Coupled Vibration and Fermi Resonance**

# 1) Physical State

- **Non-polar solvents** increase absorption frequency.
- **Polar solvents** decrease absorption frequency due to **solvent-carbonyl interaction**.
- Overall range of solvent effect **does not exceed 25 cm<sup>-1</sup>**.



## 2) Electronic Effect of Substituents

Three types of electronic effects are

1. Inductive effect.

2. Hyperconjugation.

3. Mesomeric Effects.

4. Field Effect

# Introduction of alkyl group

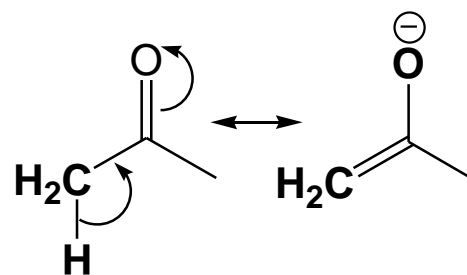
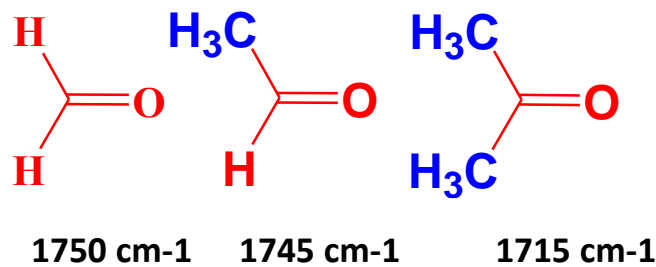
Causes **Hyperconjugative effect**

**C=O** bond get single bond character due to **Hyperconjugative effect**

increases the length of the **C=O** bond

- **decreases** its **force constant**

- the **frequency** of absorption will **decrease**.

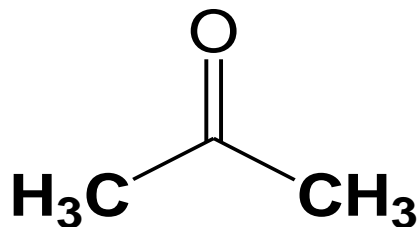


Higher the number of H.P conjugative structure, more will be the decrease of C=O bond order and  $\nu$  (C=O) decreases further.

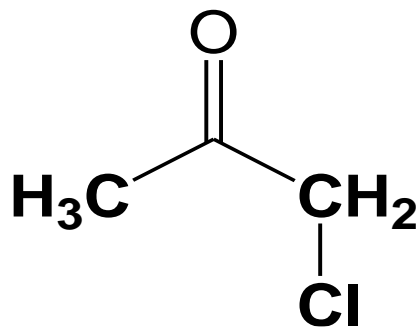
# Introduction of electronegative atom or group

(Causes -I effect)

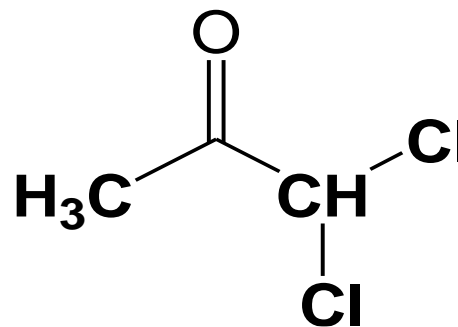
- I effect increases bond order.
- increases its force constant
- the frequency of absorption will increase.



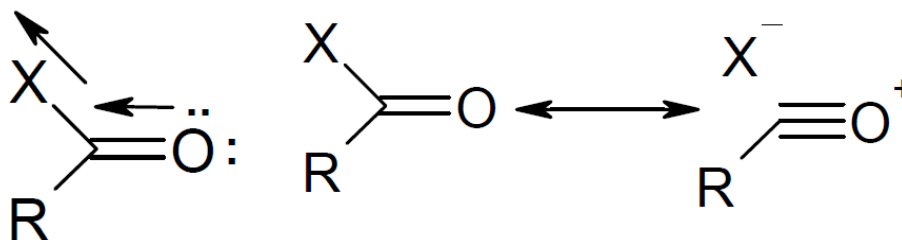
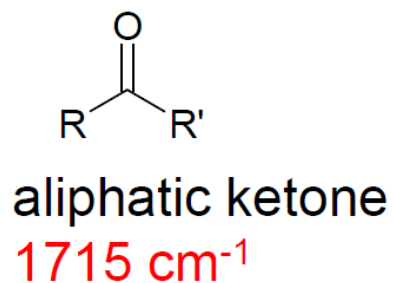
$\nu$  (C=O) 1715 cm<sup>-1</sup>



1725 cm<sup>-1</sup>



1740 cm<sup>-1</sup>

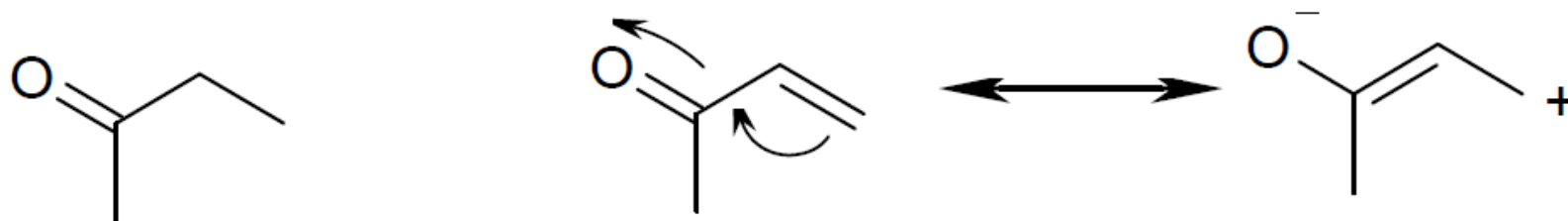


### Inductive Effect

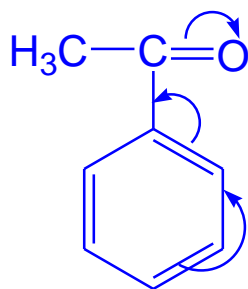
X	C=O absorption (cm <sup>-1</sup> )
F	1869
Cl	1815-1785
Br	1812
OH	1760
OR	1750-1735

In these cases –I effect of X is greater than + R effect

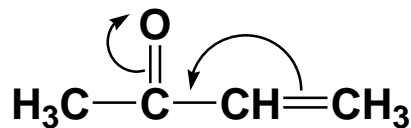
## • Conjugation lower the frequency of C=O stretching



- This is because the carbonyl **bond order** (double bond character) is **reduced** and hence the **force constant falls** (reduces).

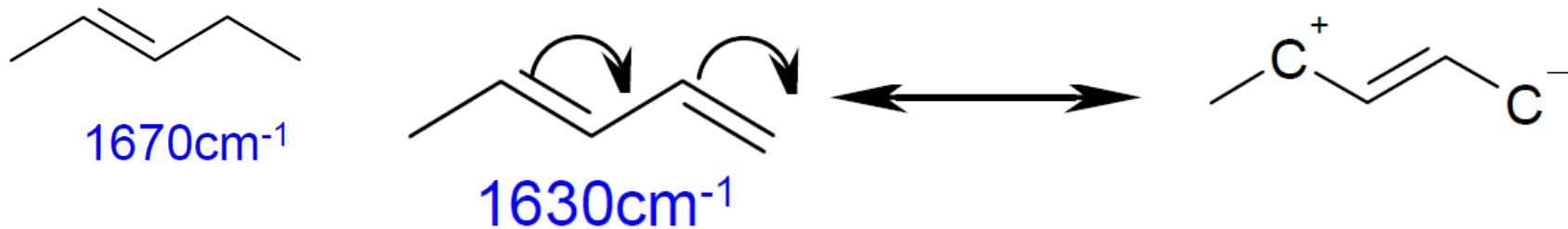


Acetophenone  
 $\nu$  (C=O) 1693 $\text{cm}^{-1}$



Methyl Vinyl ketone  
 $\nu$  (C=O) 1706 $\text{cm}^{-1}$



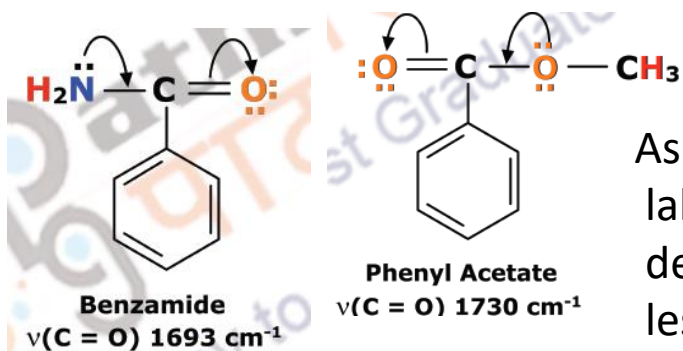
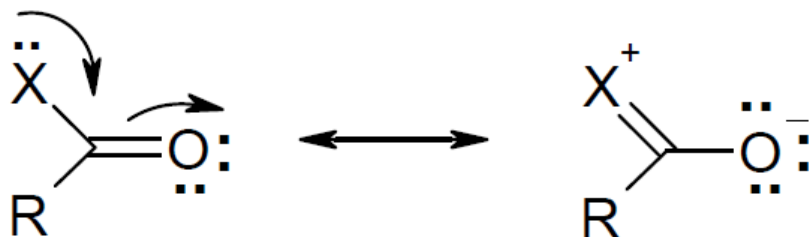


Conjugation of a double bond provides a **single bond character** through resonance, which **lowers** force constant  $K$ , thus a **lower frequency** of vibration.

# Mesomeric Effect

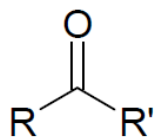
Causes **increase of the length of the C=O bond** and weaken the bond.

- **reduces its force constant.**
- **the frequency of absorption will be decreased.**



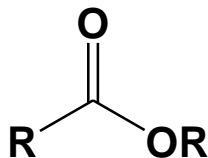
As N is less electronegative than O, So N in amide is more labile and participate more in resonance. Due to this greater degree of conjugation C=O absorption frequency is much less in amide than ester.

## When -I effect is greater than +R effect



aliphatic ketone

1715  $\text{cm}^{-1}$

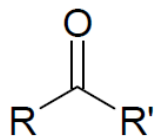


Ester

1750-1735 $\text{cm}^{-1}$

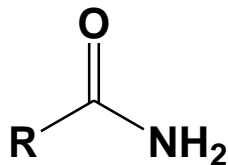
The predominant effect of the oxygen of an ester is inductive electron withdrawal, therefore the carbonyl group of an ester has **more double bond character** than the carbonyl group of a ketone, so the former appears at larger frequency value.

## When +R effect is greater than -I effect



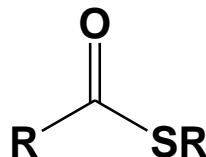
aliphatic ketone

1715  $\text{cm}^{-1}$



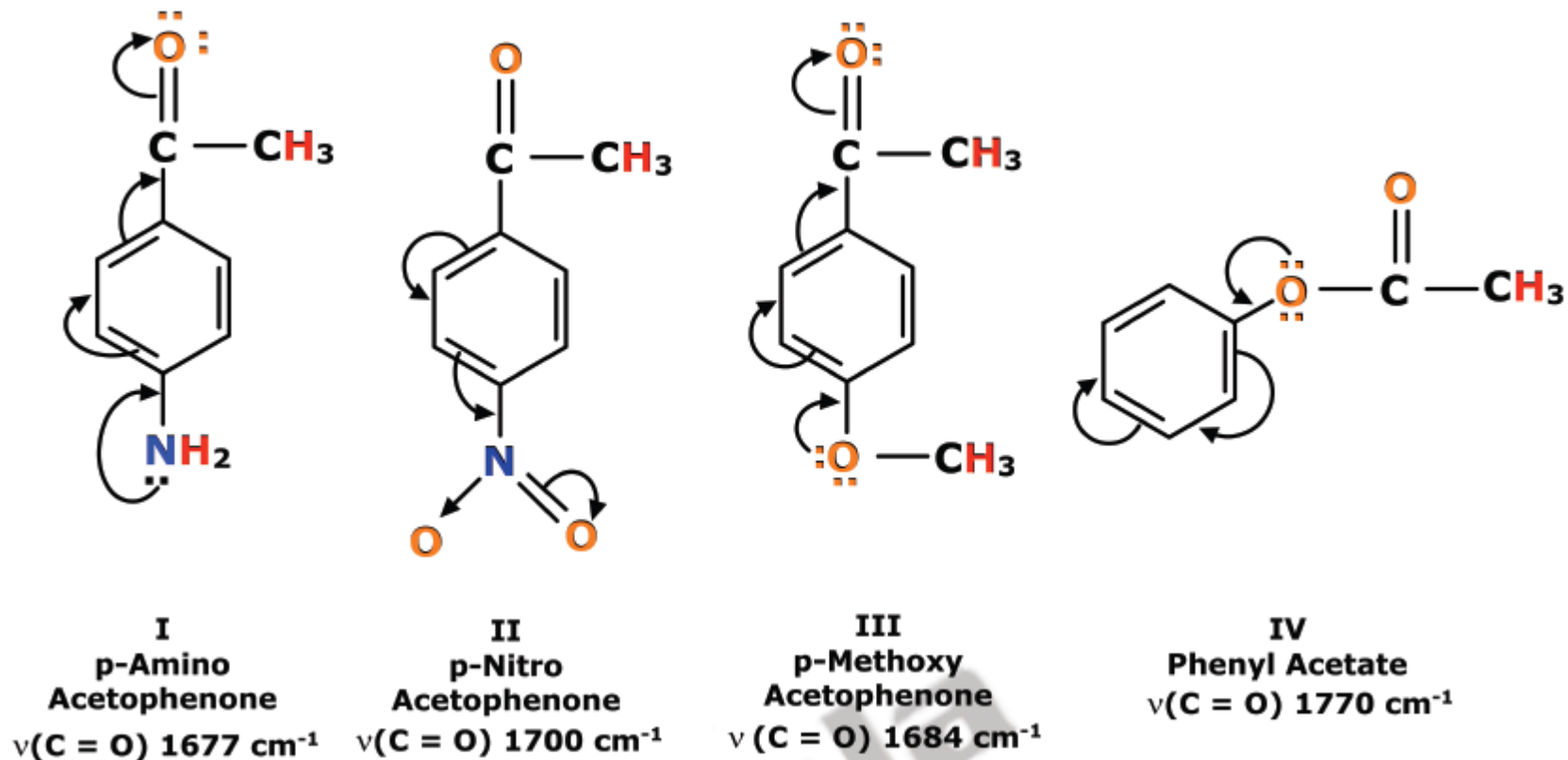
amide

1695 - 1650 $\text{cm}^{-1}$



1710-1690 $\text{cm}^{-1}$

The predominant effect of the nitrogen of an amide is electron donation by resonance. Therefore, the carbonyl group of an amide has **less double bond character** than the carbonyl group of a ketone and hence **amide has low C=O bond IR frequency** than the ketone

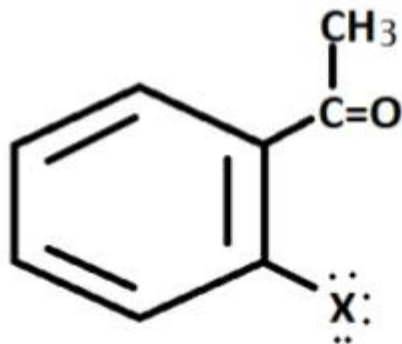


As N is less electronegative than O, so N lone pairs participate more in conjugation in I than O lone pairs in III. So  $\nu(\text{C}=\text{O})$  of I is less than III.

In II and IV inductive effect dominates over mesomeric effect hence absorption takes place at comparatively higher frequencies.

# Field Effect

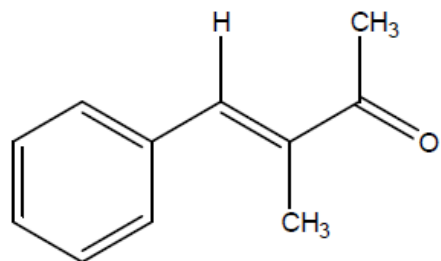
Lone pair of electrons present on the atoms influence each other through space interactions and changes the vibrational frequencies of both the groups. This effect is called as Field effect.



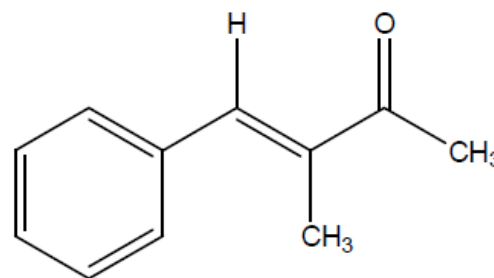
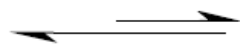
The non-bonding electrons present on oxygen atom and halogen atom cause electrostatic repulsion. This causes a change in the state of hybridisation of C=O group and also make it to go out of plane of the double bond. Thus conjugation is diminished and absorption occur at higher frequency.

**Thus for ortho substituted compound cis absorbs at a higher frequency than trans isomers.**

**(E)-3-Methyl-4-phenylbut-3-en-2-one** shows two C=O bands at 1674 and 1699  $\text{cm}^{-1}$ . Why?



*s-trans* 1674  $\text{cm}^{-1}$



*s-cis* 1699  $\text{cm}^{-1}$

Steric effects in *s-cis* reduces co-planarity of the conjugated system and reduces the effect of conjugation.