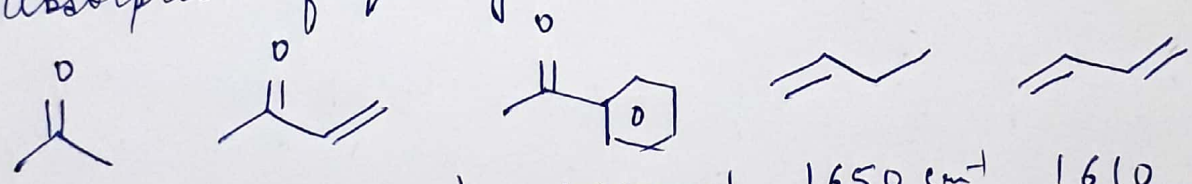
Electronic effects :-

→ Changes in the absorption frequency for a particular gp takes place, when substituent in the neighbourhood of that particular group is changed.

→ Frequency shifts are due to electronic effects - Inductive, Mesomeric & field effect.

→ Due to these effects, the force constant or the bond strength changes & its absorption freq. changes from the normal value.

a) Conjugation (~~C=C-C=O~~) causes lengthening or weakening of a bond leading to lowering of absorption frequency.



1720 cm^{-1} 1706 cm^{-1} 1693 cm^{-1} 1650 cm^{-1} 1610 cm^{-1}

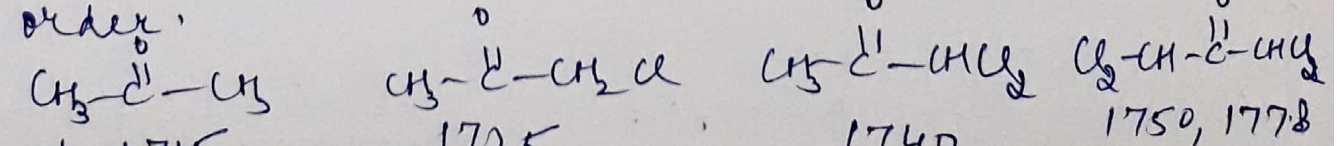
b) Introduction of +I gp results in weakening of bond.

HCHO 1750 cm^{-1}

CH_3CHO 1745 cm^{-1}

$CH_3-CO-CH_3$ 1715 cm^{-1}

c) Introduction of -I gp. results in Dse of bond order.



$CH_3-C(=O)-CH_3$ 1715 cm^{-1}

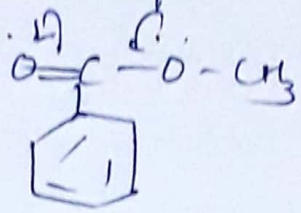
$CH_3-C(=O)-CH_2Cl$ 1725

$CH_3-C(=O)-CHCl_2$ 1740

$Cl_2-CH-C(=O)-CHCl_2$ 1750, 1778

a) when lone pair of e⁻ + ve on an atom is in conjugation ~ =bond of a gp. eg. C=O gp, the mobility of lone pair of e⁻s matters.

Benzamide
1693 cm⁻¹



Methyl benzoate
1730 cm⁻¹

e⁻ pair on N atom in amide is more labile & participate more in conjugation.

iii) H-Bonding :-

→ brings about remarkable downward freq. shifts.

More H-bonding, more absorption shifts towards lower wave no. than normal value.

→ Due to intramolecular H-bonds, bands are sharp. & intermolecular H-bonds, intense broad bands & these depends on concentration.

→ On dilution, the intensities of intermolecular H bond become independent of concentration.

→ H bonding in amines is weaker than that in alcohols.

→ Amines show N-H str. at 3500 cm⁻¹ in dil. sol. while in condensed phase, at 3300 cm⁻¹.

In aliphatic alcohols, band due to free O-H is less intense & appears at 3650 cm^{-1}, in dil. soln while due to H bonded OH gp, is broad, at 3350 cm^{-1}.

iv) Bond angle :-

→ When the value of normal bond angle ↓ses in any molecule, it ↑ses strength of vibrating bond & absorption band shifts towards higher wave no..

→ Increase in bond angle shifts the absorption band towards lower wave no.

↑se in s character results in shortening of C=O bond thus >C=O stretching band occurs at higher freq.