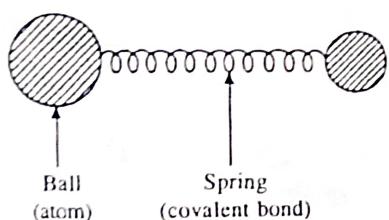


UV vs IR: Unlike UV spectra which have relatively few absorption bands, IR spectra have a large number of absorption bands and therefore provide plenty of structural information about a molecule. Different bands observed in an IR spectrum correspond to various functional groups and bonds present in the molecule. Thus, IR spectroscopy is most widely used for the detection of functional groups and identification of organic compounds.

Theory (Origin) of Infrared Spectroscopy: IR absorption spectra originate from transitions in vibrational and rotational energy levels within a molecule. When a molecule absorbs IR radiation in the range 100-10,000 cm⁻¹, the absorbed radiation causes transitions in its vibrational energy levels. These energy levels are also quantized, but vibrational spectra appear as bands rather than discrete lines. Again, a single transition in vibrational energy levels is accompanied by a large number of transitions in rotational energy levels and so the vibrational spectra appear as vibrational-rotational bands instead of discrete lines. Organic chemists are mainly concerned with these vibrational-rotational bands, especially with those occurring in the region 4000-667 cm⁻¹.



$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$T = \frac{1}{I_0} \quad \propto T = \frac{f}{I_0} \\ A = \omega_0 \sqrt{\frac{1}{\mu}} \\ \bar{v} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

Hooke's law $K = f =$ force constant of the bond

Various atoms in a molecule may be regarded as balls of different masses and the covalent bonds between them as weightless tiny springs holding such balls together. Atoms in a molecule are not still but they vibrate. The two types (modes) of fundamental molecular vibrations known are: (a) stretching and (b) bending vibrations (deformations).

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(i) Stretching Vibrations: In stretching vibrations, the distance between two atoms increases or decreases, but the atoms remain in the same bond axis.

Stretching vibrations are of two types:

(a) Symmetrical stretching. In this mode of vibration, the movement of atoms with respect to the common (or central) atom is simultaneously in the same direction along the same bond axis (Fig. 3.2(a)).

(b) Asymmetrical Stretching. In this vibration, one atom approaches the common atom while the other departs from it (Fig. 3.2(b)).

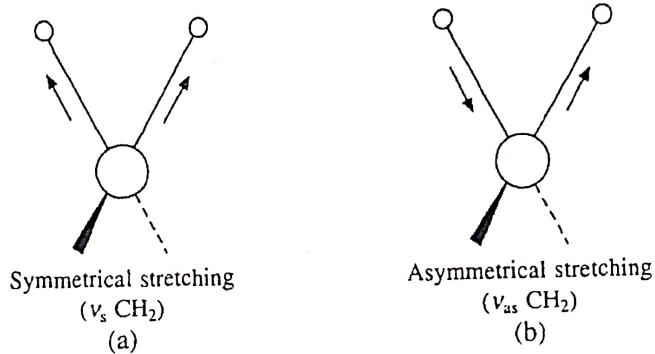


Fig. 3.2 Stretching vibrations of a CH_2 group ($v \text{ CH}_2$)

(ii) Bending Vibrations (Deformations): In such vibrations, the positions of the atoms change with respect to their original bond axes.

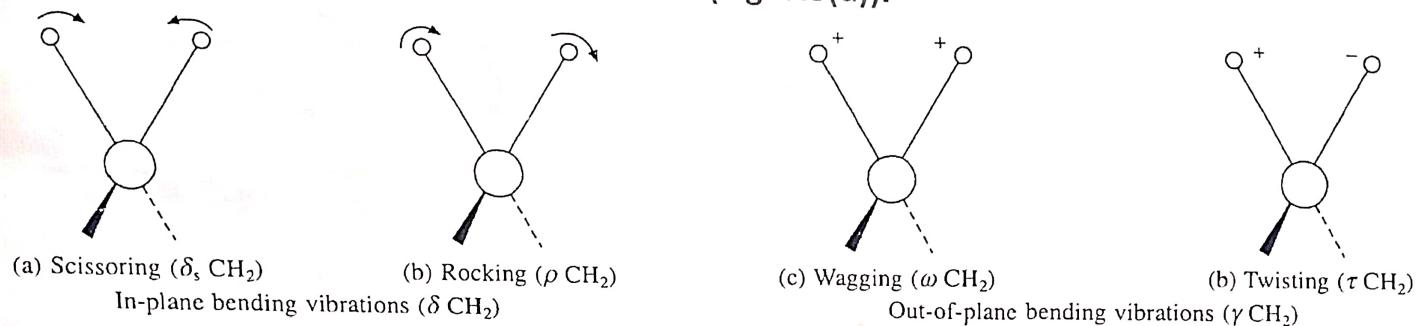
Bending vibrations are of four types:

(a) Scissoring. In this mode of vibration, the movement of atoms is in the opposite direction with change in their bond axes as well as in the bond angle they form with the central atom (Fig. 3.3(a)).

Scissoring. In this vibration, the movement of atoms takes place in the same direction with respect to their original bond axes (Fig. 3.3(b)). Scissoring and rocking are in-plane bending's.

(c) **Wagging.** In this vibration, two atoms simultaneously move above and below the plane with respect to the common atom (Fig. 3.3(c)).

(d) **Twisting.** In this mode of vibration, one of the atom moves up and the other moves down the plane with respect to the common atom (Fig. 3.3(d))).



Origin of Spectra: Infrared radiation is absorbed when the oscillating dipole moment, due to a molecular vibration, interacts with the oscillating electric field of the infrared beam. This interaction occurs and hence, an absorption band appears only when a molecular vibration produces a change in the dipole moment of the molecule. Otherwise, the vibration is said to be *infrared inactive* and it will show no absorption band in the infrared spectrum. Usually, larger the change in dipole moment, the higher is intensity of absorption. It is not necessary for a molecule to have a permanent dipole moment for IR absorption.

There are various interrelated factors which shift the vibrational frequencies from their expected values. For this reason, the values of vibrational frequencies of the bonds calculated by the application of Hooke's law are not exactly equal to their observed values. The force constant of a bond changes with the electronic and steric effects of the other groups present in the molecule, and so the vibrational frequencies are shifted from their normal values. Also, frequency shifts may occur when the IR spectrum of the same compound is recorded in different states, viz. solid, liquid or vapour. Usually, a substance absorbs at higher frequency in the vapour state than that in the liquid or solid state.

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Hooke's law

The atomic mass of carbon is 12 and that of hydrogen is 1.

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}}$$

$$\bar{v} = \frac{1}{2\pi \times 2.998 \times 10^{10} \text{ cm sec}^{-1}}$$

$$\times \sqrt{\frac{5 \times 10^5 \text{ dynes cm}^{-1} \left(\frac{12}{6.023} + \frac{1}{6.023} \right) \times 10^{-23} \text{ g}}{\left(\frac{12}{6.023} \times 10^{-23} \text{ g} \right) \left(\frac{1}{6.023} \times 10^{-23} \text{ g} \right)}}$$

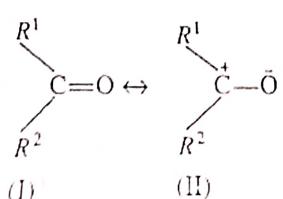
Therefore, $\bar{v}_{C-H} = 3032 \text{ cm}^{-1}$.

Factors Affecting Vibrational Frequencies:

i) Inductive and Mesomeric or Resonance Effects

Absorption frequencies of a particular group are affected by electronic effects, especially inductive and mesomeric (resonance) effects of the nearby groups. Strength (force constants) of a particular bond is changed by these effects and hence its Stretching frequency is also changed with respect to the normal values. Both of these effects may operate in the same direction or opposite to each other where one dominates the other.

A carbonyl compound may be considered as a resonance hybrid of the following structures:



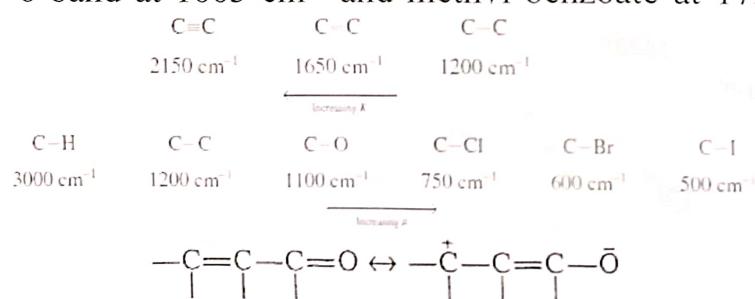
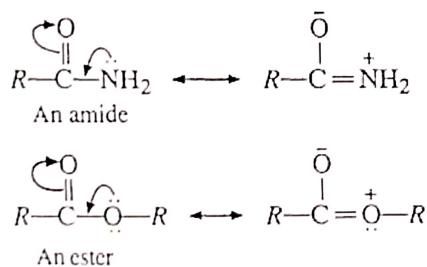
The Stretching frequency of a carbonyl group decreases with increasing number of alkyl groups attached to it. This is due to $+I$ effect of alkyl groups which favours structure (II) and lengthens (weakens) the carbon-oxygen double bond, and hence its force constant is decreased resulting in the lowering of the $C=O$ Stretching frequency.

analogous

(S)

$V_{C=O}$ (cm^{-1}) : HCHO (1750), CH_3CHO (1730) and CH_3COCH_3 (1720). It should be noted why aldehydes absorb at higher frequency than ketones. Similarly, when a group with -I effect is attached to a C=O group, its stretching frequency is increased due to increase in the bond order (force constant) of the carbon-oxygen double bond. For example, CH_3COCH_3 , CH_3COCF_3 and CF_3COCF_3 show $V_{C=O}$ bands at 1720, 1769 and 1801 cm^{-1} , respectively.

Amides show $V_{C=O}$ band at a lower frequency than that of esters. Due to lesser electronegativity of nitrogen than oxygen, its lone pair of electrons are more readily involved in resonance than that of oxygen. Thus, the carbon-oxygen double bond character is more reduced by resonance in amides than that in esters resulting in a much lower $V_{C=O}$ frequency of amides than that of esters. For example, benzamide shows $V_{C=O}$ band at 1663 cm^{-1} and methyl benzoate at 1735 cm^{-1} .



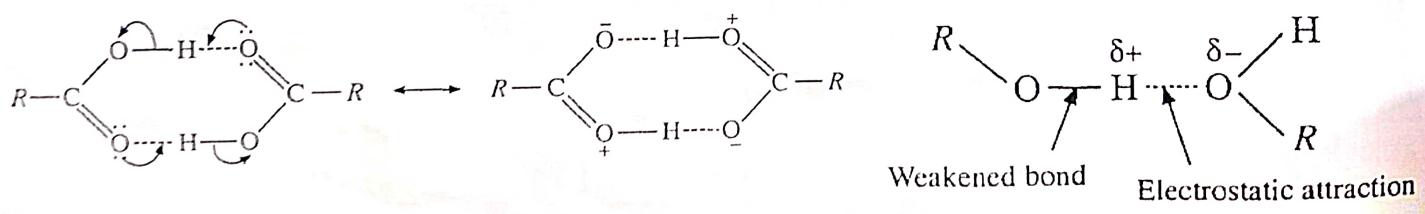
Conjugation of a carbonyl group with an olefinic double bond or an aromatic ring lowers the stretching frequency of the C=O groups by about 30 cm^{-1} . This is because the double bond character of the C=O group is reduced by mesomeric effect.

The stretching frequency of C=O group in acetone is 1720 cm^{-1} , whereas acetophenone shows a C=O band at 1697 cm^{-1} due to its conjugation with the aromatic ring. In this case, -I effect of the sp^2 -carbon of the ring is dominated by the +M effect of the ring. *Andabat*

Hydrogen Bonding

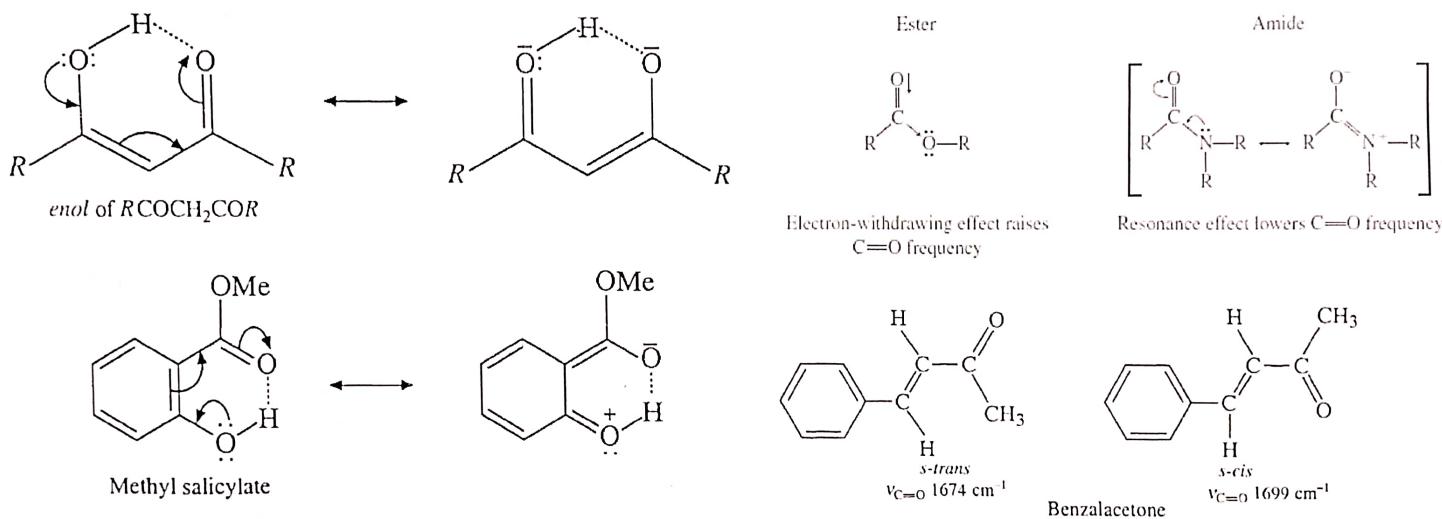
Hydrogen bonding remarkably lowers the Stretching frequencies of both the groups involved in it, and also changes the shape and intensity of the absorption bands. Usually, absorption bands become more intense and broad on hydrogen bonding. The stronger the hydrogen bond, lower is the O-H Stretching frequency. Thus, the value of O-H stretching frequency is a test for hydrogen bonding as well as a measure of the strength of hydrogen bonds. Non-hydrogen-bonded (free) O-H group of alcohols and phenols show sharp and strong absorption bands in the region $3590\text{--}3650\text{ cm}^{-1}$.

In liquid or solid state, and in concentrated solutions, carboxylic acids exist as dimers due to strong intermolecular hydrogen bonding. The strong hydrogen bonding between C=O and OH groups lowers their Stretching frequency. Because of more polar O-H bond, carboxylic acids form stronger hydrogen bond than alcohols. Carboxylic acid dimers show very broad, intense O-H Stretching absorption in the region $2500\text{--}3000\text{ cm}^{-1}$, whereas nonhydrogen-bonded carboxylic acids (monomers) show the O-H absorption near 3550 cm^{-1} . Hydrogen bonding weakens the C=O bond, i.e. its force constant is reduced, resulting in absorption at a lower frequency than the monomer. Thus, C=O stretching bands of monomers of saturated carboxylic acids appear at 1760 cm^{-1} , whereas that of dimers appear at about 1710 cm^{-1} .



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Distinction between inter- and intramolecular hydrogen bondings: In very dilute solutions (in non-polar solvents), intermolecular distances are too large to form intermolecular hydrogen bonds. On the other hand, in pure liquids, solids and concentrated solutions, the molecules are closer to form intermolecular hydrogen bond. Thus, intermolecular hydrogen bonding is concentration dependent. Intramolecular hydrogen bonding is within the same molecule, hence it is not affected by change in intermolecular distances. Thus, intramolecular hydrogen bonds are unaffected by dilution, and so the absorption band is also unaffected.

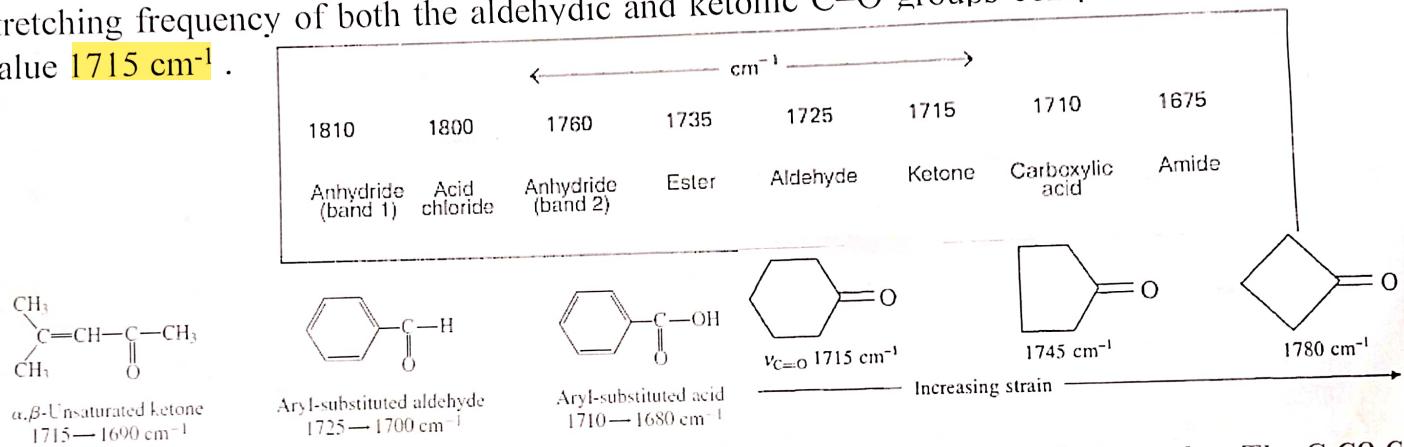


In enols, the O-H group involved in chelation shows broad absorption band in the range $2500\text{-}3200 \text{ cm}^{-1}$, whereas the C=O stretching band in enolic form occurs at 1630 cm^{-1} and that in the keto form at 1725 cm^{-1} . From the relative intensities of the two bands, it is possible to determine ratio of the keto and enol forms

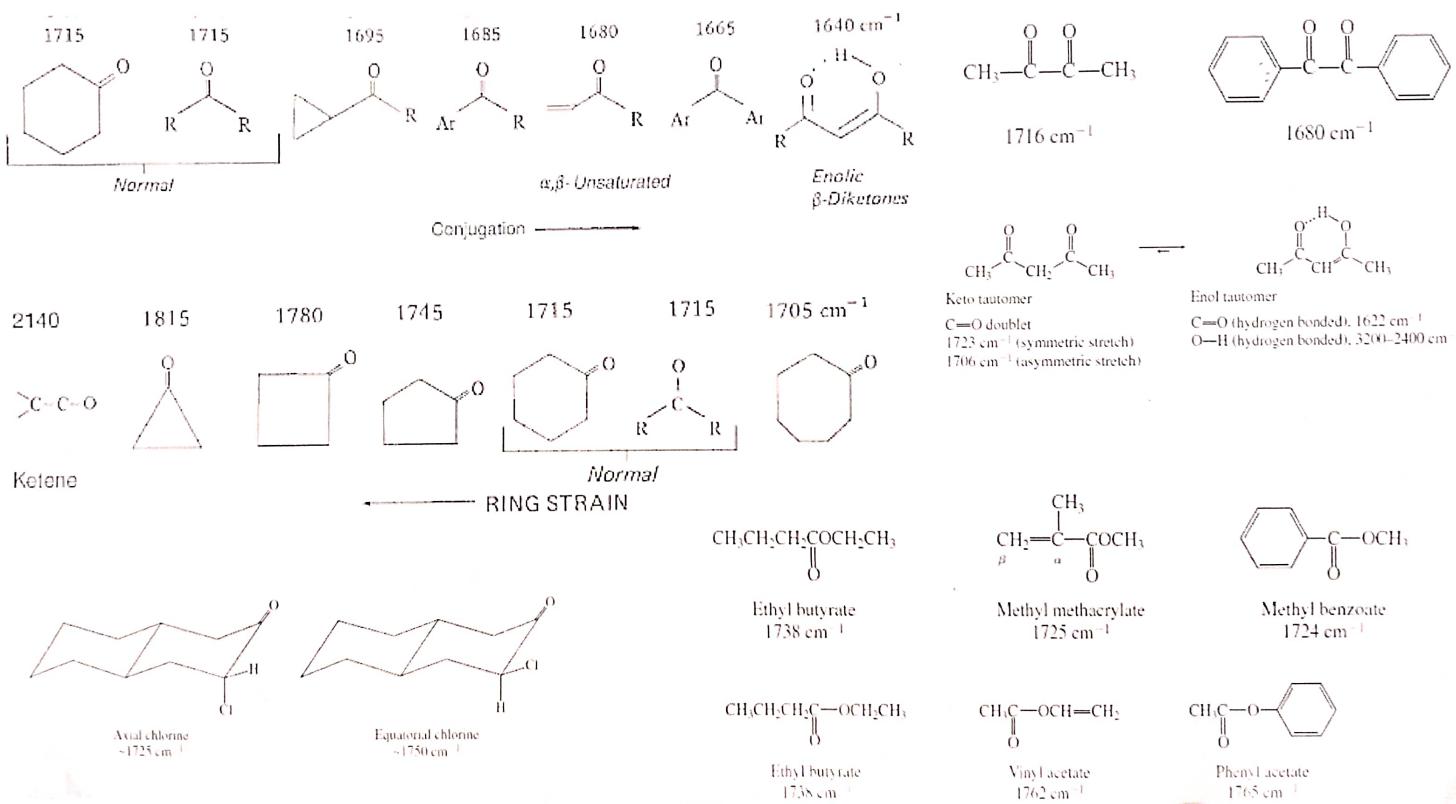
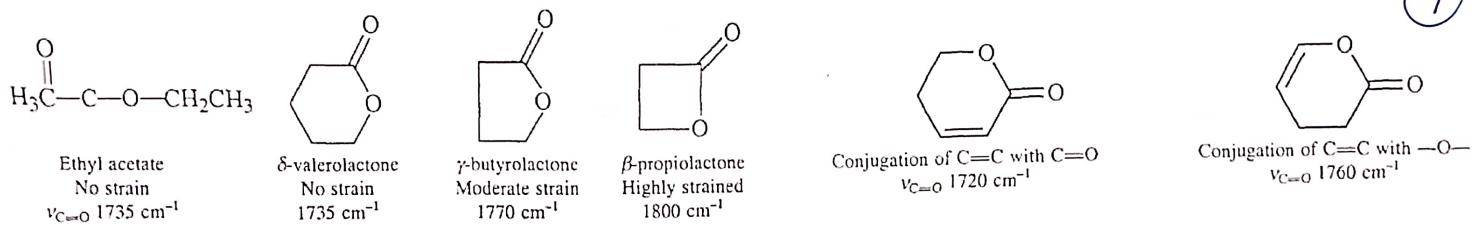
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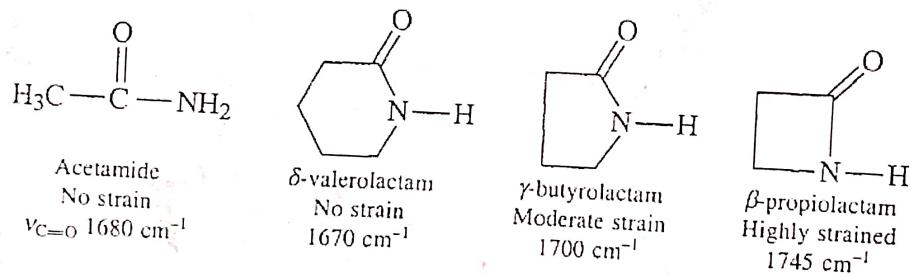
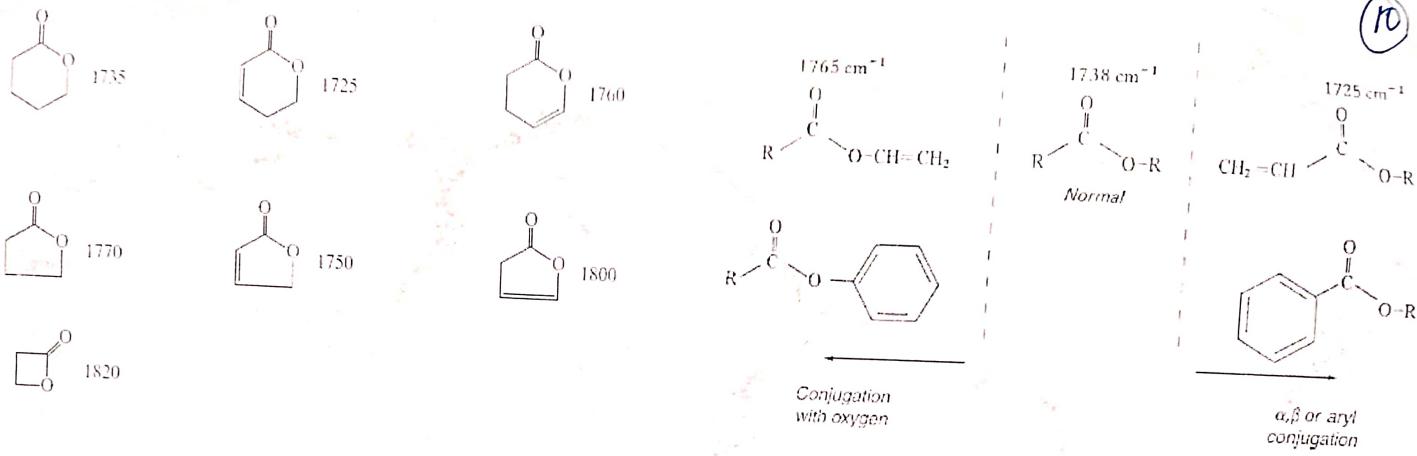
Aldehydes and Ketones:

Aldehydes, ketones, carboxylic acids, carboxylic esters, lactones, acid halides, anhydrides, amides and lactams show a strong C=O Stretching band generally in the region 1630-1870 cm⁻¹. This band has relatively constant position, high intensity and has far less interfering bands in its region making it one of the most readily recognizable bands in IR spectra. The C=O stretching frequency depends on inductive effect, mesomeric effect, hydrogen bonding, field effect, steric effect and ring strain. These factors either increase or decrease the stretching frequency of both the aldehydic and ketonic C=O groups compared to the normal value 1715 cm⁻¹.



The carbonyl stretching frequency in cyclic ketones having ring strain is shifted to a higher value. The C-CO-C bond angle in strained rings is reduced below the normal value of 120° (acyclic and six-membered cyclic ketones have the normal C-CO-C angle of 120°). This leads to an increase in *s character in the sp² orbital of carbon involved in the C=O bond. Hence, the C=O bond is shortened (strengthened) resulting in an increase in the ν_{C=O} frequency. This increase in the *s character of the outside sp² orbital is there because it gives more p character to the sp² orbitals of the ring bonds which relieves some of the strain, as the preferred bondangle of p orbitals is 90°. In ketones where C-CO-C angle is greater than the normal angle (120°), an opposite effect operates and they have lower ν_{C=O} frequency. For example, in di-t-butyl ketone, where the C-CO-C angle is pushed outward above 120°, it has very low ν_{C=O} frequency (1698 cm⁻¹). Anahatadr**





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open chain
has very low energy