Selection Rule :-

When oscillating dipole moment interact with the oscillating electric vector of infrared beam, infrared radiation is absorbed.
For this absorption, dipole moment at one extreme of a vibration must be different from dipole moment at the other extreme of the vibration.

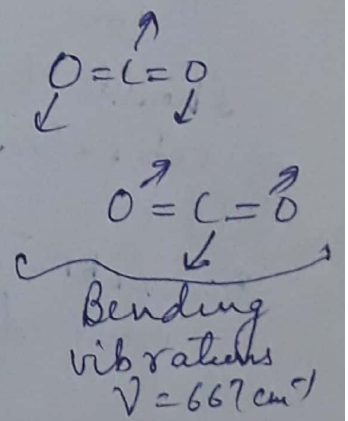
→ Some of the fundamental vibrations are infrared active & some are not. It is governed by some selection rules:-

a) If a mol. has a centre of symmetry, then the vibrations are centrosymmetric & are inactive in IR.

b) Vibrations which are not centrosymmetric are active in infrared.

Eg. $\overleftarrow{O=C=O}^{\rightarrow}$
Sym. st. vibration
D.M = 0
IR inactive

$\overrightarrow{O=C=O}$
asym. stretching
$\bar{\nu} = 2350\ cm^{-1}$
IR active



$CO_2 = 3n = 9$ Translational = 3

Linear mol. = Rot = 2.

Vib = $3n - 5 = 3 \times 3 - 5$
= 4 vibrational

But IR spectrum of CO_2, two bands only.

Conditions for Infrared Spectrum :-

→ Any molecule will absorb infrared radiation only, if it obey following :-

i) $\bar{\nu}$ radiation = $\bar{\nu}$ vibration, means the frequency of mol. vibration & frequency of IR should be same.

ii) During vibration of a molecule, there should be net change in the dipole moment. It occurs only if permanent dipole moment is present in the molecule.

for eg. H_2 & N_2 will not give IR spectrum

In Sym. str. vibration of CO_2, there is no change in D.M. & thus IR inactive.

iii) For a mol. undergoing vibrational transition within an electronic state, there should be a unit ↑ or ↓ in quantum no. of vibrations. $\Delta \bar{\nu} = \pm 1$

* Vibrational transition $0 \to 2$, $1 \to 3$ etc. do not occur for a strictly harmonic oscillator.

* Only one band is possible for each fundamental vibration.

$\Delta \bar{\nu} = +1$ (vibrational spectrum is an absorption spectrum)

Factors affecting Vibrational Frequencies :-

→ The vibrational frequency or $\bar{\nu}$ (wave no.) of absorption band can be calculated by Hooke's Law.

→ The calculated value of freq. of absorption for a particular bond is never exactly equal to its experimental value. b'coz vibration of each group is influenced by the structure of the molecule in the immediate neighbourhood of the bond.

→ Freq. shifts also occur while working with the same substance in different states. eg. In vapour phase, a sub- usually absorbs at higher freq. than that in liq or solid state.

Factors which affect the shifting of vibrational freq. from their normal values are :-

a) Coupled Vibrations & Fermi Resonance :-

~~Sometimes~~ An isolated -CH bond exhibit only one C-H Str. freq. but in $(-CH_2)$ gp, the two C-H str. vibrations are coupled & give two absorption bands of diff. freq. than required for isolated C-H str. corresponding to sym. & asym. vibrations.

In CH_3 gp, coupled vibrations occur at diff. frequencies compared to $-CH_3$ gp.

Similarly two coupled vibrations bands are obtained in primary amine & primary amide due to coupling of two N-H stretching vibrations.

* Asym & Sym stretching vibrations of CH_3 gp are k/n as coupled vibrations b'coz these vibrations occur at diff. freq. than that required for an isolated C-H stretching.

→ When a fundamental vibration may couple with the overtone or combination band of some other vibration, Then it is called Fermi Resonance.

→ Fermi resonance is given by aldehydes in which C-H str. absorption usually appears as a doublet (~2820 & ~2720 cm^{-1}) due to the interaction b'n C-H str. (fundamental) & the overtone of C-H deformation (bending).

Overtones (2x, 2y)

Combination bands (x+y, x+2y, 2x+y etc)

Diff. bands (x-y, x-2y, 2y-x) etc..

Degenerate vibrations :- Fundamental vibrations that are too weak to be observed as bands or these may be so close that may overlap.