Number of fundamental Vibrations :-

The IR Spectra of polyatomic molecule may exhibit more than one vibrational absorption bands.
The number of three bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degree of freedom of the molecule
The degree of freedom of a molecule are equal to the total degree of freedom of its individual atom. Each atom has three degrees of freedom corresponding to three Cartesian Coordinates (x, y, z) necessary to describe its position relative to other atoms will have 3n degrees of freedom.

In Case of a non linear molecular, three degrees of freedom describes rotation and three describe translation
Then the remaining degree of freedom are Vibrational

$vib = 3n-6$

Total degree of freedom $3n$ = Translational + Rotational + vibrational degrees of freedom

In Case a linear molecule, only two degrees of freedom describe rotation (because rotation about its axis of linearity does not Change the positions of the atom) three describe Translation.

$vib = 3n-5$

(1) CO_2 (linear)

$n = 3$ (no of atoms, Rotational = 2, Translational = 3

Total degree of freedom = $3 \times 3 = 9$

$vib = 3 \times 3 - 5 = 4$

(2) C_2H_6 (non-linear)

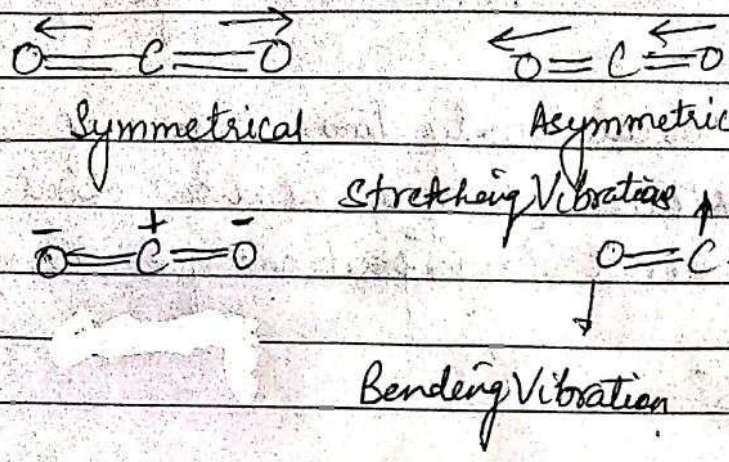
$vib = 3 \times 8 - 3 - 3 = 18$

(3) C_6H_6 (non-linear)

$vib = 3 \times 12 - 3 - 3 = 30$

The Carbon dioxide molecule is linear & has four fundamental vibrations. Thus, four theoretical fundamental bands are expected but actually it shows only two. The Symmetrical stretching vibration in CO_2 is IR inactive because it produces no change in dipole moment of the molecule. The two

bending vibrations are equivalent and absorb at the same number (667.3 cm^{-1}). Thus IR Spectrum of CO_2 shows only two fundamental absorption bands, one at 2350 cm^{-1} due to asymmetrical stretching and other at 667.3 cm^{-1} due to the bending vibrations.



Overtone bands:-

These may arise if a molecule is excited eg from Vibrational energy level to third vibrational energy level; the energy required is almost twice of that required for the excitation to second vibrational energy level. In this way, if there are two fundamental bands x & y cm^{-1}, then the overtone bands can be expected eg at 2x, 2y, 3x, & 3y cm^{-1}

The intensity of the overtone decrease as the order of the overtone increases - eg second overtone (3x or 3y) is less intense than first overtone (2x or 2y).

Consequently, second & higher overtones are rarely observed whereas first overtones are observed only strong bands

Combination Bands:-

If there are two fundamental bands at x & y cm^{-1} then combination bands can be expected at (x+y), (x+2y), (2x+y) cm^{-1}. It is another

type of overtone, it occurs when a single photon has precisely the correct energy to excite two vibrations at once. For this to happen, the energy of the combination band must be the exact sum of the two independent absorption.

Difference Bands:-

If there are two fundamental bands at x & y cm^{-1}, then the difference bands can be expected at (x-y), (x-2y), (2x-y) cm^{-1}.

CALCULATION OF VIBRATIONAL FREQUENCIES

The stretching vibrations of two bonded atoms may be regarded as the vibration of two balls connected by a spring, a situation for which Hooke's law applies. Thus, an approximate value for the stretching vibrational frequency, i.e. the stretching absorption frequency of a bond, can be calculated by Hooke's law

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

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, m_1 & m_2 are the masses (g) of the atoms linked to the particular bond.

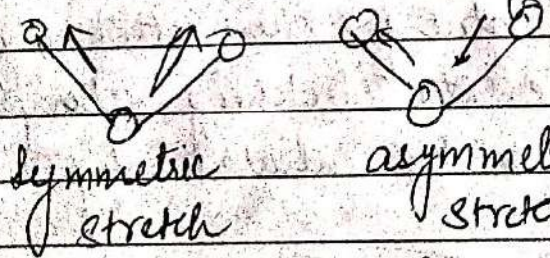
f = force constant of bond in dynes/cm

c = Velocity of light

$\bar{\nu}$ = stretching vibrational frequency of the bond in cm^{-1} (wavenumber)

The force constant is related to its bond strength.

Coupled Vibrations :-
(It involves interaction between two similar or different vibrating groups.)
An isolated C–H bond has only one stretching vibrational frequency, where as methylene group shows two stretching vibrations, symmetrical and asymmetrical.
This is because there is mechanical Coupling or interaction between C–H stretching vibrations in the CH_2 group. In all such cases, asymmetric stretching vibrations occur at higher frequencies or wavenumber than the symmetric stretching vibrations. The C–H Coupled vibrations of CH_2 groups are of different frequencies than that of CH_3 groups.
These are known as Coupled vibrations because these vibrations occur at different frequencies than that required for an isolated C–H stretching.



A strong vibrational Coupling is present in Carboxylic acid anhydrides in which Symmetrical and asymmetrical vibrations appear in the region 1720–1825 cm^{-1}. Here two Carbonyl groups are Coupled through the oxygen. The interaction is very effective probably because of partial double bond character in the Carbonyl oxygen bonds due to resonance which also keeps the system planar for effective Coupling.