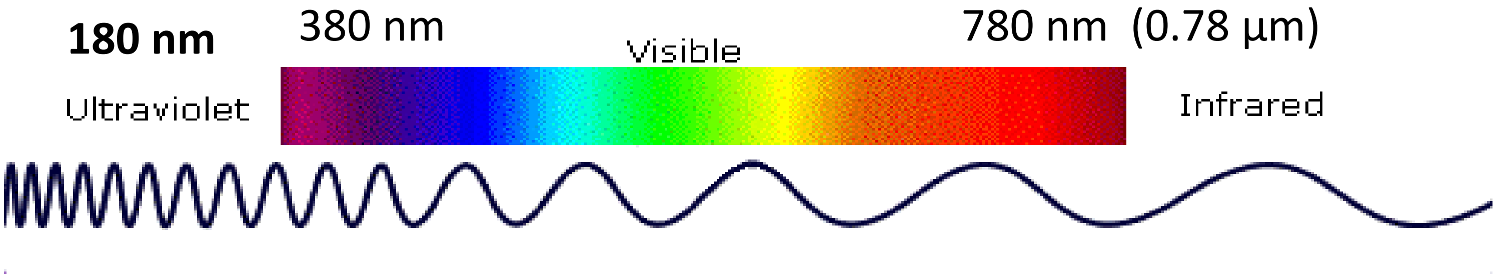
INFRARED (IR)
SPECTROSCOPY

- Infrared spectrum is an important record which gives sufficient information about the structure of a compound.
- The ordinary infrared region covers 4000 cm-1 to 667 cm-1.
- Infrared spectra of organic compounds are plotted as percentage transmittance against wave number.



Region	Energy (kJ/mol)	Wavenumber (cm^{-1})	Wavelength (µm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

Interaction of Molecules with IR Radiation

Vibrational frequencies of molecules correspond to the frequencies of absorbed radiation.

i.e. Infrared light is absorbed when the **oscillating dipole moment** (due to molecular vibration) interacts with the oscillating electrical vector of the infrared beam.

Band intensities are expressed as transmittance (T)

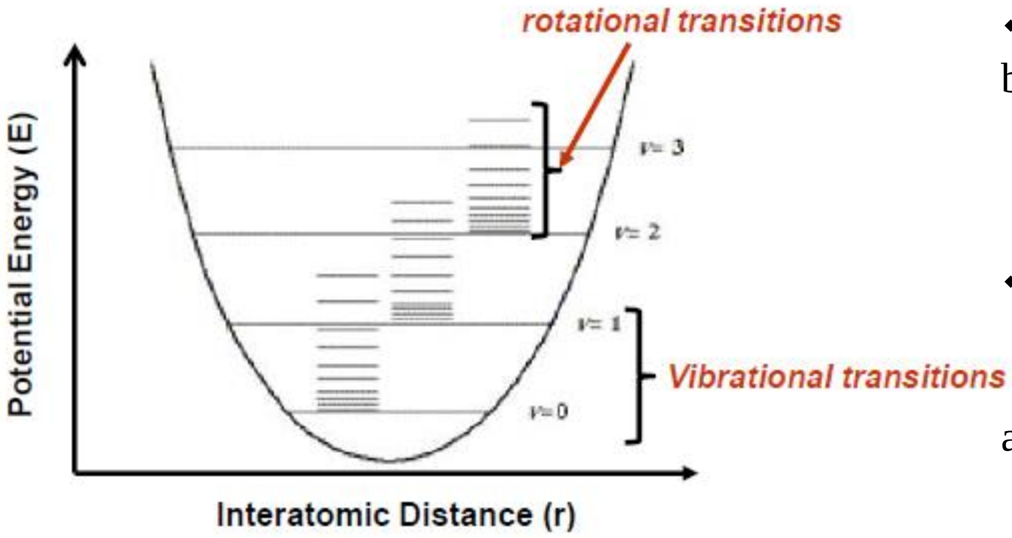
($T = I/I°$)

I= intensity of light transmitted

I° = Intensity of initial light from the source

Principle of IR spectra

- The absorption of IR radiation causes an excitation of a molecule from lower to higher vibrational level. We know that each vibrational level is associated with a number of closely spaced rotational level. So IR spectra is considered as **vibrational-rotational spectra.**
- Only those bonds which are accompanied by **a change in dipole moment** will absorb in the IR region.



- Vibrational transitions of C=O, N-H, O-H bands are accompanied by a change in dipole moment and thus absorbs strongly in the IR region.

- But transitions in C-C bonds in symmetrical alkene and alkynes are not accompanied by change in dipole moment and hence do not absorb in IR region.

The energy in the IR region, absorbed by a molecule depends on

1. Masses of the atom present in the molecule.
2. Strength of the bond.
3. The arrangements of atoms in the molecule.

No two compounds except the enantiomers can have similar Infrared Spectra

When Infra-red light is passed through the sample, the vibrational and the rotational Energies of the molecules are increased.

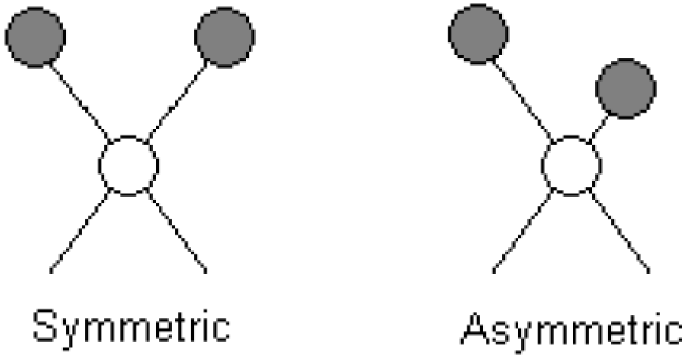
Two kinds of fundamental vibrations are:

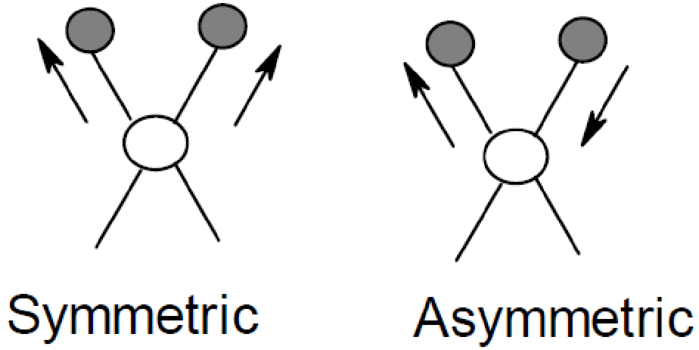
1. **Stretching**
2. **Bending.**

Stretching absorption of a bond appear at high frequencies than bending absorption of the same bond.

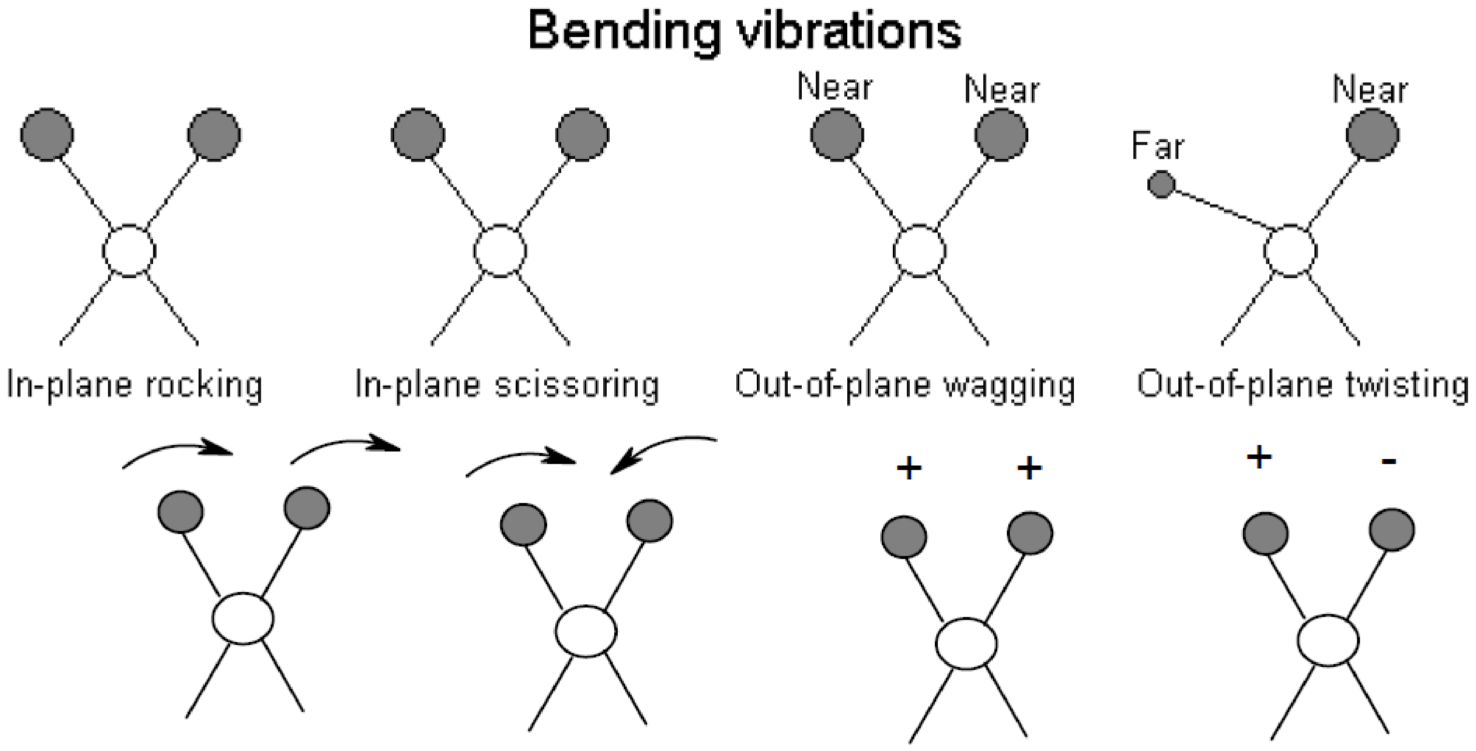
1) Stretching:- a rhythmic movement along the bond axis such that the interatomic distance is **increased** or **decreased**.

Stretching vibrations



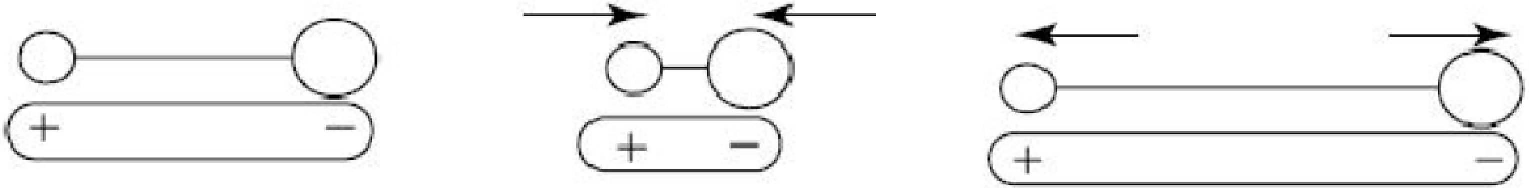


- 2) Bending:- a change in bond angle between bonds with a common atom or
- the **movement of a group of atoms** with respect to the remainder of the molecule,
- with out movement of the atoms in the group with respect to one another.



Selection Rule

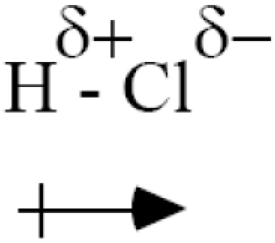
- Only those vibrations that result in rhythmical change of dipole moment of the molecule are observed in IR.



Homonuclear diatomic molecules such as H_2 or O_2 do not **absorb IR radiation** (they are IR-inactive), since there is no over-all electric (Dipole) moment in the molecule.

O – O

No dipole moment



$\overset{\delta+}{H}-\overset{\delta-}{Cl}$

HCl, H_2O, NO

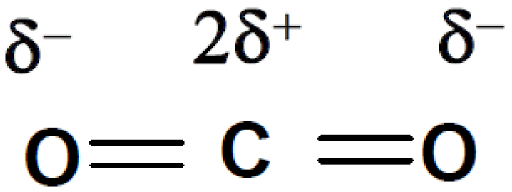
IR active

Atoms, O_2, H_2, Cl_2

IR inactive

- It is not necessary for polyatomic molecules to possess permanent dipole moment in order exhibit IR absorption,
- provided that some polar bonds are present in the molecule.

Example

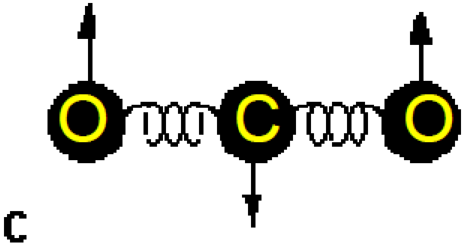


$$\overset{\delta^-}{O}=\overset{2\delta^+}{C}=\overset{\delta^-}{O}$$

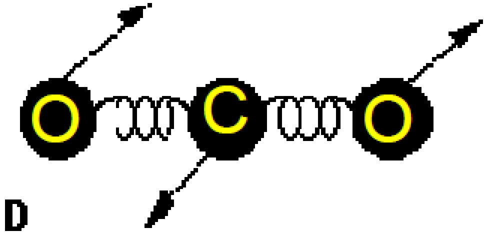
Symmetrical stretching

Anti-symmetrical stretching

ν = 2350 cm-1



In plane bending



Out of plane bending

ν = 667 cm-1

- A is not IR active
- B, C and D are **IR active**
- its positive and negative electrical centres are no longer coincident,
- a dipole moment is **temporarily induced**.

Vibrational frequency

The value of the stretching vibration frequency of a bond can be calculated fairly accurately By the application of Hooke's law which may be represented as:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

Where:

μ = reduced mass = $\frac{m_1 m_2}{m_1+m_2}$

m1 and m2 are the masses of the atoms concerned in grams in a particular bond

In terms of the wavenumber ($\bar{\upsilon}$)

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

k is **force constant** of the bond related to the strength of the bond.

Higher the bond strength higher will be k value.

c = speed of light = 3 x 10^{10} cm/sec

Force constants (k):

Single bond = 5x10^5 dyne/cm

Double bond = 10x10^5 dyne/cm

Triple bond = 15x10^5 dyne/cm

The value of vibrational frequency or wave number depends on

1. Bond strength
2. Reduced mass

Note: If the bond strength increases or reduced mass decreases the vibrational frequency increases.

- ➢C=C stretching (higher bond strength) absorb at higher frequency than C-C (lower bond strength).
- ➢O-H stretching (small reduced mass) absorb at higher frequency than C-C bond (higher reduced mass).

C–N bond $\bar{\upsilon} = 1145\ cm^{-1}$

C=N bond $\bar{\upsilon} = 1619\ cm^{-1}$

C≡N bond $\bar{\upsilon} = 1983\ cm^{-1}$

C–S bond $\bar{\upsilon} = 985\ cm^{-1}$

C–H bond $\bar{\upsilon} = 3023\ cm^{-1}$

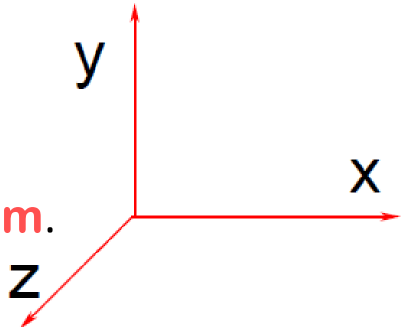
Number of fundamental vibrations

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands.

The number of fundamental bands is related to the degrees of freedom in a molecule.

The number of degrees of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space.

- ❑Molecules of n atom will have 3n degrees of freedom.
- ❑A molecule have always 3 translational degrees of freedom.



For a linear molecule of n atoms

Total degrees of freedom = 3n

Translational degrees of freedom= 3

Rotational degrees of freedom=2

Therefore, **vibrational degrees of freedom = 3n-3-2=3n-5**

For a non-linear molecule of n atoms

Total degrees of freedom = 3n

Translational degrees of freedom= 3

Rotational degrees of freedom=3

Therefore, **vibrational degrees of freedom = 3n-3-3=3n-6**

H_2O

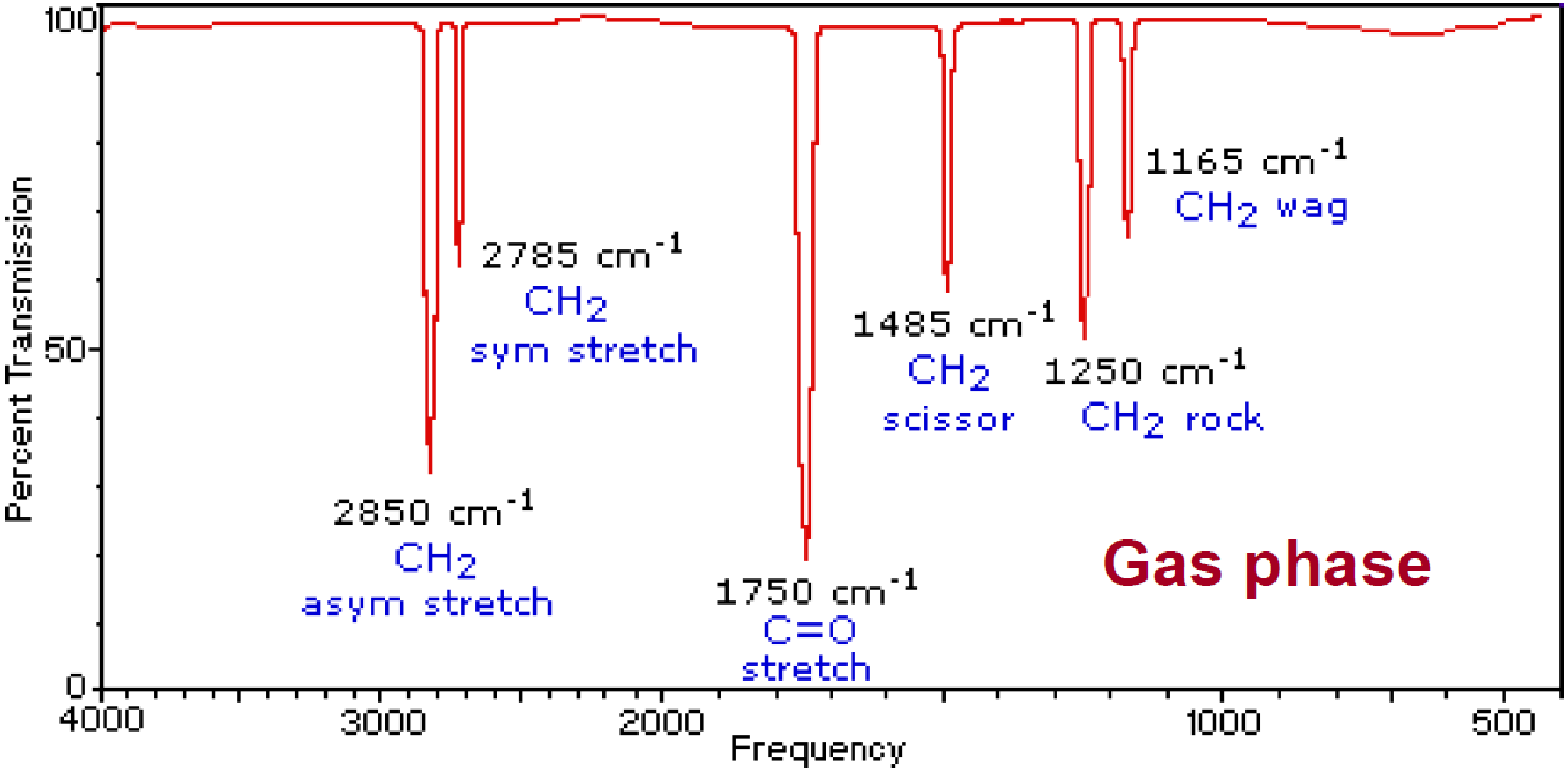
- Three atoms (non-linear).
- 3 X 3= **9 degrees of freedom**.
- 3n-6 (fundamental vibrations).
- 9 - 6 = 3 (fundamental vibrations).
- **CO_2**
- Three atoms (linear).
- 3 X 3 = **9 degrees of freedom**.
- 3n-5 (fundamental vibrations).
- 9 - 5 = 4 (fundamental vibrations).

Formaldehyde, $H_2C=O$

Four atoms (non-linear).

3 X 4= **12 degrees of freedom**.

12 - 6 = 6 (fundamental vibrations).



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