<u>B.Sc. Sem IV</u>

Unit III: Molecular Spectroscopy

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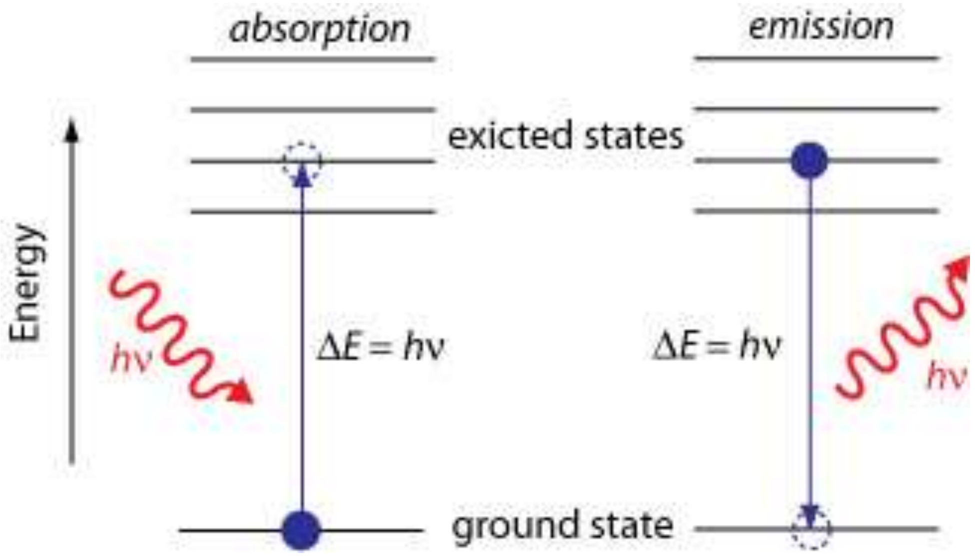
Spectroscopy

Spectroscopy: *Study of the interaction of electromagnetic waves and matter*

Due to interaction, the absorption or emission of electromagnetic wave by the molecules happen

It provides important information about the molecular structure (bond length, bond energy etc.)

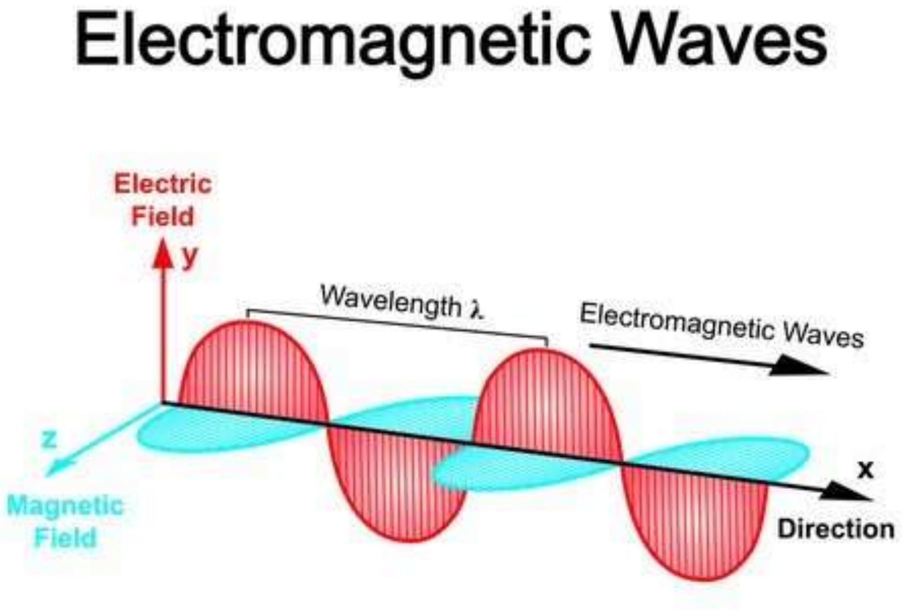


Electromagnetic wave

- Electromagnetic wave shows dual nature (particle & wave nature)

- A light ray consists of a stream of particles (photons) moving in the form of waves each with energy $E = hv$

- Electromagnetic waves have electric and magnetic fields associated with them at right angle to one another. Thus if the radiation is propagating along X axis, the magnetic field is along Z axis and the electric field is oriented along Y axis.



$$c_0(vaccum) = 2.9978\ \times 10^8\, m\, s^{-1}$$

Electromagnetic wave

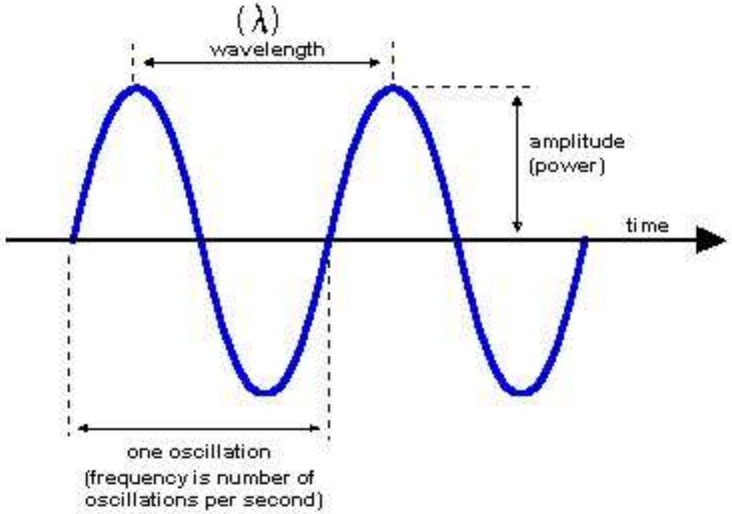
Electromagnetic wave are characterized by wavelength (λ), amplitude, frequency(ν) or wavenumber ($\bar{\nu}$)

Wavelength (λ) : Distance between two successive crests or troughs.
Unit: cm or m or nm

Frequency (ν) : The no. of waves that pass by a given point in one second. Unit: Hz or s^{-1}

wavenumber ($\bar{\nu}$) : The no. of waves per unit length is called wavenumber cm^{-1}

Amplitude : The maximum displacement or distance moved by a point on a vibrating body or wave measured from its equilibrium position



Relation,

$$\lambda\nu = c$$

$$\nu = c\bar{\nu}$$

$$\bar{\nu} = \frac{1}{\lambda}$$

Energy of photons given by Planck equation

$$E = hv = \frac{hc}{\lambda} = hc\bar{v}$$

Regions of the electromagnetic spectrum

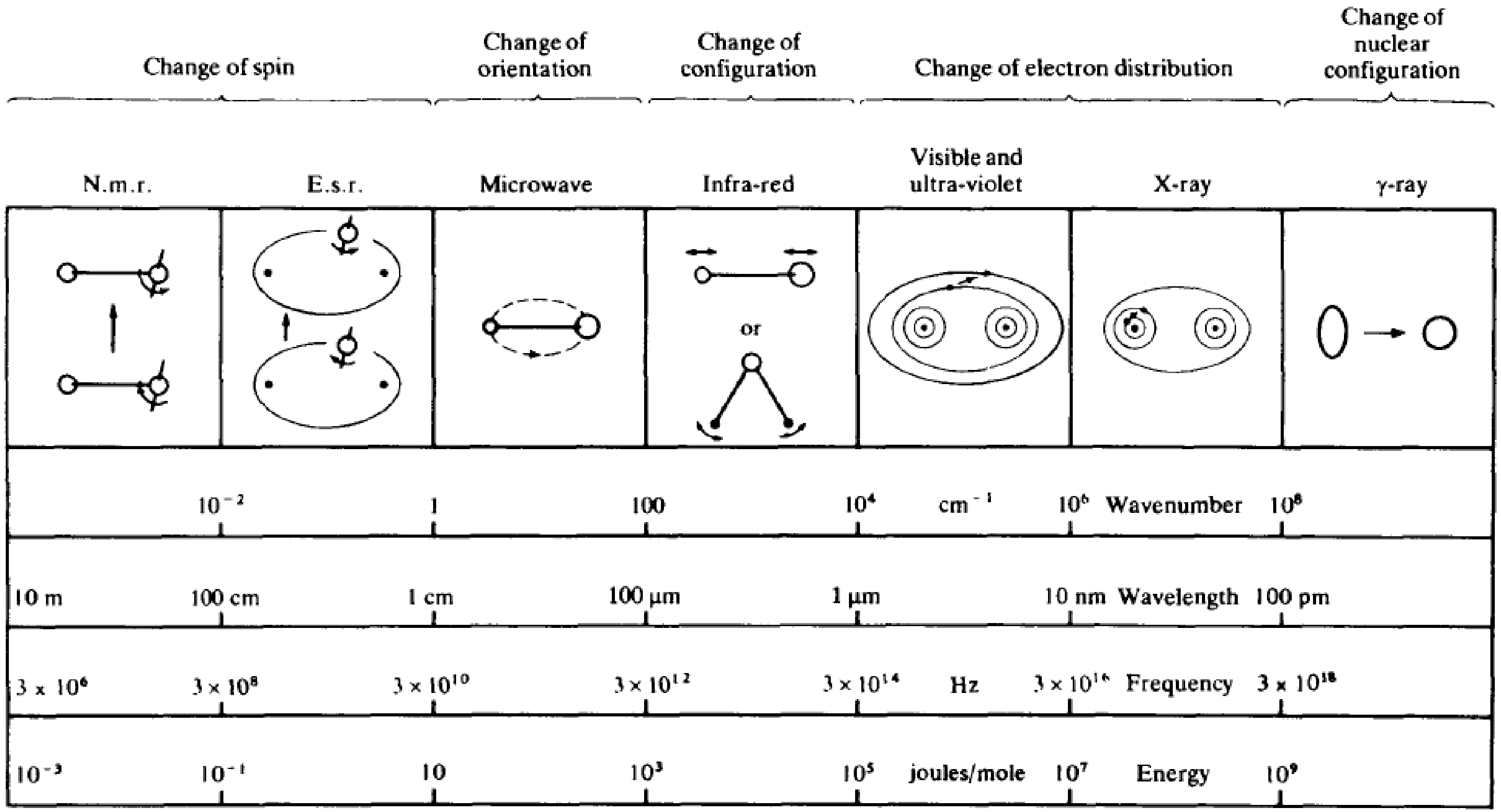
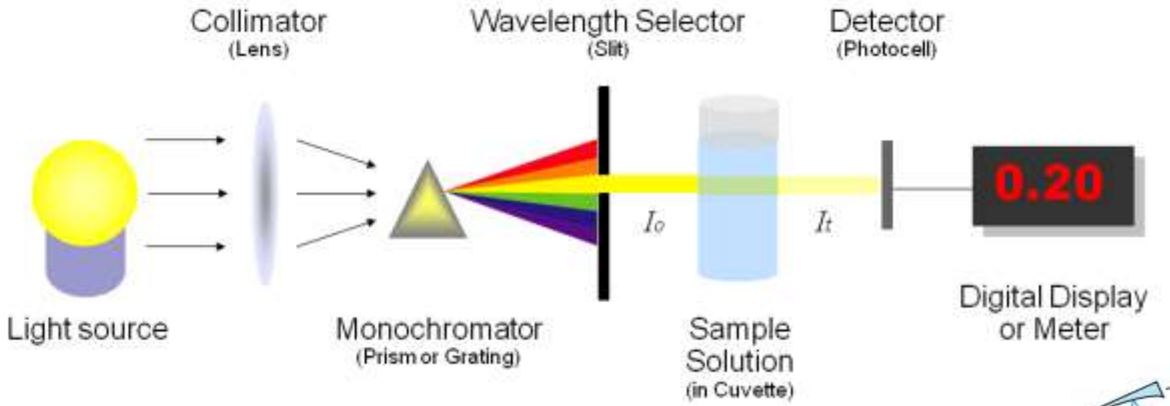


Figure 1.4 The regions of the electromagnetic spectrum.

Regions of the electromagnetic spectrum

Spectrum Region	Process	Information
Radio frequency $(3 \times 10^{6} - 3 \times 10^{10}\ Hz)$ 10 m – 1 cm wavelength	Change in spin orientation of electron (EPR)/nuclei (NMR)	Magnetic environment of spinning nuclei from which structure may be concluded (NMR). EPR is used in studying compounds containing paramagnetic electrons
Microwave region $(3 \times 10^{10} - 3 \times 10^{12}\ Hz)$ 1 cm – 100 µm wavelength	Change in rotational energy state of the molecule	Bond length
Infra-red region $(3 \times 10^{12} - 3 \times 10^{14}\ Hz)$ 100 µm - 1 µm wavelength	Change in vibrational energy state of the molecule	Type of bonds (Functional groups)
Visible and ultra-violet region $(3 \times 10^{14} - 3 \times 10^{16}\ Hz)$ 1 µm - 10 nm wavelength	Transition of valence(outer) electrons	Details of valence electronic structure, Bond dissociation energy
X-ray region $(3 \times 10^{16} - 3 \times 10^{18}\ Hz)$ 10 nm – 100 pm wavelength	Transition of inner elctrons	Details of inner electronic structure, Crystal structure
gamma-ray region $(3 \times 10^{18} - 3 \times 10^{20}\ Hz)$ 100 pm – 1 pm wavelength	Rearrangement of nuclear particles	Used in identifying various radioactive isotopes in a sample

Spectrophotometry

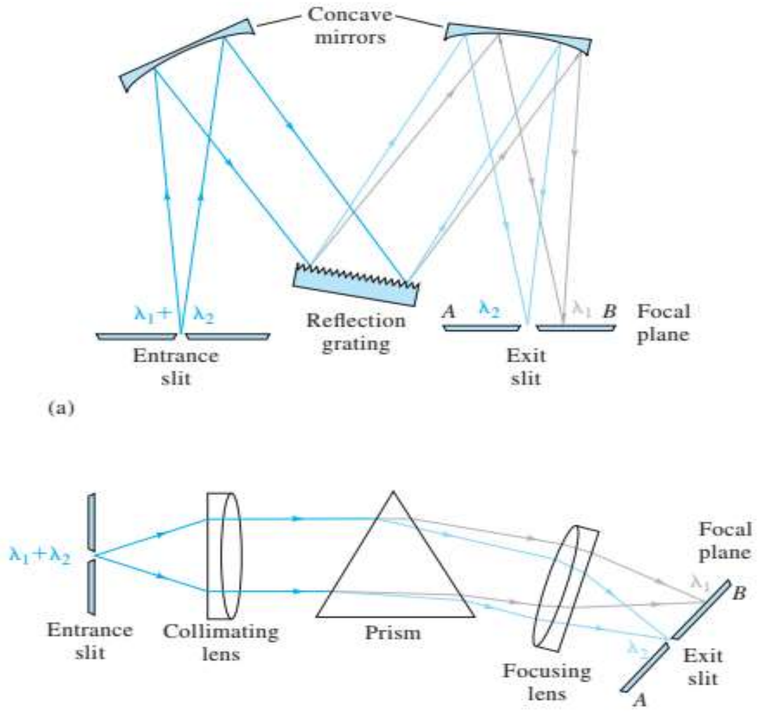


Working principle of spectrophotometer

Spectrophotometry is a measurement of how much a chemical substance absorbs or transmits light

A spectrophotometer is an instrument that measures the amount of photons (the intensity of light) absorbed after it passes through sample solution.

Using it, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected.



Types of monochromators

Born-Oppenheimer Approximation

The electronic energy, rotational energy, vibrational energy and translational energy are totally independent of each other and total energy of a molecule can be expressed as sum of these quantities.

$$E_{total} = E_{el} + Ev_{ib} + Er_{ot} + Et_{rans}$$
$$\Delta E_{total} = \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot} + \Delta E_{trans}$$

The mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times) and nuclei move much slowly than the electrons.

Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule.

Thus the electronic wave function can be separated from the nuclear wave function

Degrees of freedom

Defined as the no. of coordinates required to explain the position of all the atoms in a molecule in space

A molecule made up of N atoms has 3N no. of degrees of freedom.

Energy absorbed by a molecule is stored within the molecule in the form of

- *Translational motion*
- *Internal movements of the atom within the molecule, i.e. rotational motion and vibrational motion*

Translational motion of the molecules means the motion of the centre of mass of the molecule as a whole. Centre of mass can be represented by 3 coordinates.

For a rotational motion, there are 2 degrees of freedom for a linear molecule and 3 for a non-linear molecular molecule.

No. of vibrational degrees of freedom in linear molecules are equal to (3N-5) and for non linear molecule (3N-6)

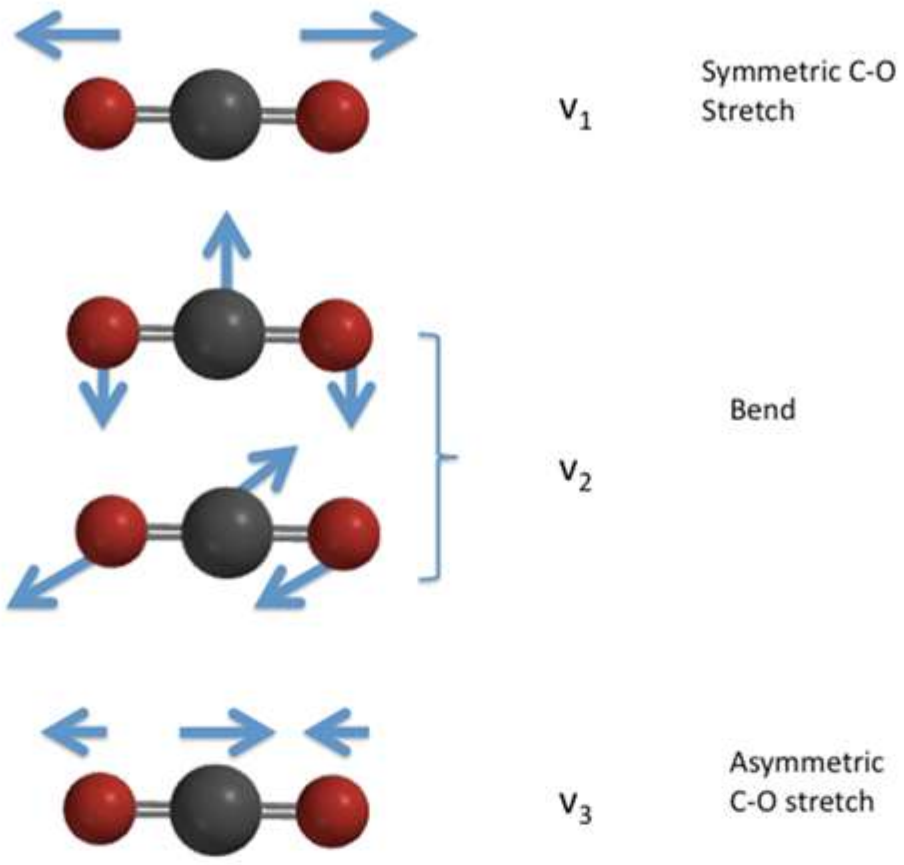


Fig. 1 Vibrational modes of CO_2

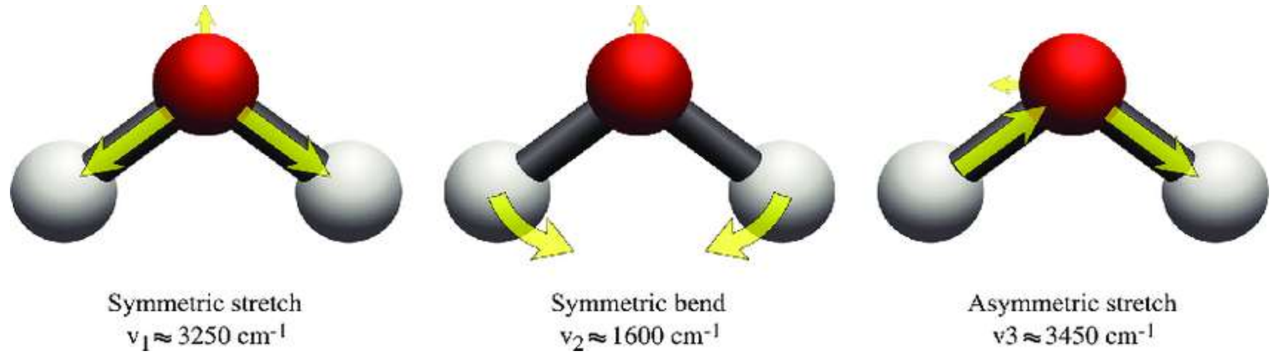


Fig. 2 Vibrational mode of H_2O