Interaction with matter:

- Photon is the elementary particle which carries the EM radiation and has properties of a wave as well as particle, albeit having a mass of zero.
- **As a particle, photon interacts with matter by transferring its energy**

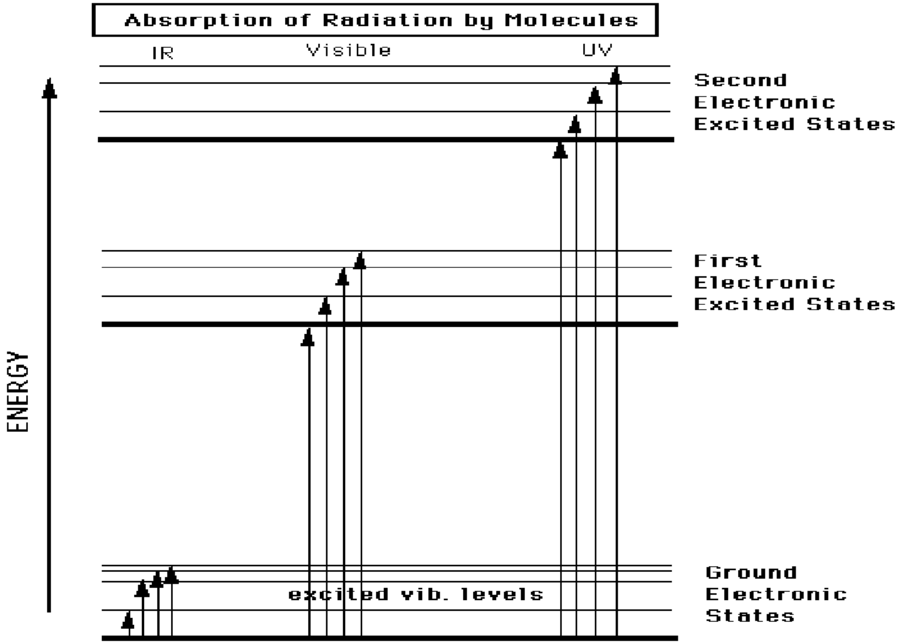
$$\mathbf{E = \frac{hc}{\lambda} = h\upsilon}$$

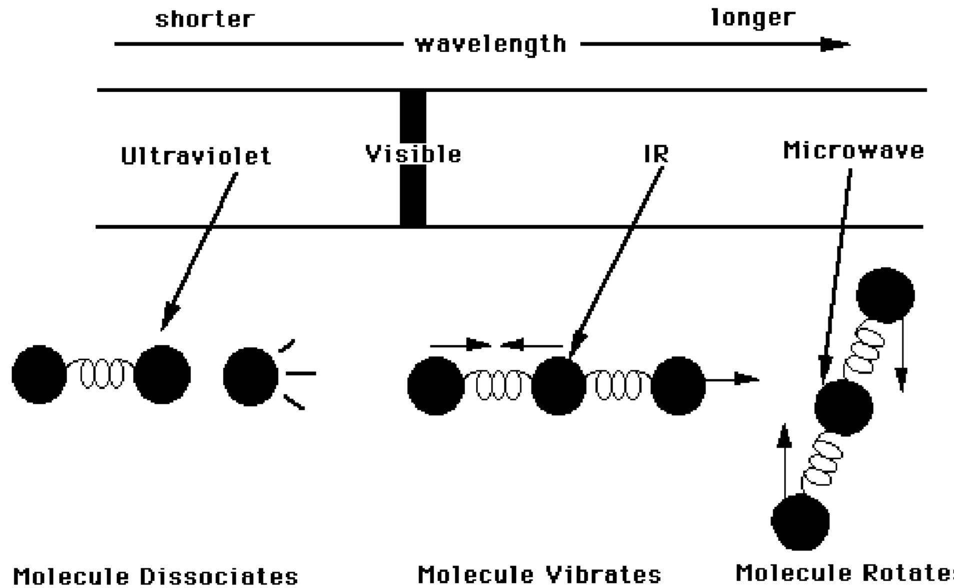
where, h is Planck constant ($h = 6.63\ 10^{-34}$ Js) and υ is the frequency of the radiation.

- Considering a diatomic molecule, each electronic state of a molecule possesses its own set of rotational and vibrational levels. In order for a transition to occur in the system, energy must be absorbed. The energy change (ΔE) needed is defined in quantum terms by the difference in absolute energies between the final and the starting states as

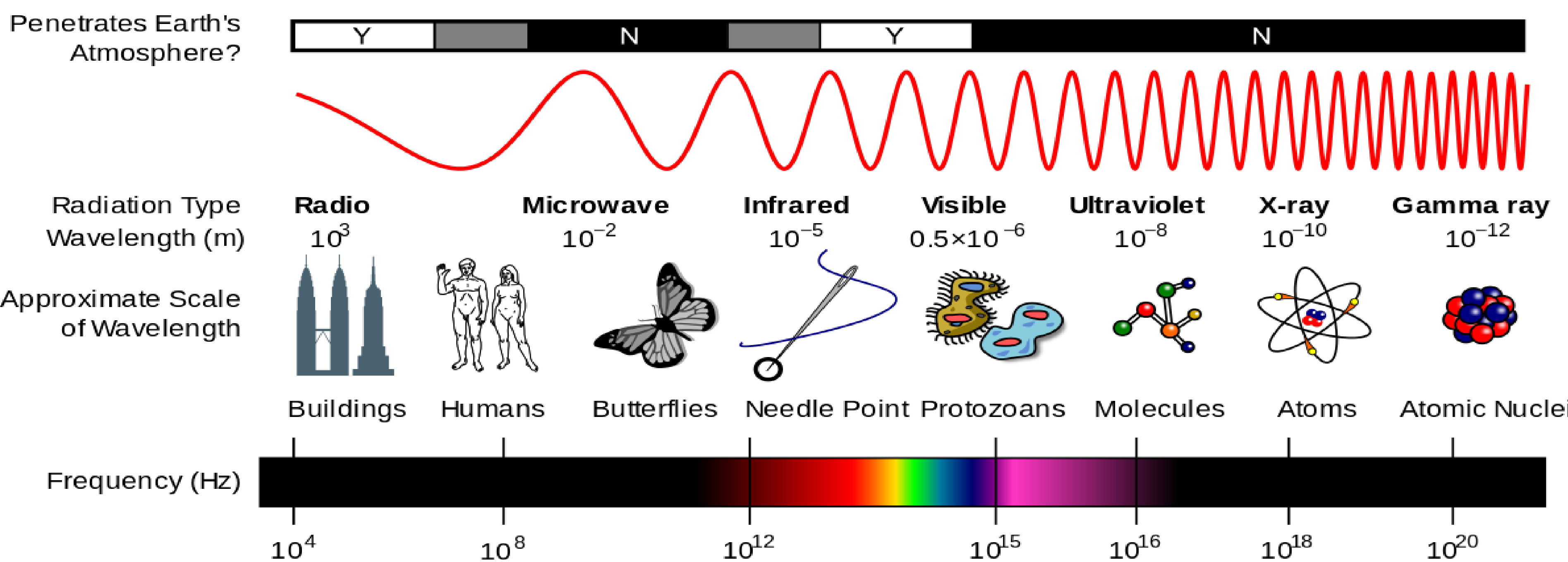
$$\Delta E = E_{final} - E_{start} = h\upsilon.$$

- **Electrons in either atoms or molecules** may be distributed between several energy levels but **principally reside in the lowest levels (ground state).** In order for an electron to be promoted to a higher level (**excited state**), energy must be put into the system.
- **If this energy $E = h\upsilon$ is derived from EM radiation, this gives rise to an absorption spectrum,** and an electron is transferred from the electronic ground state (S_0) into the first electronic excited state (S_1).
- The molecule will also be in an excited vibrational and rotational state. Subsequent relaxation of the molecule into the vibrational ground state of the first electronic excited state will occur. The electron can then revert back to the electronic ground state.
- **For non-fluorescent molecules, this is accompanied by the emission of heat (ΔH).**





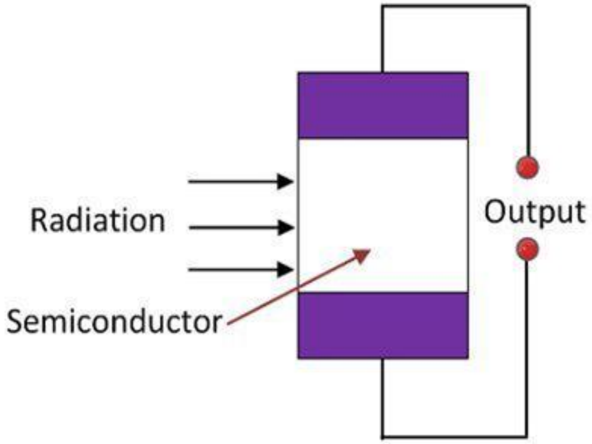
Frequency range of each transition during the spectroscopic analysis



Type of radiation	Frequency range (Hz)	Wavelength range	Type of transition
Radio waves	$<3x10^{11}$	>1 mm	excitement of nucleus to a higher spin state
Microwaves	$3x10^{11}-10^{13}$	1 mm-25 mm	molecular rotations, electron spin flips
Infrared	$10^{13}-10^{14}$	25 mm-2.5 mm	molecular vibrations
Near-infrared	$1\sim4x10^{14}$	2.5 mm-750 nm	outer e^- molecular vibrations
Visible	$4\sim7.5x10^{14}$	750 nm-400 nm	outer electron
Ultraviolet	$10^{15}-10^{17}$	400 nm-1 nm	outer electron
X-rays	$10^{17}-10^{20}$	1 nm-1 pm	inner electron
Gamma-rays	$10^{20}-10^{24}$	$<10^{-12}$ m	Nuclear

Spectrometric Instruments:

- Ultraviolet-Visible (UV-Vis), Atomic Absorption Spectroscopy (AAS) and Atomic Emission Spectroscopy (AES) are used for **measurement of substances**.
- IR, Raman, X-ray Fluorescence (XRF), Energy-dispersive X-ray (EDX) and Nuclear Magnetic Resonance (NMR) spectroscopy techniques are mainly used for **characterization of substances**.



Photoelectric Transducer

- Intensity of the radiation is mostly measured with a photoelectric transducer.
- The large number of wavelengths emitted by these systems makes it possible to investigate their electron configurations of ground and various excited states.

(b). Principle and applications of UV-Visible Spectroscopy technique

- In UV-Vis spectroscopy, energy is absorbed by a molecule in the UV region (1 nm-400 nm) or visible region (400 nm-750 nm) resulting in electronic transition of valence electrons.
- Different molecules absorb radiation of different wavelengths depending on their structure. An absorption spectrum will show a number of absorption bands corresponding to structural (functional) groups within the molecule.
- For ex. absorption by carbonyl group in acetone is of the same wavelength as the absorption by carbonyl group in diethyl ketone.

Three types of electronic transitions involving:

(i). π, σ and *n* electrons; (ii). charge-transfer electrons and (iii). *d* and *f* electrons.

- Inorganic species show charge-transfer absorption and are called *charge-transfer complexes*.
- For a complex to demonstrate charge-transfer behaviour, one of its components must be able to donate electrons and other component must be able to accept electrons.
- Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor (ε will be very high > 10,000 $dm^3 mol^{-1} cm^{-1}$).
- Absorption of UV-Vis radiation in organic molecules is restricted to certain functional groups (***chromophores***) that contain valence electrons of low excitation energy. The spectrum of a molecule containing these chromophores is complex and broad.