

# IR Spectroscopy

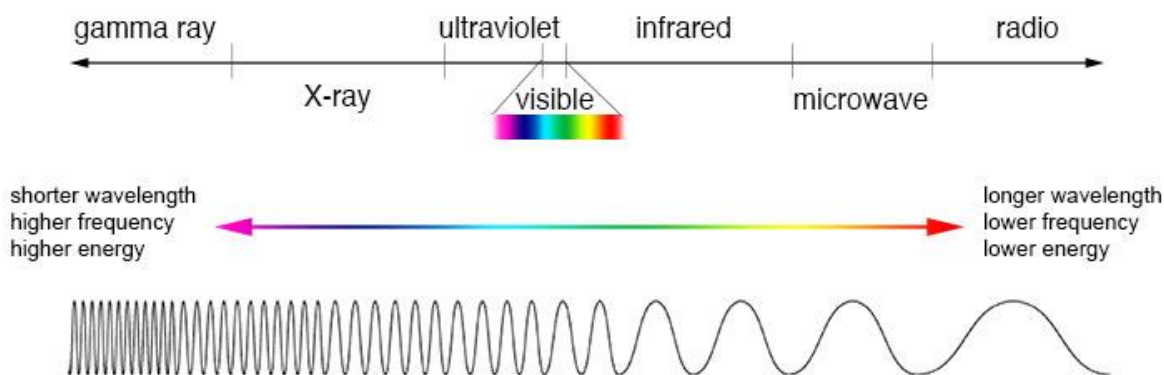
## Electromagnetic radiation and Spectroscopy

Spectroscopy is the branch of science concerned with the investigation and measurement of spectra produced when matter interacts with electromagnetic radiation.

Spectroscopy is the technique of splitting light (or more precisely electromagnetic radiation) into its constituent wavelengths (a spectrum), in much the same way as a prism splits light into a rainbow of colors. However, in general, a spectrum is generally more than a simple 'rainbow' of colors. The energy levels of electrons in atoms and molecules are quantized, and the absorption and emission of electromagnetic radiation only occurs at specific wavelengths.

The frequency and wavelength of electromagnetic radiation varies over many orders of magnitude. The electromagnetic spectrum is divided according to the type of atomic or molecular transition that gives rise to the absorption or emission of photons; UV, IR, microwave, radio wave etc.

Absorption spectroscopy relies on the absorption of energy from a photon which subsequently promotes the analyte from a lower-energy state to a higher-energy, or excited, state. As the energy of the photon changes the type of transition that the analyte undergoes will change. For example in IR spectroscopy, the absorption of relatively low IR radiation results in the vibration of chemical bonds within the analyte; a process which requires a fairly low energy input. Whereas, higher energy photons, such as those found in the UV-visible region of the electromagnetic spectrum, will promote valence electrons to move from their ground state to excited state energy levels within the atoms of an analyte; a process that requires a much greater energy input.



## IR Spectroscopy

IR spectroscopy (which is short for infrared spectroscopy) deals with the infrared region of the electromagnetic spectrum, i.e. light having a longer wavelength and a lower frequency than visible light. Infrared Spectroscopy generally refers to the analysis of the interaction of a molecule with infrared light.

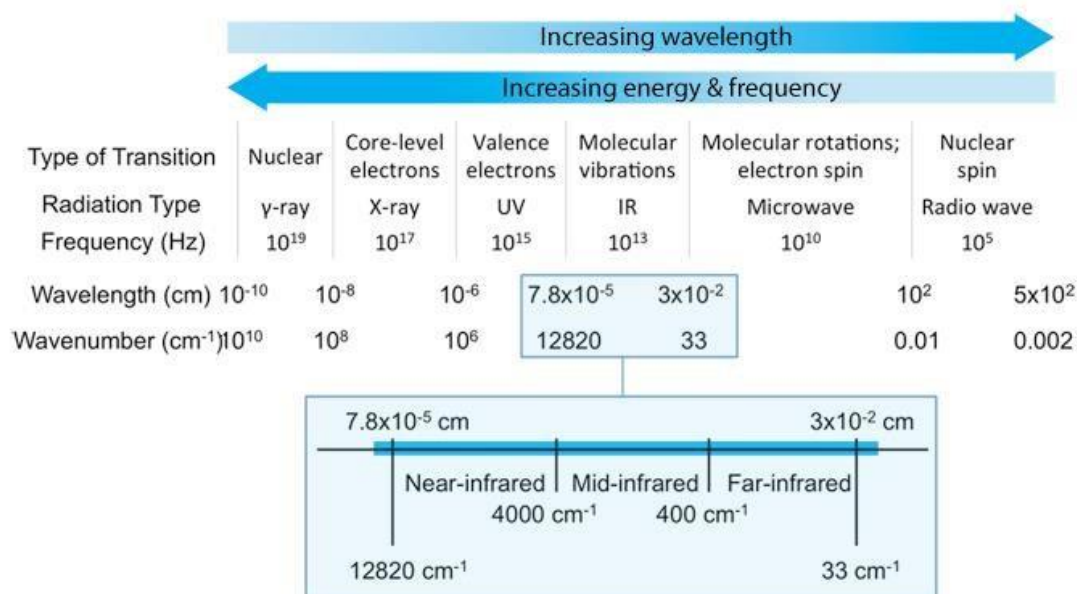
There are three well defined IR regions (near, mid and far). The boundaries between them are not clearly defined and debate still persists, but broadly they are defined as:

**Near infrared (12820-4000  $\text{cm}^{-1}$ ):** poor in specific absorptions.

**Mid-infrared (4000-400  $\text{cm}^{-1}$ ):** provides structural information for most organic molecules.

**Far Infrared (400-33  $\text{cm}^{-1}$ ):** has been less investigated than the other two regions; however, it has been used with inorganic molecules.

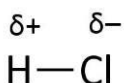
The low energies, typically encountered within the infrared region, are not sufficient to cause electronic transitions; however, they are large enough to cause changes in the frequency and amplitude of molecular vibrations.



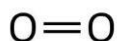
## Molecular Vibrations

The absorption of light will increase both amplitude and frequency of molecular vibrations. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. Molecules with a permanent dipole moment, such as water, HCl, and NO, are infrared active.

The HCl molecule possesses a permanent dipole moment, so it is infrared active.



The O<sub>2</sub> molecule does not possess a permanent dipole moment, so it is not infrared active.



In the case of alkenes (C=C) and alkynes (C≡C) if the bond is symmetrically substituted no band will be seen in the IR spectrum, however, if the bond is asymmetrically substituted a stretching frequency corresponding to the alkene or alkyne bond will be present.

In order to understand molecular vibrations, a bond can be treated as a simple harmonic oscillator composed of two masses (atoms) joined by a spring. Figure depicts a diatomic molecule with two generic atoms (of masses  $m_1$  and  $m_2$ ) connected by a spring.

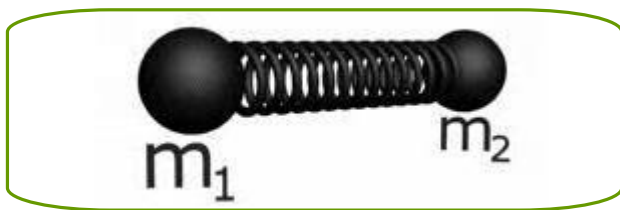
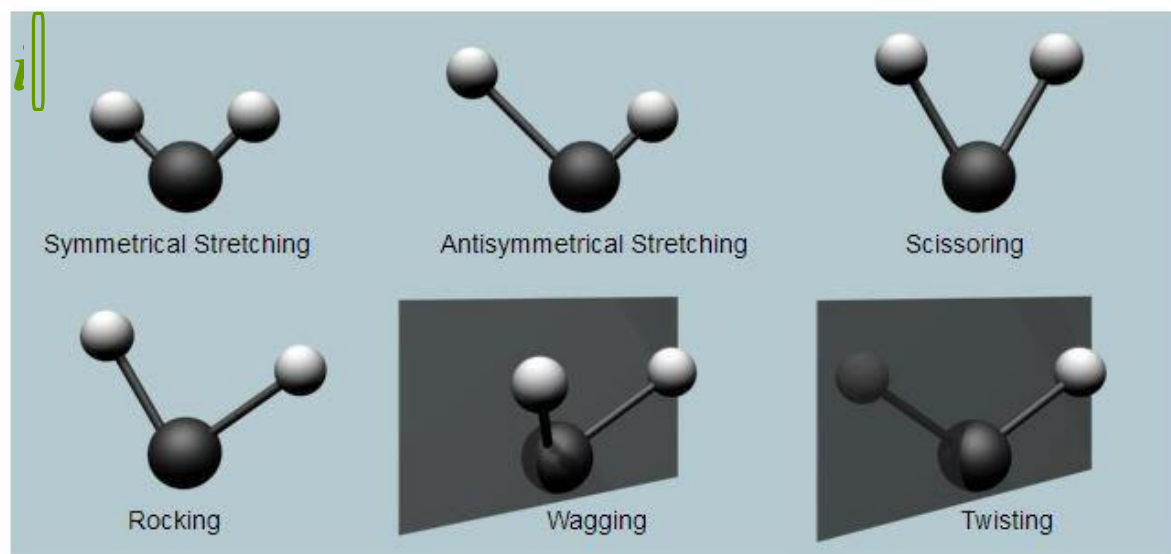


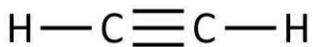
FIG: Representation of a diatomic molecule. If masses  $m_1$  and  $m_2$  are equal, no change in the dipole moment will occur as the molecule vibrates.

## Infrared Active Modes

A molecule that is infrared active must undergo a change in its dipole moment when vibrating. The simplest modes of vibration that are infrared active are stretching and bending modes.



For simplicity, we are going to illustrate the vibration modes in a linear molecule (acetylene in this case).



The symmetric  $\text{C}\equiv\text{C}$  stretching will not alter the acetylene's dipole moment and it is not infrared active.

However, substitution of either of the H atoms in acetylene produces an asymmetric alkyne bond which will be IR active. Homonuclear diatomic molecules such as  $\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , etc. will exhibit no infrared active modes as no change in their dipole moment is experienced during vibrations.

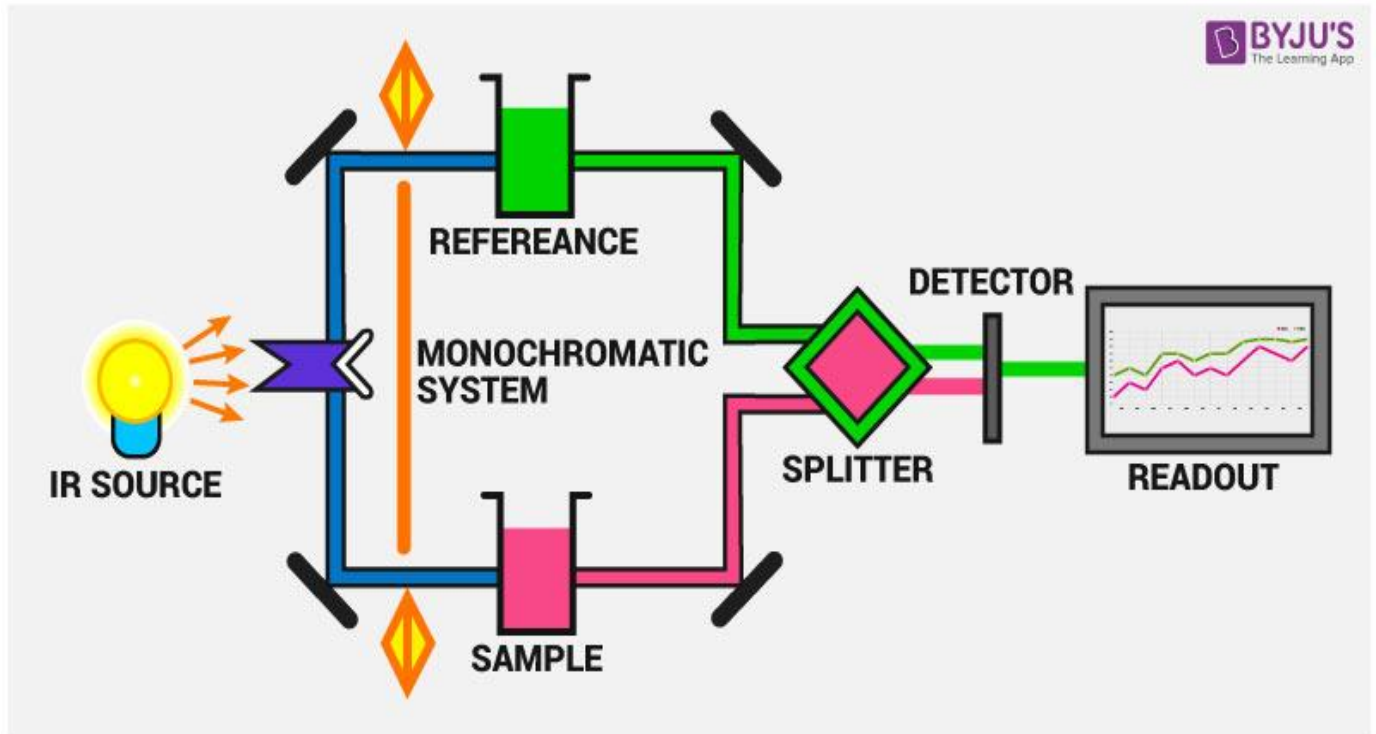
## Samples in Infrared Spectroscopy

The samples used in IR spectroscopy can be either in the solid, liquid, or gaseous state.

- a-** Liquid samples are generally kept between two salt plates and measured since the plates are transparent to IR light. Salt plates can be made up of sodium chloride, calcium fluoride, or even potassium bromide.
- b-** Since the concentration of gaseous samples can be in parts per million, the sample cell must have a relatively long path length, i.e. light must travel for a relatively long distance in the sample cell.
- c-** Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually mineral oil). A thin film of the mull is applied onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified potassium bromide finely. This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non-hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis.

## IR Spectroscopy Instrumentation

The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference and the sample respectively.



Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

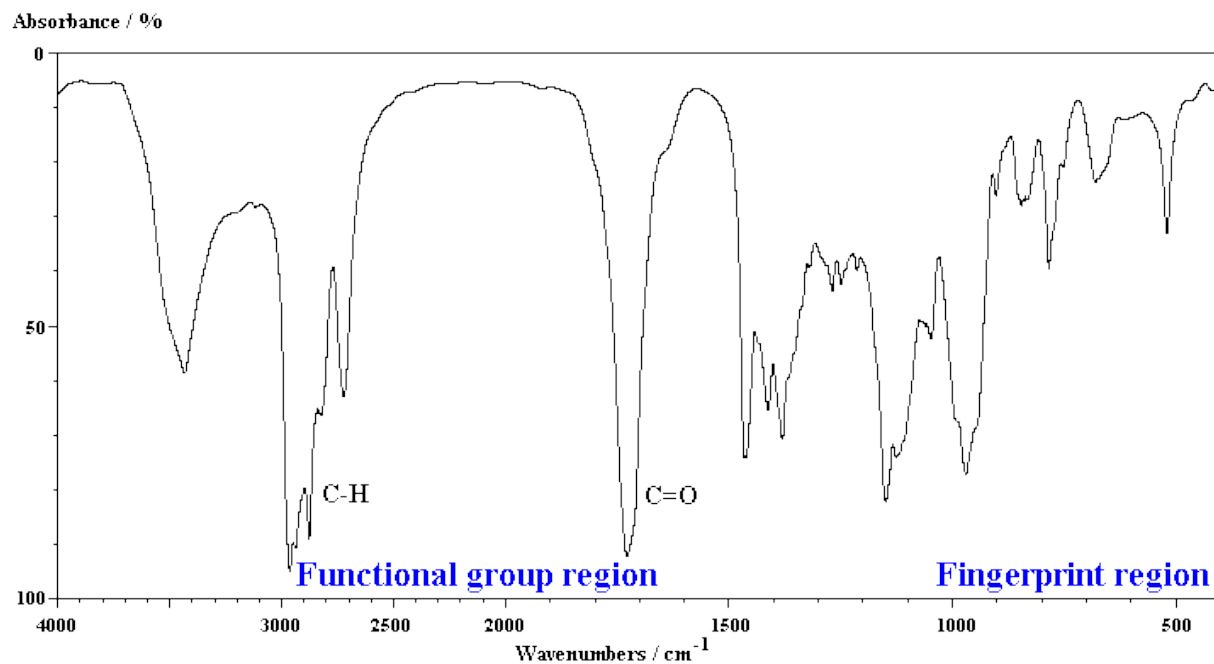
## Graph and Regions of the Infrared spectrum

Most of the bands that indicate what functional group is present are found in the region from  $4000\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$ . Their bands can be identified and used to determine the functional group of an unknown compound.



Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from  $1300\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . These bands are only used to compare the spectra of one compound to another

Given below is a sample of typical Infrared Absorption Frequencies



<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm<sup>-1</sup>)</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)