Spectroscopy

The branch of science which deals with the interaction of electromagnetic radiation with matter is called spectroscopy

The energy absorbed or emitted in each transition corresponds to a definite frequency or wavelength

A plot of intensities of radiation emitted or absorbed against the corresponding frequencies or wavelengths is called a spectrum.

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These methods have three major advantages over chemical methods

(i). Spectroscopic method is easier and faster than any other chemical method and reactions.

(ii). Spectroscopic method provides more information about molecular structure as functional groups and structural features

(iii). Spectroscopic method is non-destructive and , if necessary , the entire sample can be recovered

There are four spectroscopic methods which are used in organic chemistry.

(i). Ultraviolet –visible spectroscopy

(ii). Infrared spectroscopy.

(iii). Nuclear magnetic resonance spectroscopy.

(iv). Mass spectroscopy.

Electromagnetic radiation

Electromagnetic radiation is the ordinary white light , which can be dispersed into spectrum of colours by a prism.

This visible light represents only a small part of the entire electromagnetic spectrum. It extends from high-energy cosmic rays to low-energy radio or radar waves.

Electromagnetic radiation can be described as the stream of energetic particles called photons or as a wave motion.

The energy of the particles may be given as –

$$E = h\,\nu$$

$$\nu = c / \lambda$$

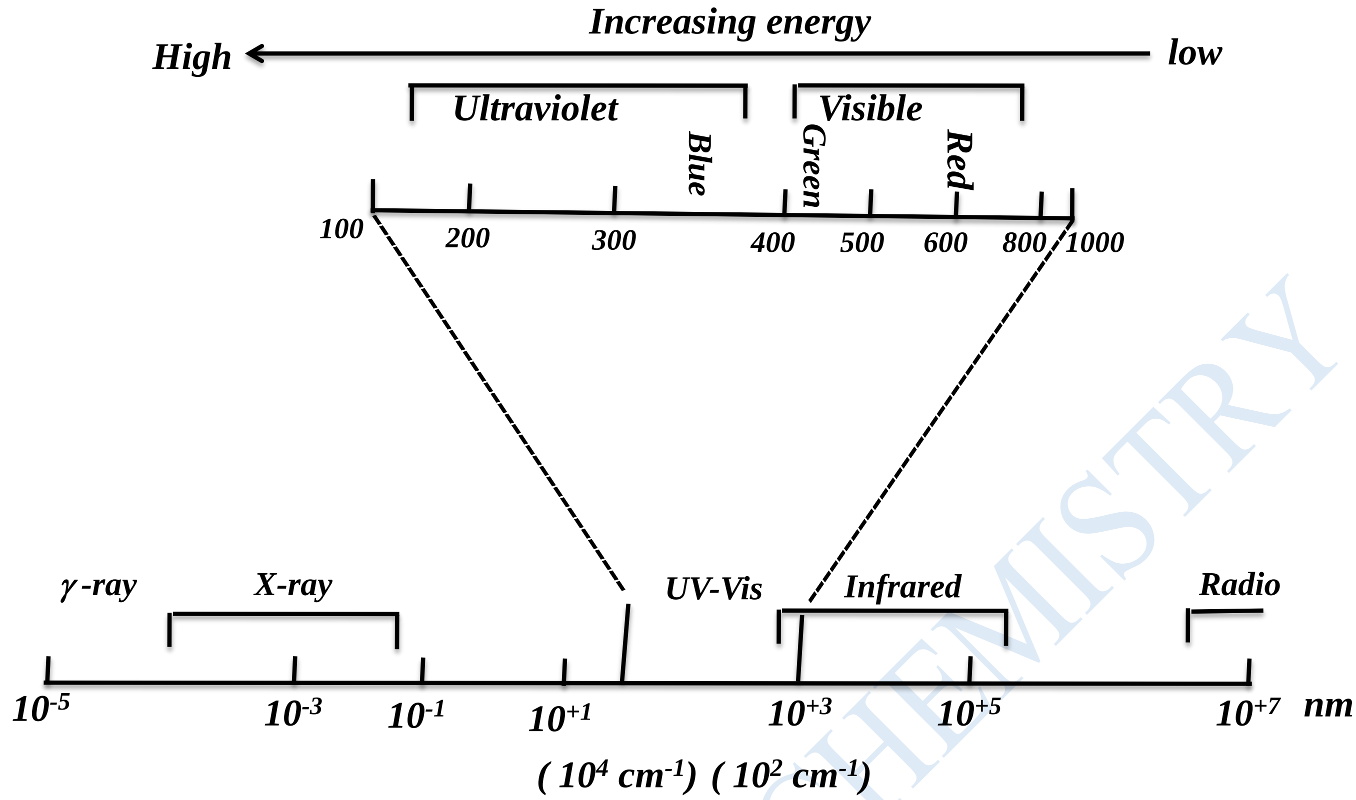
E – energy of the particles

h – Planck's constant.

ν – frequency of radiation

c – speed of light

λ – wave length of radiation



In the above figure various components of the electromagnetic spectrum. In organic chemistry , the important wavelength regions are the ultraviolet, visible and infrared.

The ultraviolet and visible region are adjacent, and the boundary is arbitrary. The unit for the wavelength in this region is the Nanometer (1 nm = 10^{-9} meter = $0.1A^0$).

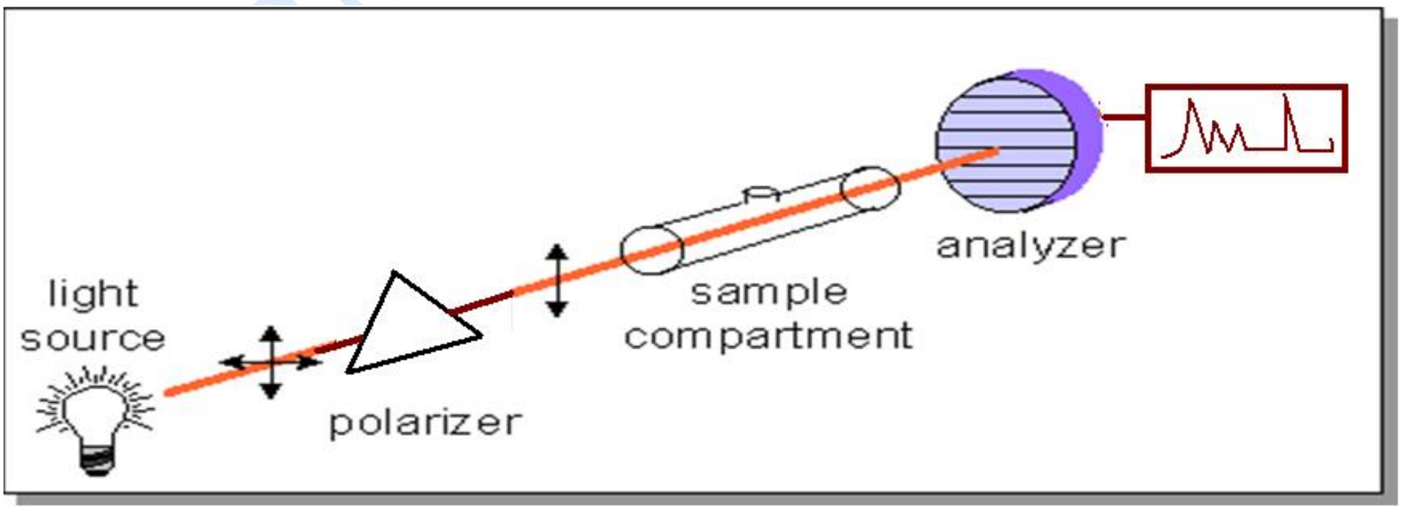
The infrared region is at longer wavelength.

Principles of spectroscopy

All the organic compounds interact with the electromagnetic radiation and absorb energy. When a molecule absorb energy, a transformation occurs that may be either temporary or permanent.

Lower energy radiation may cause a molecular rotation or a bond vibration. Higher energy radiation may cause the promotion of electrons to higher energy levels or bond cleavage.

The transformation involves molecular rotation, bond vibration or electronic transition, the molecule absorbs only the wavelengths of radiation is selective for a particular transition which depends on the structure of the molecule.

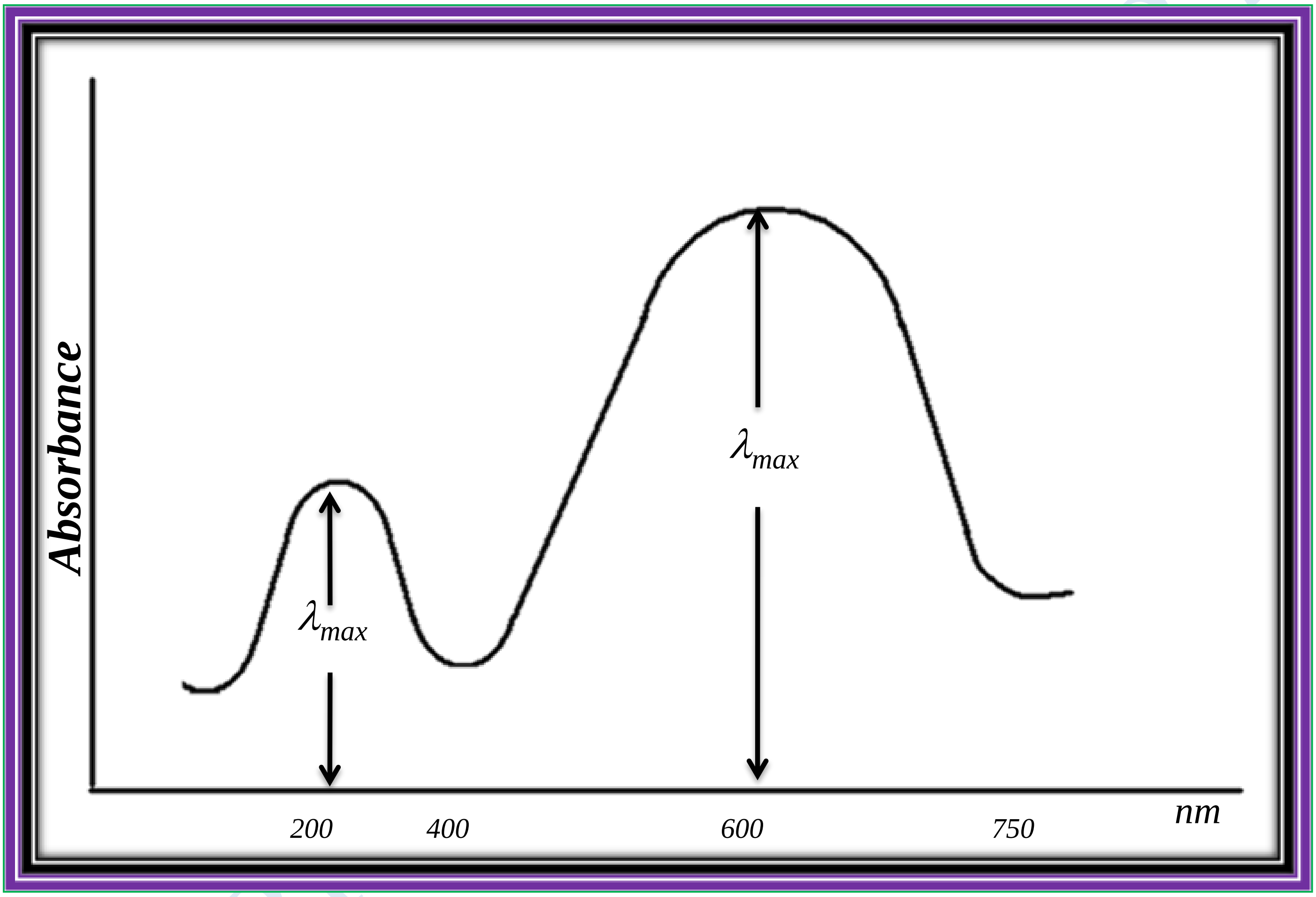


The instrument that is used to measure the amount of electromagnetic radiation absorbed *by an organic molecule is called spetrophotometer or spectrometer. It consists of a light source of radiation, with a prism that can select the desired wavelengths , which are passed through the sample of the compound being investigated. Sample can be detected ,analyse, recorded. The recording is called spectrum.*

Ultraviolet-Visible spectroscopy

In UV-Visible spectroscopy , 200-750 nm region is used. This includes both the visible region (400-750 nm) and near ultraviolet region (200-400 nm) . These wavelength is sufficiently energetic to cause the promotion of loosely held electrons , such as nonbonding electrons or electrons involved in a pi-bond to higher energy levels.

For absorption in this region molecule must contain conjugated double bonds.



The ultraviolet-visible spectrum is composed of only a few broad bands of absorption as shown in the figure.

The wavelength of maximum absorbance is referred to as λ_{max}. UV-Vis. Spectrum depends upon the following points.

(i). Nonconjugated alkenes show absorption below 200 nm and is therefore used UV spectrometers.

e.g.

Ethylene has λ_{max} = 171 nm. The absorption comes from the light-induced promotion of a π-electron to the next higher energy level.

(ii). Non-conjugated carbonyl compounds have a very weak absorption band in the 200-300 nm region.

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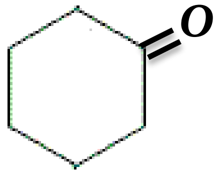
$CH_3 - C - CH_3$

Acetone

279 nm



Cyclohexanone

291 nm

(iii). When a molecule contains two or more nonconjugated carbon-carbon double bonds , molecule is expected a simple alkene in UV spectrum. However when the double bonds are conjugated, λ_{max} is shifted to longer wavelengths.

$CH_2 = CH - CH_2 - CH_2 - CH = CH_2$

1,5- Hexadiene

178 nm

$CH_3 - CH = CH - CH = CH - CH_2$

2,4- Hexadiene

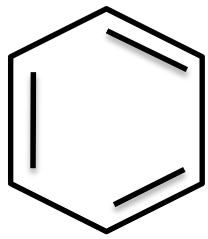
227 nm

(v). As the no. of double bonds in conjugation increases , λ_{max} also increases.

$CH_2 = CH - CH = CH_2$

1,3-butadiene

215 nm



Benzene

257 nm

(iv). Conjugation of carbon-carbon double bond and a carbonyl group shifts the λ_{max} of both group to longer wavelengths.

$(CH_3)_2C = CH - CH_2 - CH_3$

2-methyl pentene-2

180 nm

$$\overset{O}{\overset{\|}{}}$$
$(CH_3)_3CH - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$

4-methyl pentanone -2

283 nm

$(CH_3)_3C = CH - \overset{\overset{O}{\|}}{C} - CH_3$

4-methyl pent – 3-en-2-one

230 nm (for C = C)

327 nm (for C = O)

summary

(i). Absorption of UV-Vis. Radiation (200-700 nm) causes electrons within molecules to be promoted from one energy level to a higher electronic energy level.

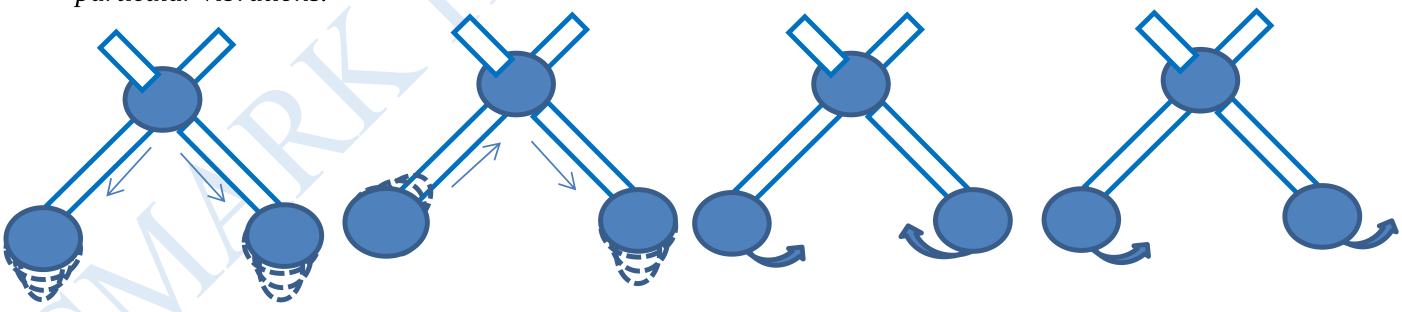
(ii). If an organic compound does not absorb UV-Vis radiation , it means that the compound does not contain conjugated double bonds.

(iii). If an organic compound absorb UV-Vis radiation , it means that the compound contains a carbonyl group or conjugated double bonds.

e.g. conjugated dienes , carbonyl compounds, and aromatic compounds all absorbs in the UV-Vis region.

Infrared spectroscopy (IR spectroscopy)

An infrared spectrometer subjects a compound to infrared radiation in the 5000-667 cm^{-1} range. It supply sufficient energy for bonds in the molecule to vibrate by stretching or bending. The atoms are considered as linked by springs that are set in motion by the application of energy. It absorb only those energy radiations which causes particular vibrations.



Stretching vibrations **Bending vibrations**

since different bonds and functional groups absorb at different wavelengths, an infrared spectrum is used to determine the structure of an organic molecules.

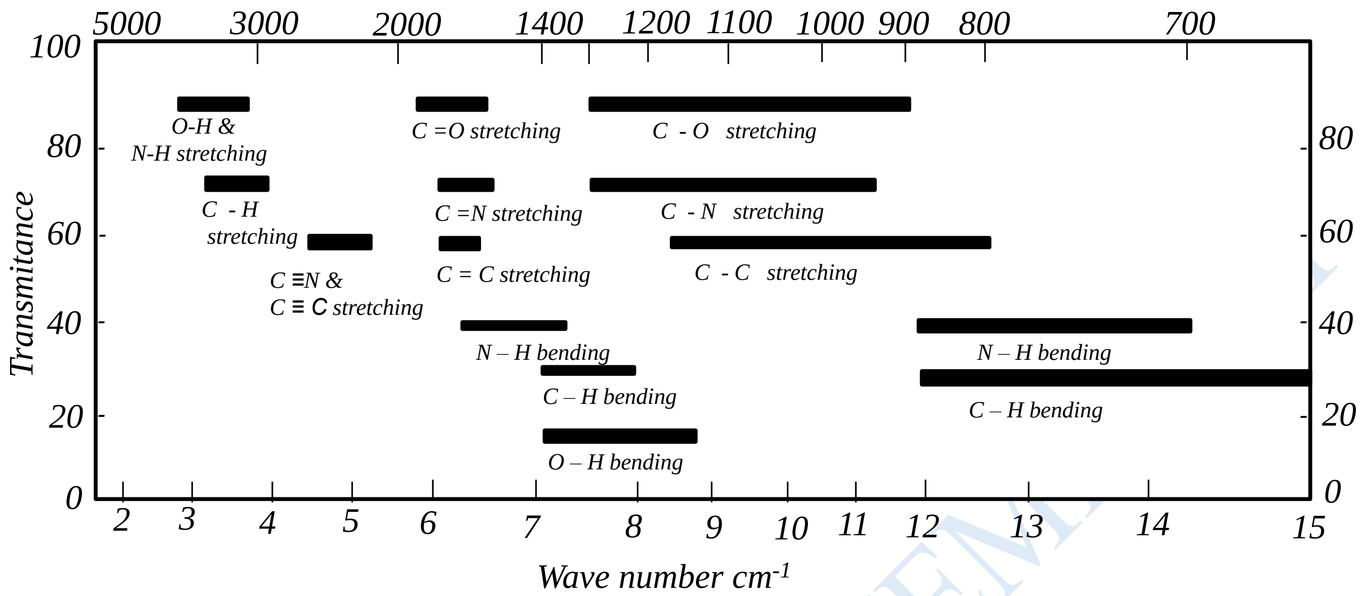
e.g.

C=C *C = C ,*

C = O , *C – O*

C =N ,   *C – N*

From the position of absorption peak , one can identify the group that caused it, the general areas in which various bonds absorb in the infrared



An infrared spectrum is usually studied in two sections:

(i). Functional group region

(ii). Finger print region

Functional group region

The area from 5000 cm-1 to 1300 cm-1 is called functional group region. The bands in this region are particularly useful in determining the type of functional groups present in the molecule.

Finger print region

The area from 1300 cm^{-1} to 667 cm^{-1} is called the finger print region. A peak-by-peak match of an unknown spectrum with the spectrum of the suspected compound in this region can be used, much like a fingerprint, to confirm its identity.

summary

(i). Absorption of infrared Radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to a higher vibrational energy level. .

(ii). Stronger bonds require greater energy to vibrate (stretch or bend). Therefore such bonds absorb infrared radiation of shorter wavelengths.

(iii). Different functional groups absorb infrared radiation at different wavelengths and their presence or absence in a molecule can be determined by examination of an IR spectrum.

(iv). No two compounds have exactly identical infrared spectra.