Spectroscopy

Spectroscopy is the study of the interaction between matter and radiated energy. Spectroscopy originates through the study of visible light dispersed according to wavelength. Later the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency.

Spectroscopy data is often represented by a spectrum, a plot of the response of interest as a wavelength or frequency.

Spectroscopy & spectrography are terms used to refer to the measurement of radiation intensity as a function of wavelength & are often used to describe experimental spectroscopic methods. Spectral measurement devices are referred to as spectrometers, spectrophotometers, spectrographs or spectral analyzer.

Theory :- The main concept of spectroscopy is resonance & its corresponding resonance frequency.

Spectrum:- there are two types of spectrum

Absorption Spectrum:- It results when an atom or molecule undergo a transition from the lower energy level to higher energy level, with the absorption of a photon energy.

Emission spectrum:- It results when the atom or molecule falls from the excited state to the ground state with the emission of a photon of energy.

The spectrum can be classified in to two categories:

(i) **Atomic Spectra**:- Arises from the transition of an electron between the atomic energy levels.
(ii) **Molecular Spectra**:-this arises from the transition of a electron between the molecular energy levels.

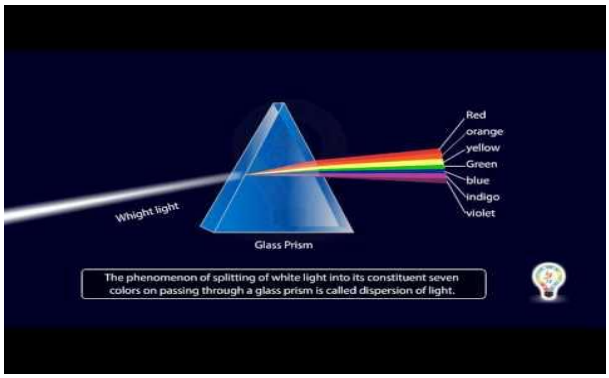
Following are the spectroscopic methods which are widely used in chemistry

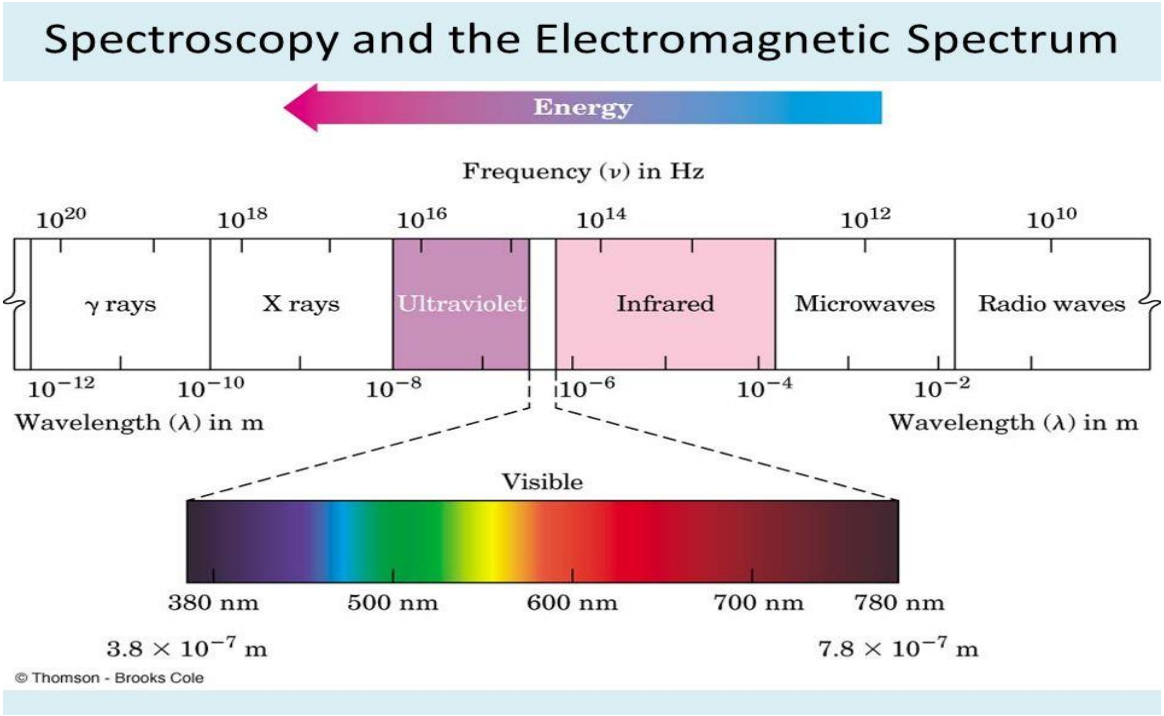
(a) Ultra Voilet Spectroscopy
(b) InfraRed Spectroscopy
(c) Nuclear Magnetic Resonance (NMR)
(d) Mass Spectroscopy
(e) Atomic Absorption Spectroscopy

Importance of Spectroscopy

Spectroscopy has many advantages over the classical techniques

(1) They require very small amount of the compound, element under investigation.
(2) They take very less time for analysis.
(3) They are highly reliable in establishing the identity of the compound.
(4) They are generally cheap in the long run.
(5) This method does not destroy the sample under investigation.
(6) Most effective in milligram and even in micrograms of compound.
(7) The compound remains unchanged during spectroscopic analysis.
(8) Highly reliable in establishing identity of two compounds.





Infra Red Spectroscopy

Infrared radiation lies between the visible and microwave portions of the electromagnetic spectrum. Infrared waves have wavelengths longer than visible and shorter than microwaves, and have frequencies which are lower than visible and higher than microwaves.

The Infrared region is divided into: near, mid and far-infrared.

- Near-infrared refers to the part of the infrared spectrum that is closest to visible light and far-infrared refers to the part that is closer to the microwave region.
- Mid-infrared is the region between these two.

The primary source of infrared radiation is thermal radiation. (heat)

It is the radiation produced by the motion of atoms and molecules in an object. The higher the temperature, the more the atoms and molecules move and the more infrared radiation they produce. Any object radiates in the infrared. Even an ice cube, emits infrared.

It is absorption spectroscopy, in which absorption of energy occurs. It is molecular spectroscopy. In this after absorption of energy bond shows some changes in their length, bond angle and orientation in space.

Theory:- IR spectroscopy is based on this fact that molecule absorb specific frequencies that are characteristics of their structure. These absorptions are resonance frequencies. The resonance frequency can be related to the strength of the bond, the mass of the atom or either end of it. The frequency of the vibrations can be associated with a particular bond type. It is also related or affected by the arrangement of the atom within the molecule.

Only enantiomers can be able to show similar IR spectra.

When IR light is passed through the sample, the vibrational & rotational energies of the molecule are increased.

Then following types of vibrations takes place:

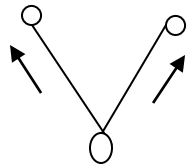
(i) **Streching:-** In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.

(ii) **Bending:-** In this type of vibration, the positions of the atoms change with respect to the original bond axis. It requires more energy than stretching vibrations. Thus it appears at higher frequencies.

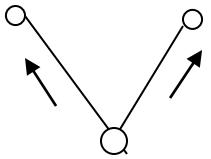
Types of stretching vibrations

Here are two types of stretching vibrations

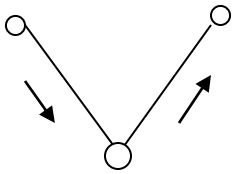
(a) Symmetrical stretching – In this type the movement of the atoms with respect to a particular atom in a molecule is in the same direction.
(b) Asymmetrical stretching – In this type of vibration, one atom apparaoches to central atom while the other departs from it.



Stretching



symmetrical

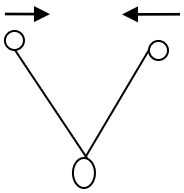


Asymmetrical

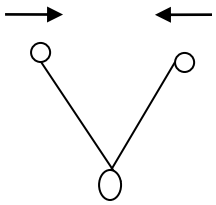
Types of bending vibrations

Bending vibrations are of four types

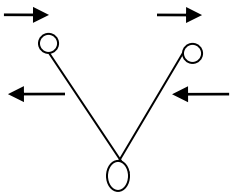
(a) Scissoring – In this type two atoms or bond approaches each other.
(b) Rocking – In this type the movement of the atom takes place in the same direction.
(c) Wagging – Two atoms move up & below the plane with respect to the central atom.
(d) Twisting – In this type one of the atom moves up in the plane while the other moves down the plane with respect to the central atom.



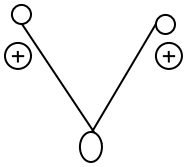
Simple Bending



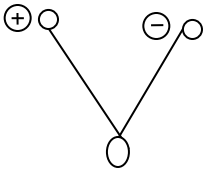
Scissoring



Rocking



Wagging



Twisting

Ultra Violet Spectroscopy

UV-visible spectrometers can be used to measure the absorbance of ultra violet or visible light by a sample, either at a single wavelength or perform a scan over a range in the spectrum. The UV region ranges from 190 to 400 nm and the visible region from 400 to 800 nm.

The technique can be used both quantitatively and qualitatively. A schematic diagram of a UV-visible spectrometer is shown above. The light source (a combination of tungsten/halogen and deuterium lamps) provides the visible and near ultraviolet radiation covering the 200 – 800 nm. The output from the light source is focused onto the diffraction grating which splits the incoming light into its component colours of different wavelengths, like a prism (shown below) but more efficiently.

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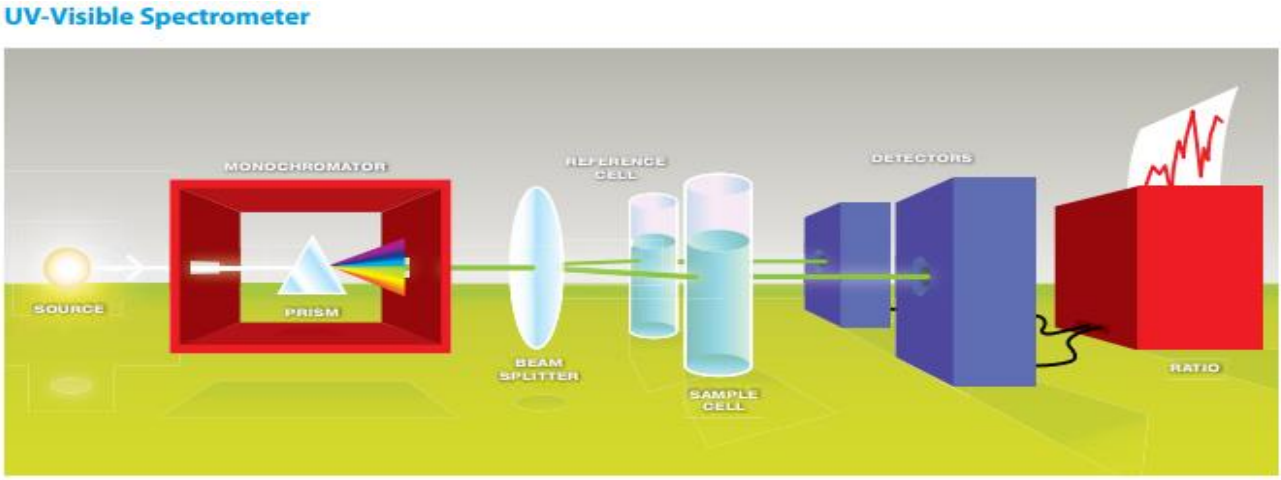
For liquids the sample is held in an optically flat, transparent container called a cell or cuvette. The reference cell or cuvette contains the solvent in which the sample is dissolved and this is commonly referred to as the blank.

$$A = \log_{10} \frac{I_o}{I}$$

For each wavelength the intensity of light passing through both a reference cell (Io) and the sample cell (I) is measured. If I is less than Io, then the sample has absorbed some of the light. The absorbance (A) of the sample is related to I and Io according to the following equation: The detector converts the incoming light into a current, the higher the current the greater the intensity. The chart recorder usually plots the absorbance against wavelength (nm) in the UV and visible section of the electromagnetic spectrum.



The detector converts the incoming light into a current, the higher the current the greater the intensity. The chart recorder usually plots the absorbance against wavelength (nm) in the UV and visible section of the electromagnetic spectrum. (Note: absorbance does not have any units).

Applications of Absorption Spectroscopy (UV, Visible)

1.Detection of Impurities

UV absorption spectroscopy is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material. By also measuring the absorbance at specific wavelength, the impurities can be detected.
Benzene appears as a common impurity in cyclohexane. Its presence can be easily detected by its absorption at 255 nm.

2. Structure elucidation of organic compounds.

UV spectroscopy is useful in the structure elucidation of organic molecules, the presence or absence of unsaturation, the presence of hetero atoms.
From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc.

3. Quantitative analysis

UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on

Beer's law which is as follows.
$A = \log I0 / It = \log 1/ T = - \log T = abc = \varepsilon bc$
Where ε is extinction co-efficient, c is concentration, and b is the length of the cell that is used in UV spectrophotometer.

4. Qualitative analysis

UVabsorption spectroscopy can characterize those types of compounds which absorbs UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds.
UV absorption spectroscopy is generally used for characterizing aromatic compounds and aromatic olefins.

5. Dissociation constants of acids and bases.

$PH = PKa + \log [A^-] / [HA]$
From the above equation, the PKa value can be calculated if the ratio of $[A^-] / [HA]$ is known at a particular PH. and the ratio of $[A^-] / [HA]$ can be determined spectrophotometrically from the graph plotted between absorbance and wavelength at different PH values.

6.Chemical kinetics

Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

7. Quantitative analysis of pharmaceutical substances

Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

8. Molecular weight determination

Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

9. As HPLC detector

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response which can be assumed to be proportional to the concentration. For more accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; as in the case of calibration curve.