UV SPECTROSCOPY

M. Sc. Chemistry
3rd Sem (301)
Ph. D. Course Work- Paper-II / Unit-II

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Introduction

- **Spectroscopy** is the branch of science that deals with the study of interaction of EMR with matter.

- $$\text{EMR+Matter} \xrightarrow{\text{Condition}} \text{Spectra}$$
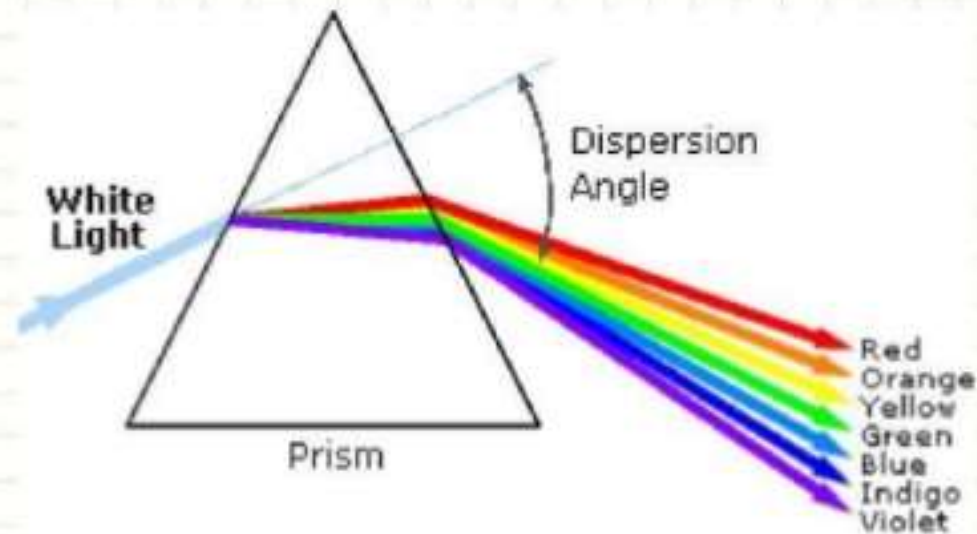
Here,

   EMR= UV–Visible Radiation (100-800 nm)

   Matter = Compounds having sigma, pie & non bonding electron

      Condition imposed by selection rule

It is the most powerful tool available for the study of atomic & molecular structure and is used in the analysis of a wide range of samples .

Electromagnetic Radiation

Violet	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm
Green	490 - 570 nm		

Principles of UV-Visible Spectrometer

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.

- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).

- Spectrometer is an instrument design to measure the spectrum of a compound.

Absorption Spectroscopy:

- An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

- The UV radiation region from 10 nm to 400 nm

    visible radiation region from 400 nm to 800 nm

.   Near UV Region: from 200 nm to 400 nm

                         Far UV Region: below 200 nm

- This energy corresponds to EMR in the UV region 100-350 nm & visible region 350-700 nm of the spectrum.

- The difference in energy between molecular bonding, non-bonding & anti-bonding orbitals ranges from 125-650 KJ/mole.

- Far UV spectroscopy is studied under vacuum condition.

- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane

- When white (continuum of l) light passes through, or is reflected by a surface, those ls that are absorbed are removed from the transmitted or reflected light respectively

- What is "seen" is the complimentary colors (those that are not absorbed)
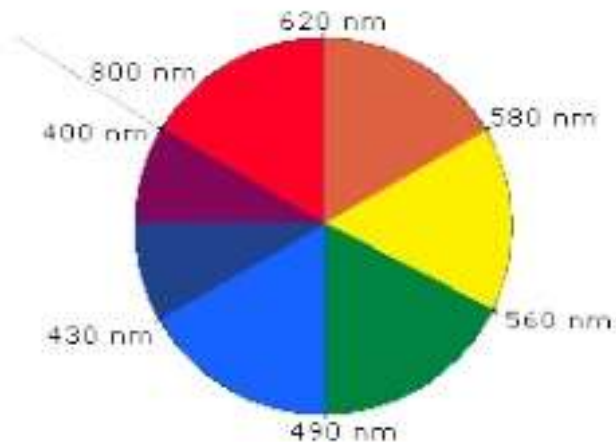
- This is the origin of the "color wheel"

Table 1 Relationship between light absorption and color

Color absorbed	Color observed	Absorbed radiation(nm)
Violet	Yellow-green	400-435
Blue	Yellow	435-480
Green-blue	Orange	480-490
Blue-green	Red	490-500
Green	Purple	500-560
Yellow-green	Violet	560-580
Yellow	Blue	580-595
Orange	Green-blue	595-605
Red	Blue-green	605-750

I. Introduction
    A. UV radiation and Electronic Excitations
        1. The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole

        2. This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum

        3. For comparison, recall the EM spectrum:

        4. Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm

        5. For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV

THE LAWS OF ABSORPTION

The absorption of light by any absorbing material is governed by two laws .

❖ Bouger-Lambert law

❖ Beer's law

Bouger-Lambert law

This law is suggested by Picre Bouguer in 1729, its often attributed to Johann Heinrich Lambert .

Bouger-Lambert law

- This law is states that " The amount of the light absorbed is proportional to the thickness of the absorbing material & is independent of the intensity of the incident light "

Second law – Beer's law

It states that, the amount of light absorbed by a material is proportional to the number of
Absorbing molecules(concentration)

Beer Lamberts Law:

This combined law states that the amount of light absorbed is proportional to the
Concentration of the absorbing substance & to the thickness of the absorbing material.

$$A = \varepsilon \, b \, c$$

A = absorbance
ε = molar absorbtivity with units of L /mol.cm
b = path length of the sample (cuvette)
c = Concentration of the compound in solution, expressed in mol /L

Cont'd

1.Electronic Energy Levels:

- At room temperature molecules are in the lowest energy levels E_0.

- When molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E_1, E_2, …E_n, etc is called as electronic transition and the difference is as:

$$\Delta E = h\,\nu = E_n - E_0 \quad \text{where } (n = 1, 2, 3, … \text{ etc})$$

$$\Delta E = 35 \text{ to } 71 \text{ kcal/mole}$$

Electronic Transitions

- The possible electronic transitions are:
- $\sigma \to \sigma^*$ transition
- $\pi \to \pi^*$ transition
- $n \to \sigma^*$ transition
- $n \to \pi^*$ transition
- $\sigma \to \pi^*$ transition
- $\pi \to \sigma^*$ transition

σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.

- The energy required is large for this transition.

- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

π → π* transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.

- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.

- e.g. Alkenes generally absorb in the region 170 to 205 nm.

n → σ* transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of n → σ* transition.

- These transitions usually requires less energy than σ → σ* transitions.

- The number of organic functional groups with n → σ* peaks in UV region is small (150 – 250 nm).

n → π* transition

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.

- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.

- n → π* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

σ → π* transition & π → σ* transition

- These electronic transitions are forbidden transitions & are only theoretically possible.

- Thus, n → π* & π → π* electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.

- The UV spectrum is of only a few broad of absorption.

# The possible electronic transitions can graphically shown as:
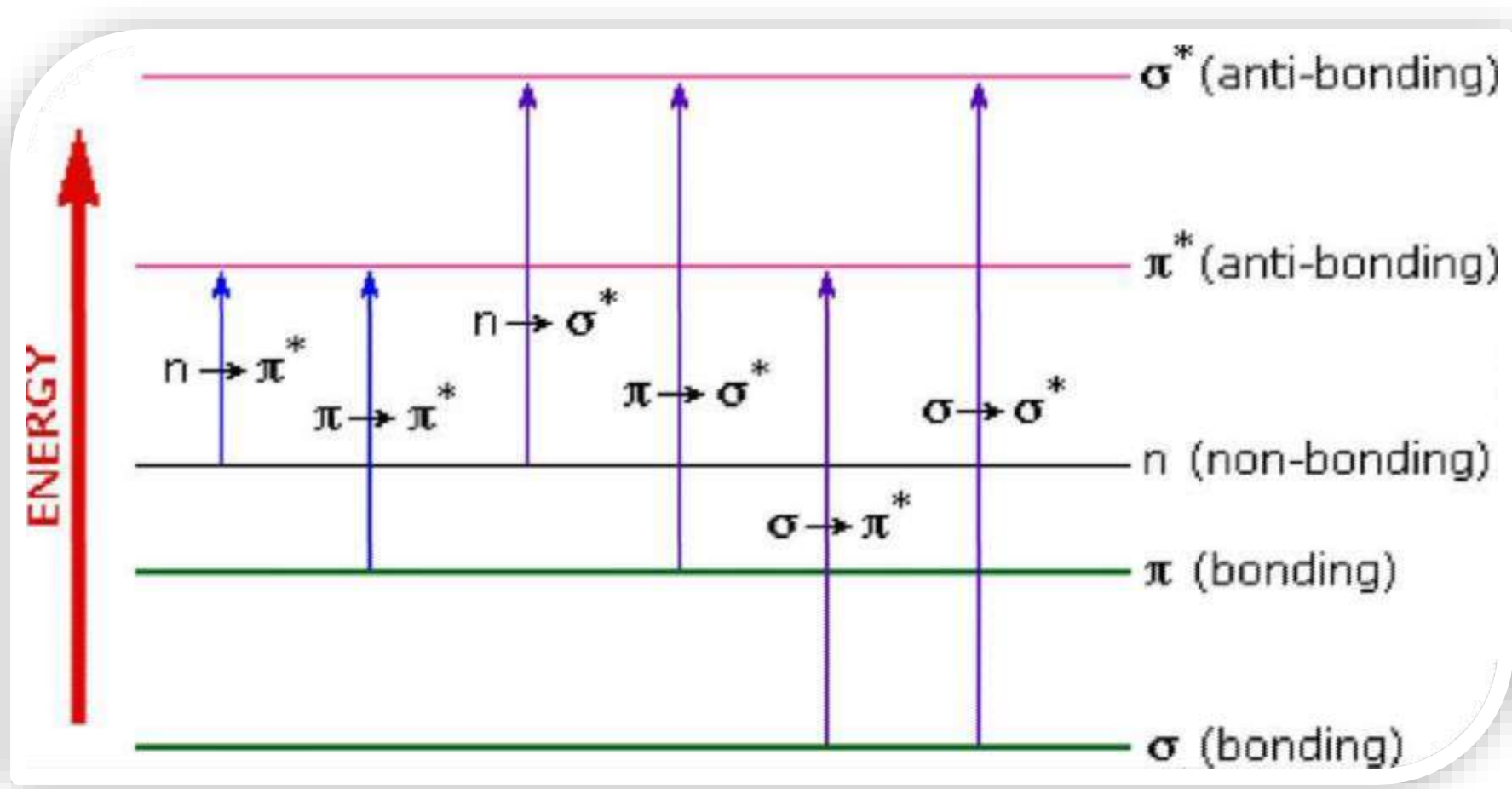
Applications of U.V. Spectroscopy:

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.

U.V. Spectra of Paracetamol (PCM)
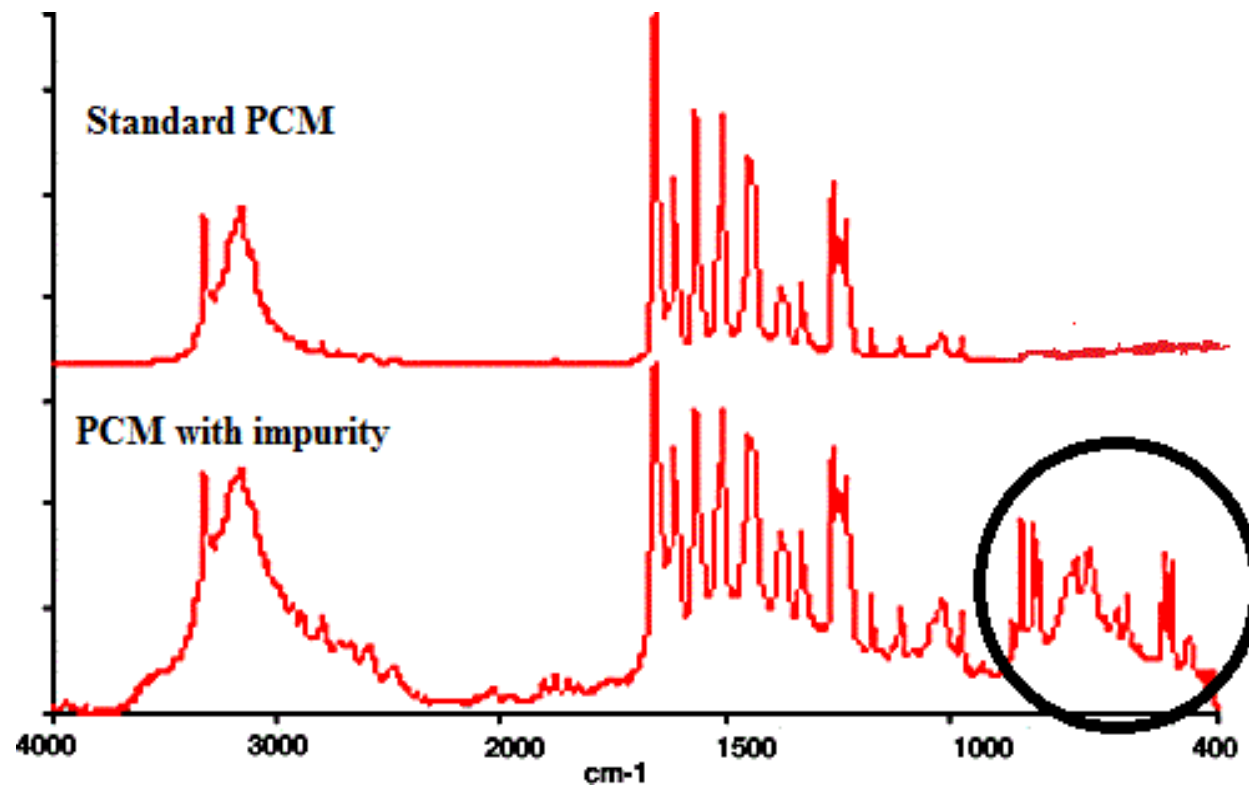
2. Structure elucidation of organic compounds.

- 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.

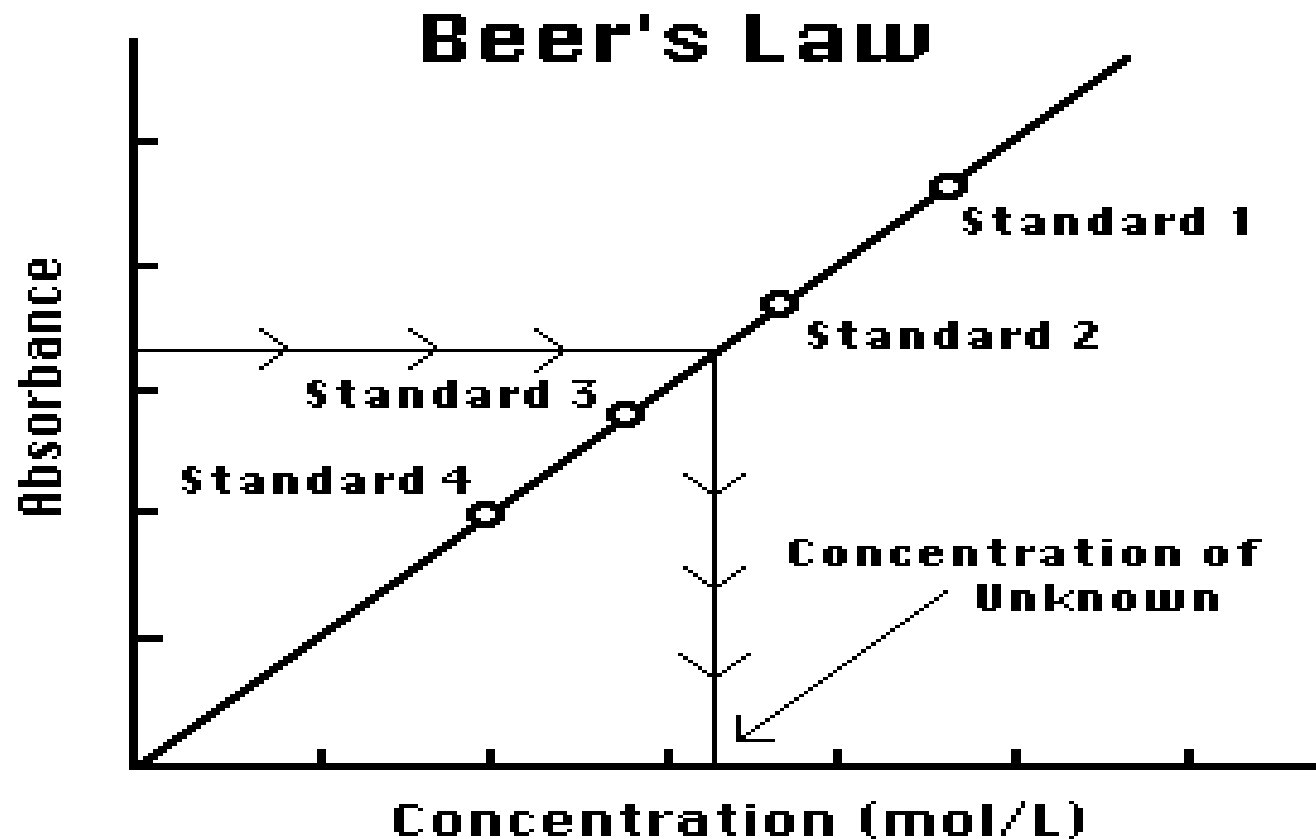$$A = \log I_0 / I_t = \log 1/ T = - \log T = abc = \varepsilon bc$$

Where :

ε -is extinction co-efficient,

c- is concentration, and

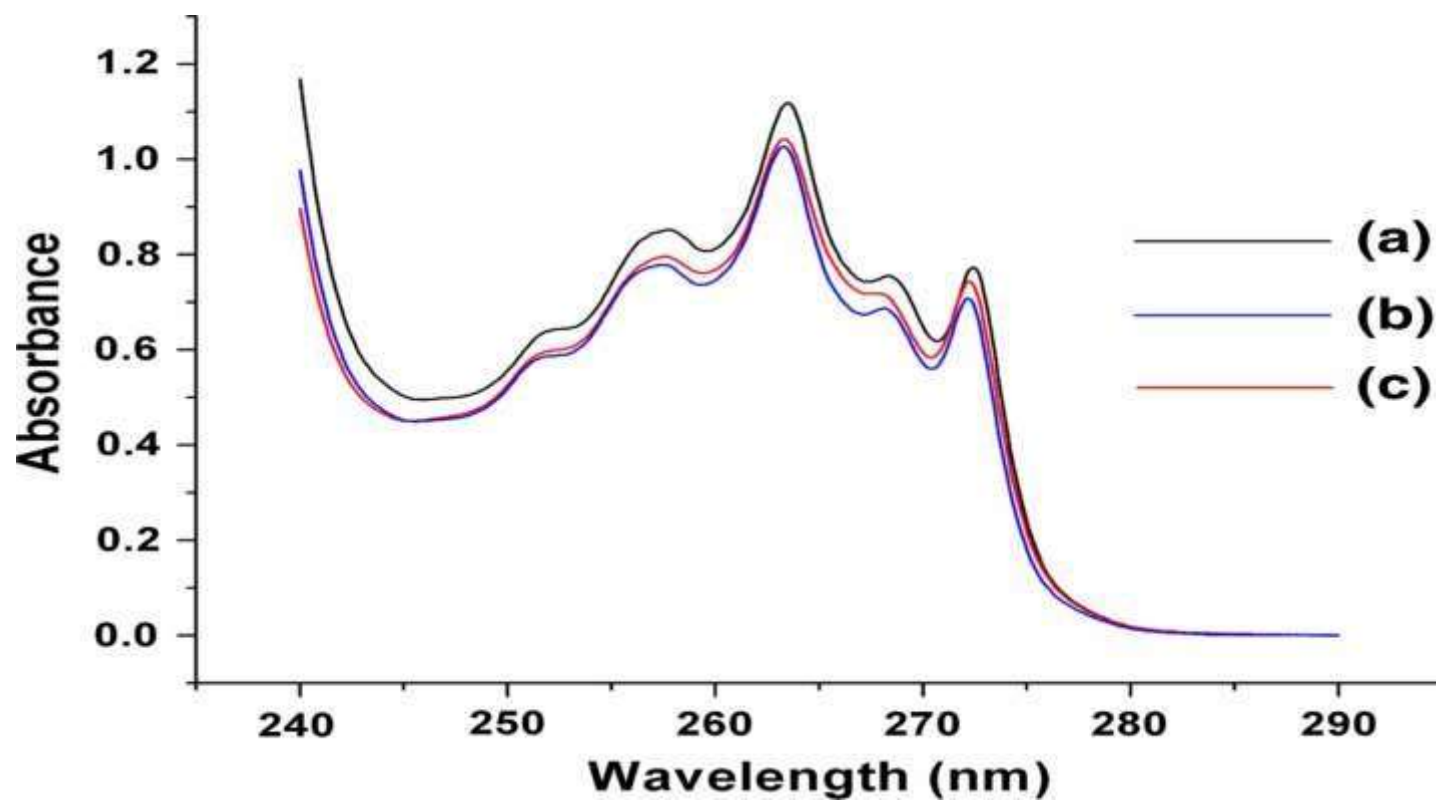b- is the length of the cell that is used in UV spectrophotometer.

Beer's law

4. Qualitative analysis

- UV absorption 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.

U.V. Spectra's of Ibuprofen

5.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.
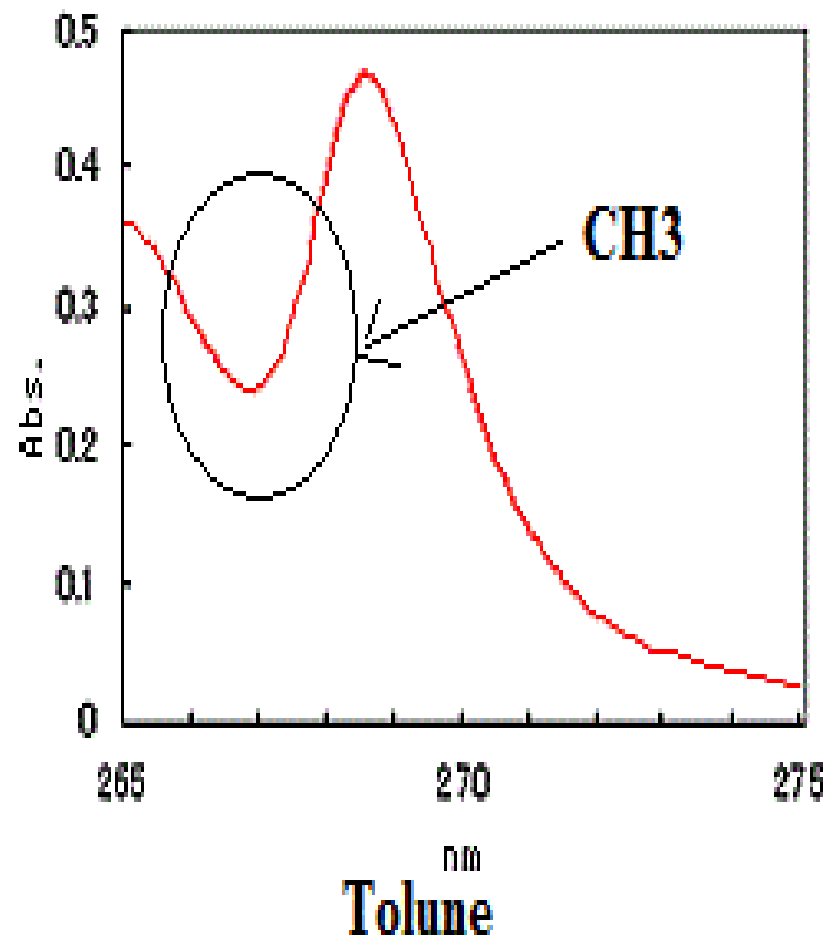
6. **Detection of Functional Groups**

- This technique is used to detect the presence or absence of functional group in the compound

- Absence of a band at particular wavelength regarded as an evidence for absence of particular group
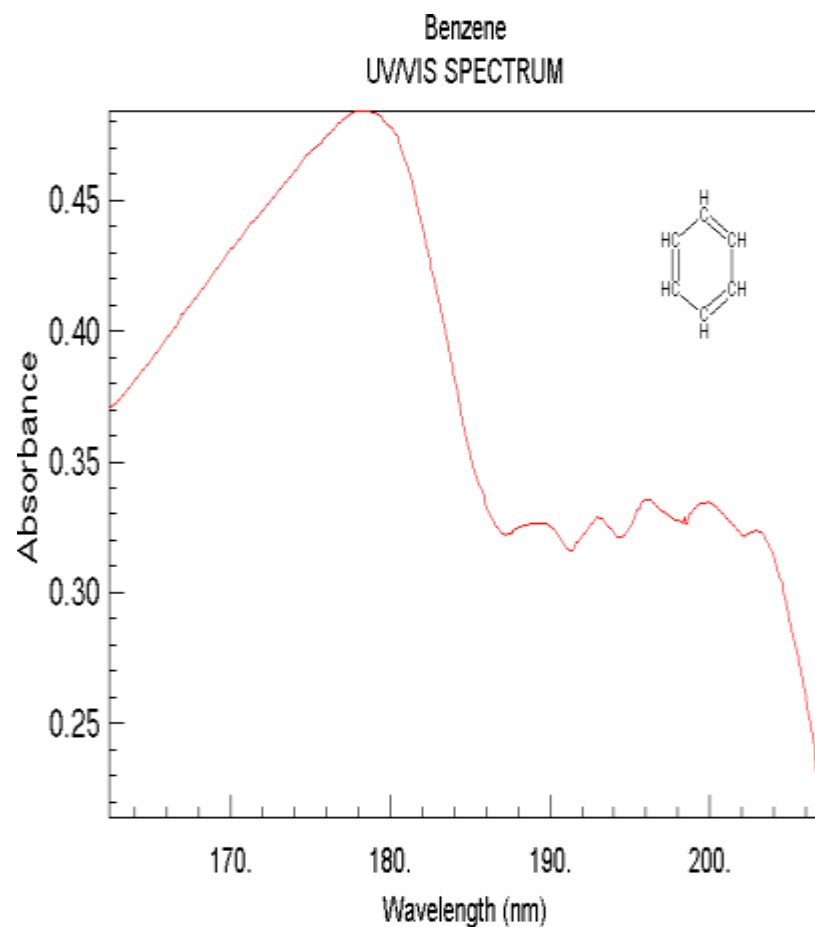
Benzene

# 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.

- Diazepam tablet can be analyzed by 0.5% H_2SO_4 in methanol at the wavelength 284 nm.

8. Examination of Polynuclear Hydrocarbons

- Benzene and Polynuclear hydrocarbons have characteristic spectra in ultraviolet and visible region. Thus identification of Polynuclear hydrocarbons can be made by comparison with the spectra of known Polynuclear compounds.

- Polynuclear hydrocarbons are the Hydrocarbon molecule with two or more closed rings; examples are naphthalene, $C_{10}H_8$, with two benzene rings side by side, or diphenyl, $(C_6H_5)_2$, with two bond-connected benzene rings. Also known as *polycyclic hydrocarbon*.

Naphthalene

DIPHENYL
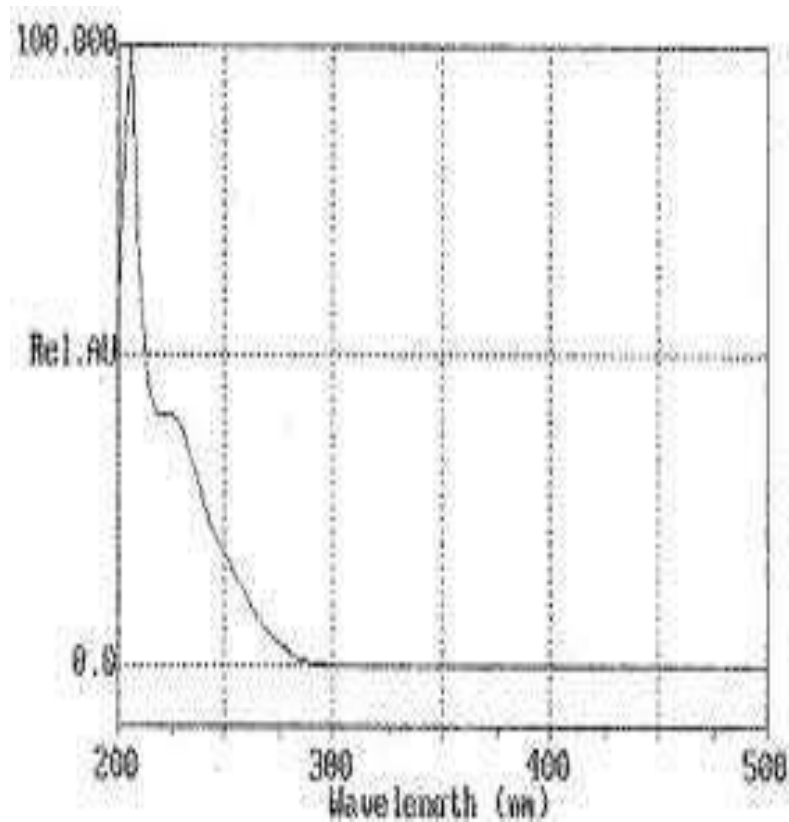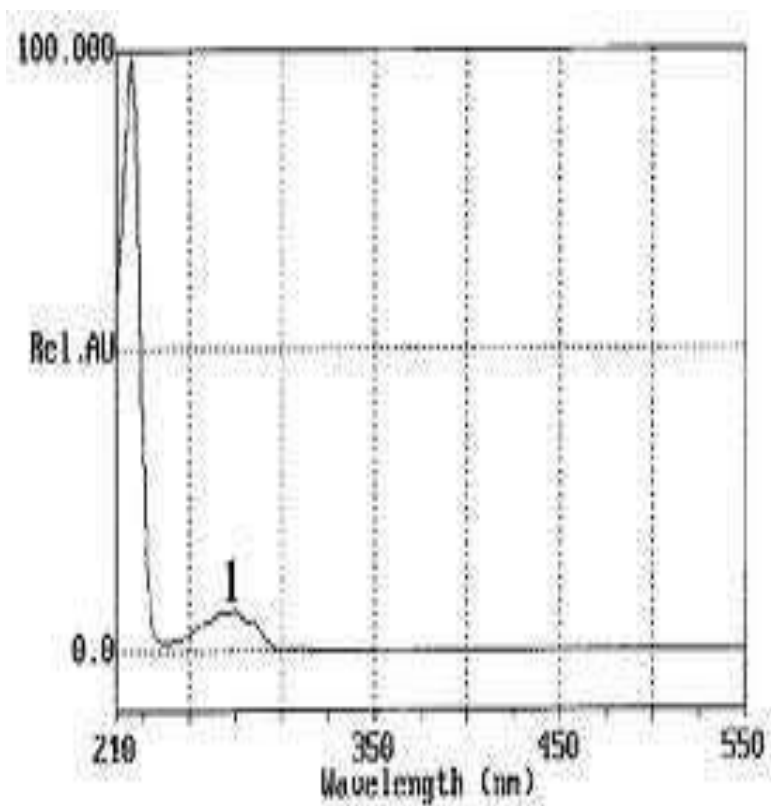
References & further reading

B.K. Sharma Molecular Spectroscopy Application of Spectroscopy

Thank You