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Introduction

Spectroscopy

✓ Spectroscopy is the branch of science dealing the study of interaction of electromagnetic radiation with matter.

OR

- ✓ It is the measurement of electromagnetic radiation (EMR) absorbed or emitted when molecule or ions or atoms of a sample move from one energy state to another energy state.
- Spectroscopy 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.

Principle of Spectroscopy

- ✓ 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 (v) or wavelength (λ).
- Spectrometer is an instrument design to measure the spectrum of a compound.
- a. Absorption Spectroscopy: An analytical technique which concerns with the measurement of absorption of electromagnetic radiation. e.g. UV (185 400 nm) / Visible (400 800 nm) Spectroscopy, IR Spectroscopy (0.76 15µm)
- b. Emission Spectroscopy: An analytical technique in which emission of a particle or radiation is dispersed according to some property of the emission & the amount of dispersion is measured. e.g. Mass Spectroscopy

Electromagnetic Radiation:

- ✓ Electromagnetic radiation consist of discrete packets of energy which are called as photons.
- ✓ A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.



Properties of Electromagnetic radiation:

- (a) Wave length: It is the distance between two successive maxima on an Electromagnetic wave. Units are:- m, cm, mm, nm and micro meter.
- (b) Frequency: Number of wavelength units pass through a given point in unit time is called as frequency. It is denoted by "v" and units are cycles per second, Hertz.

(c) Wave number $\bar{v} = \frac{1}{\text{wave length}}$ as the number of waves per cm in

(d) Velocity: it is the product of wavelength and frequency and is equal to the velocity of the wave in the medium.

 $\mathbf{V} = \mathbf{n} \times \lambda$

- The relationship between wavelength & frequency can be written as: $c = v \lambda$
- ✓ As photon is subjected to energy, so $E = h v = h c / \lambda$

Interaction of EMR with matter

1.Electronic Energy Levels:

- \checkmark At room temperature the molecules are in the lowest energy levels E₀.
- ✓ When the molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E1, E2, ... En, etc is called as electronic transition and the difference is as:

 $\Delta E = h v = En - E_0$ where (n = 1, 2, 3, ... etc)

 $\Delta E = 35$ to 71 kcal/mole

- 2. Vibrational Energy Levels:
- \checkmark These are less energy level than electronic energy levels.
- ✓ The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.

 e.g. when IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.

- 3. Rotational Energy Levels:
- ✓ These energy levels are quantized & discrete.
- ✓ The spacing between energy levels are even smaller than vibrational energy levels.

 $\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$

Electronic Transitions

- 1. $\sigma \rightarrow \sigma^*$ transition:
- ✓ An electron in a bonding s-orbital is excited to the corresponding anti-bonding orbital and observed with saturated compounds.
- \checkmark The energy required is large.
- ✓ For example, methane (which has only C-H bonds, and can only undergo σ → σ^* transition transitions) shows an absorbance maximum at 125 nm.
- ✓ Absorption maxima due to $\sigma \rightarrow \sigma^*$ transition are not seen in typical UV-VIS spectra (200 700 nm) but in UV-region (125-135nm)

2. n $\rightarrow \sigma^*$ transition:

- ✓ Saturated compounds containing atoms with lone pairs (nonbonding electrons) like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.
- ✓ These transitions usually need less energy than $n \rightarrow \sigma^*$ transition.
- They can be initiated by light whose wavelength is in the range 150
 250 nm.
- ✓ The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

3. $\pi \rightarrow \pi^*$ transition:

- $\checkmark \pi$ electron in a bonding orbital is excited to corresponding antibonding orbital π^* and observed in conjugated compounds.
- ✓ Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.
- ✓ e.g. Alkenes generally absorb in the region 170 to 205 nm.

4. n $\rightarrow \pi^*$ transition:

- ✓ An electron from non-bonding orbital is promoted to antibonding π^* orbital and required lower energy.
- ✓ Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.
- \checkmark n $\rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.



Terms used in UV / Visible Spectroscopy

Chromophore:

- ✓ The part of a molecule responsible for imparting color, are called as chromospheres.
 OR
- ✓ The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n→ π* & π → π* transitions. e.g. NO₂, N=O, C=O, C=N, C=N, C=C, C=S, etc

Auxochrome:

- ✓ The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption. OR
- ✓ The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption. e.g. Benzene λ_{max} =255 nm, Phenol λ_{max} =270 nm, Aniline λ_{max} =280 nm

Absorption & Intensity Shifts

- 1. Bathochromic Shift (Red Shift): When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- 2. Hypsochromic Shift (Blue Shift) When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.
- Hyperchromic Effect: When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.
- Hypochromic Effect: When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.



UV- Visible Spectroscopy

Theory Involved

- When a beam of light falls on a solution or homogenous media, a portion of light is reflected ,from the surface of the media, a portion is absorbed within the medium and remaining is transmitted through the medium.
- Thus if I_0 is the intensity of radiation falling on the media.
- I_r is the amount of radiations reflected,
- I_a is the amount of radiation absorbed &
- I_t the amount of radiation transmitted
- Then $I_0 = I_r + I_a + I_t$

Laws involved

- 1. Beer's law
- 2. Lambert's law
- 3. Beer-lambert's law

Beer's Law: When a beam of monochromatic light is passed through a homogenous absorbing medium, the rate of decrease of intensity of radiation with increase in the concentration (c) of absorbing species is directly proportional to the intensity (I) of the incident light (radiation).

-dI/dc = k I-dI/I = k d c

On integration of above equation

-ln I = k c + b (b= integration constant)(1) When conc. = 0, then there is no absorbance. Here I = I_0 Therefor substituting in equation (1)

 $-\ln I = k \times 0 + b$ $-\ln I = b$

Substituting the value of b in equation (1)

 $-\ln I = k c - \ln I_0$ $\ln I_0 - \ln I = kc$ $\ln I_0 / \ln I = kc \quad (Since \log A - \log B = \log A/B)$ $I_0 / I = e^{kc} (removing natural logarithm)$ $I / I_0 = e^{-kc} (inverse both sides)$ $I = I_0 e^{-kc} \dots (2)$

Lambert's law: When a beam of monochromatic light is passed through a homogenous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident light (radiation).

$$dI/dt = kI$$

I= intensity of incident light of wavelength λ & t= thickness of medium

Since, $I = I_0 e^{-kt}$ (3)

Now combine the eq.(2) and eq.(3), we get; $I = I_0 e^{-kct}$ Converting natural logarithm to base 10 $\mathbf{I} = \mathbf{I}_0 \ 10^{-\text{kct}}$ Inverse on both sides $I_0 / I = 10 \text{ kct}$ Taking log on both sides Here, transmittance (T) = I/I_0 and Absorbance (A) = log 1/T Hence, $A = \log I_0 / I$ (5) Using eq.(4) and eq.(5), A = kct

Instead of k we can use ε , the above equation will be as follow:

 $A = \varepsilon c t$

This is mathematical equation for Beer's- Lambert's Law.

 $A = \varepsilon c t$

Where A = Absorbance;

 $\varepsilon =$ Molecular extinction coefficient;

c = Concentration of sample;

t = Path length (normally 10mm or 1cm)

ε can be expressed as follows:

 $\frac{\varepsilon = E^{1\%}_{1cm} \times \frac{Molecular \ weight}{10}}{10}$

Instrumenation:

- ✓ Source of radiation.
- ✓ Collimating system.
- ✓ Mono-chromator system.
- ✓ Sample holder.
- ✓ Detector.
- ✓ Amplifier and Read-out devise.



Source of radiation

Requirements of an ideal source

- ✓ It should be stable and should not allow fluctuations.
- ✓ It should emit light of continuous spectrum of high and uniform intensity over the entire wavelength region in which it's used.
- ✓ It should provide incident light of sufficient intensity for the transmitted energy to be detected at the end of optic path. Tungsten-Halogen Lamp
- \checkmark It should not show fatigue on continued use.



1. Tungsten Halogen Lamp:

- \succ Its construction is similar to a house hold lamp.
- The bulb contains a filament of Tungsten fixed in evacuated condition and then filled with inert gas.
- The filament can be heated up to 3000 k, beyond this Tungsten starts sublimating.
- > It is used when polychromatic light is required.

DEMERIT

It emits the major portion of its radiant energy in near IR region of the spectrum.

2. Hydrogen Discharge Lamp:

- In Hydrogen discharge lamp pair of electrodes is enclosed in a glass tube (provided with silica or quartz window for UV radiation to pass trough) filled with hydrogen gas.
- ✓ When current is passed trough these electrodes maintained at high voltage, discharge of electrons occurs which excites hydrogen molecules which in turn cause emission of UV radiations in near UV region.

 \checkmark They are stable and widely used.



3. Xenon Discharge Lamp:

- ✤ It possesses two tungsten electrodes separated by some distance.
- These are enclosed in a glass tube (with quartz or fused silica) and xenon gas is filled under pressure.
- An intense arc is formed between electrodes by applying high voltage. This is a good source of continuous plus additional intense radiation. Its intensity is higher than the hydrogen discharge lamp.
 Envelope



DEMERIT:

The lamp since operates at high voltage becomes very hot during operation and hence needs thermal insulation

4. Mercury arc Lamp:

 In mercury arc lamp, mercury vapor is stored under high pressure and excitation of mercury atoms is done by electric discharge.



DEMERIT:

Not suitable for continuous spectral studies, (because it doesn't give continuous radiations).

Collimating System

The radiation emitted by the source is collimated (made parallel) by lenses, mirrors and slits.

Lenses:

- Materials used for the lenses must be transparent to the radiation being used.
- ✓ Ordinary silicate glass transmits between 350 to 3000nm and is suitable for visible and near IR region.
- Quartz or fused silica is used as a material for lenses to work below 300nm.

Mirrors

- ✓ These are used to reflect, focus or collimate light beams in spectrophotometer.
- ✓ To minimize the light loss, mirrors are aluminized on their front surfaces.

Slits:

- Slit is an important device in resolving polychromatic radiation into monochromatic radiation.
- \checkmark To achieve this, entrance slit and exit slit are used.
- ✓ The width of slit plays an important role in resolution of polychromatic radiation.

Momochromators

- It is a device used to isolate the radiation of the desired wavelength from wavelength of the continuous spectra.
- The essential elements of monochromators are:
- i. An entrance slit
- ii. Dispersing element
- iii. Exit slit

The entrance slit sharply define the incoming beam of heterochromatic radiation. The dispersing element disperses the heterochromatic radiation into its component wavelength. Exit slit allows the nominal wavelength together with a bond of wavelength on either side of it.

> Following types of monochromatic devices are used.

- 1. Filters
- 2. Prisms
- 3. Gratings

1. Filters

Two types of filters are used, they are:

a. Absorption filters- works by selective absorption of unwanted radiation and transmits the radiation which is required.

Examples- Glass and Gelatin filters.

Selection of absorption filter is done according to the following procedure:

- ✓ Draw a filter wheel.
- Write the color VIBGYOR in clockwise or anticlockwise manner, omitting Indigo.
- ✓ If solution to be analyzed is BLUE in color a filter having a complimentary color ORANGE is used in the analysis.
- Similarly, we can select the required filter in colorimeter, based upon the color of the solution.

An Absorption glass filter is made of solid sheet of glass that has been colored by pigments which is dissolved or dispersed in the glass.

Merits:-

- ✓ Simple in construction
- ✓ Cheaper
- ✓ Selection of the filter is easy Demerits:-
- n is easy 430 nm 490 nm

400 nm)

800 nm

- ✓ Less accurate
- ✓ Band pass (bandwidth) is more (±20-30nm) i.e. if we have to measure at 400nm; we get radiation from 370-430nm. Hence less accurate results are obtained.

580 nm

560 nm

b. Interference filter

- ✓ Works on the interference phenomenon, causes rejection of unwanted wavelength by selective reflection.
- ✓ It is constructed by using two parallel glass plates, which are silvered internally and separated by thin film of dielectric material of different (CaF2, SiO, MgF2) refractive index.
- ✓ These filters have a band pass of 10-15nm with peak transmittance of 40-60%.



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Merits –

- Provide greater transmittance and narrower band pass (10-15nm) as compare to absorption filter.
- Inexpensive
- > Additional filters can be used to cut off undesired wavelength.

2. Prism

- ✓ Prism is made from glass, Quartz or fused silica.
- ✓ Quartz or fused silica is the choice of material of UV spectrum.
- ✓ When white light is passed through glass prism, dispersion of polychromatic light in rainbow occurs. Now by rotation of the prism different wavelengths of the spectrum can be made to pass through in exit slit on the sample.
- ✓ The effective wavelength depends on the dispersive power of prism material and the optical angle of the prism.



There are two types of mounting in an instrument one is called 'Cornu type'(refractive), which has an optical angle of 60o and its adjusted such that on rotation the emerging light is allowed to fall on exit slit. Show in fig. (a)



The other type is called "Littrow type" (reflective), which has optical angle 30o and its one surface is aluminized with reflected light back to pass through prism and to emerge on the same side of the light source i.e. light doesn't pass through the prism on other side. Show in fig.(b)

3. Gratings

- They are most efficient in converting a polychromatic light to monochromatic light. As a resolution of +/- 0.1nm could be achieved by using gratings. As the gratings are expensive, they are commonly used in spectrophotometers.
- Gratings are of two types.
- 1. Diffraction grating.
- 2. Transmission gratings.

1. Diffraction grating:

- More refined dispersion of light is obtained by means of diffraction gratings.
- ✓ These consist of large number of parallel lines (grooves) about 15000-30000/ inch is ruled on highly polished surface of aluminum.
- ✓ To make the surface reflective, a deposit of aluminum is made on the surface.
- ✓ Diffraction produces reinforcement.

Mechaism:

✓ The ray which is incident on grating gets reinforced with reflected ray and hence resulting radiation has wavelength, which is governed by equation:

 $m\lambda = b (\sin i \pm \sin r)$

Where λ = wavelength of light produced, **b** = grating spacing, **i** = angle of incidence, **r** = angle of reflection, **m** = order (1,2,3.....)



2. Transmission grating:

- ✓ It is similar to diffraction grating but refraction takes place instead of reflection.
- Refraction produces reinforcement, this occurs when radiation transmitted through grating reinforces with the partially refracted radiation.
- The wavelength of radiation produce by transmission grating can be expressed by following equation:

 $\lambda = d \sin \theta / m$

Where λ = wavelength of light produced, d = 1/ lines per cm, θ = angle at deflection or diffraction, m = order (1,2,3.....)



Advantages

- Grating gives higher and linear dispersions compared to prism monochromator.
- Can be used over wide wavelength ranges.
- Gratings can be constructed with materials like aluminium which is resistant to atmospheric moisture.
- > Provide light of narrow wavelength.
- > No loss of energy due to absorption.

Sample holder or cuvettes

- ✓ The cells or cuvettes are used for handling liquid samples.
- \checkmark The cell may either be rectangular or cylindrical in nature.
- ✓ For study in UV region; the cells are prepared from quartz or fused silica where as fused glass is used for visible region.
- ✓ The surfaces of absorption cells must be kept clean. No fingerprints should be present on cells.
- Cleaning is carried out washing with distilled water or with dilute alcohol, acetone.
- The cell or cuvette that contain samples for analysis should fulfil 3 conditions:
- a) They must be uniform in construction, the thickness must be constant and surfaces facing the incident light must be optically flat.
- b) The materials of construction should be inert to solvents.
- c) They must transmit light of the wavelength used.



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Detectors

- Device which converts light energy into electrical signals, that are displayed on readout devices.
- ✓ The transmitted radiation falls on the detector which determines the intensity of radiation absorbed by sample.
- The following types of detectors are employed in instrumentation of absorption spectrophotometer
- 1. Barrier layer cell/Photovoltaic cell
- 2. Phototubes/ Photo emissive tube
- 3. Photomultiplier tube

- Requirements of an ideal detector:-
- a. It should give quantitative response.
- b. It should have high sensitivity and low noise level.
- c. It should have a short response time.
- d. It should provide signal or response quantitative to wide spectrum of radiation received.
- 1. Barrier layer cell/Photovoltaic cell:
- The detector has a thin film metallic layer coated with silver or gold and acts as an electrode.
- \checkmark It also has a metal base plate which acts as another electrode.
- ✓ These two layers are separated by a semiconductor layer of selenium.

- ✓ When light radiation falls on selenium layer, electrons become mobile and are taken up by transparent metal layer.
- ✓ This creates a potential difference between two electrodes & causes the flow of current.
- ✓ When it is connected to galvanometer, a flow of current observed which is proportional to the intensity and wavelength of light falling on it.





- 2. Phototubes/ Photo emissive tube:
- Consists of a evacuated glass tube with a photocathode and a collector anode.
- The surface of photocathode is coated with a layer of elements like cesium, silver oxide or mixture of them.
- ✓ When radiant energy falls on photosensitive cathode, electrons are emitted which are attracted to anode causing current to flow.
- ✓ More sensitive compared to barrier layer cell and therefore widely used.



3. Photomultiplier tube:

- ✓ The principle employed in this detector is that, multiplication of photoelectrons by secondary emission of electrons.
- ✓ In a vacuum tube, a primary photo-cathode is fixed which receives radiation from the sample.
- ✓ Some eight to ten dynodes are fixed each with increasing potential of 75-100V higher than preceding one.
- ✓ Near the last dynode is fixed an anode or electron collector electrode.
- ✓ Photo-multiplier is extremely sensitive to light and is best suited where weaker or low radiation is received.
 Photocathode





Read-out device

- ✓ The signals from the detector after amplification are finally received by the recoding system or read-out device.
- \checkmark The recording is done by recorder pen.



Single beam UV-Spectrophotometer

- Light from the source is carried through lens and/or through aperture to pass through a suitable filter.
- ✓ The type of filter to be used is governed by the colour of the solution.
- \checkmark The sample solution to be analysed is placed in cuvettes.



- ✓ After passing through the solution, the light strikes the surface of detector (barrier-layer cell or phototube) and produces electrical current.
- ✓ The output of current is measured by the deflection of needle of light-spot galvanometer or micro ammeter. This meter is calibrated in terms of transmittance as well as optical density.
- ✓ The readings of solution of both standard and unknown are recorded in optical density units after adjusting instrument to a reagent blank.

Double Beam UV-Spectrophotometer

Double beam instrument is the one in which two beams are formed in the space by a U shaped mirror called as beam splitter or beam chopper.

Chopper is a device consisting of a circular disc. One third of the disc is opaque and one third is transparent, remaining one third is mirrored. It splits the monochromatic beam of light into two beams of equal intensities.



Advantages of single & double beam spectrophotometer:

Single beam-

- Simple in construction, Easy to use and economical
 Double beam-
- O It facilitates rapid scanning over wide λ region.
- Fluctuations due to radiation source are minimized.
- It doesn't require adjustment of the transmittance at 0% and 100% at each wavelength.
- It gives ratio of intensities of sample & reference beams simultaneously.

Disadvantages of single & double beam spectrophotometer:

Single beam

- Any fluctuation in the intensity of radiation sources affects the absorbance.
- Continuous spectrum is not obtained.
 Double beam
- Construction is complicated.
- Instrument is expensive.

Comparison

s.no	Single beam	Double beam
1.	Calibration should be done with blank every time, before measuring the absorbance or transmittance of sample.	Calibration is done only in the beginning.
2.	Radiant energy intensity changes with fluctuation of voltage.	It permits a large degree of inherent compensation for fluctuations in the intensity of the radiant energy.
3.	It measure the total amount of transmitted light reaching the detector	It measures the percentage of light absorbed by the sample.
4.	In single beam it's not possible to compare blank and sample together.	In double beam it's possible to do direct one step comparison of sample in one path with a standard in the other path.
5.	In single beam radiant energy wavelength has to be adjusted every time.	In this scanning can be done over a wide wavelength region
6.	Working on single beam is tedious and time consuming.	Working on double beam is fast and non tedious.

Applications for UV- Visible Spectroscopy

- Qualitative & Quantitative Analysis: It is used for characterizing aromatic compounds and conjugated olefins. It can be used to find out molar concentration of the solute under study.
- Detection of impurities: It is one of the important method to detect impurities in organic solvents. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
- Structure elucidation of organic compounds: The presence or absence of unsaturation, the presence of hetero atoms like S, N, O or halogens can be determined.
- **4** Structural analysis of organic compounds:
- Effect of conjugation: Extended conjugation shifts the λ_{max} to longer λ (Bathochromatic shift) and reduction of the compound or saturation of double bonds leads to the opposite effect i.e. hypsochromic shift.

- Effect of geometric isomerism: Trans isomer absorbs at longer wavelength than cic isomers. Cis to trans conversion is bathochromic shift and hyper-chromic effect.
- ✓ Alkyl substitution shifts the λ_{max} to longer wave length (bathochromic shift).
- ✓ Number of rings: The addition of rings causes bathochromic shift.

Choice of Solvent

- The choice of the solvent to be used in ultraviolet spectroscopy is quite important.
- The first criterion for a good solvent is that it should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined. Usually, solvents that do not contain conjugated systems are most suitable for this purpose, although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation.
- A second criterion for a good solvent is its effect on the fine structure of an absorption band.
- A non- polar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed.
- In a polar solvent, the hydrogen bonding forms a solute-solvent complex, and the fine structure may disappear.

✓ Table 1, lists some common ultraviolet spectroscopy solvents and their cutoff points or minimum regions of transparency. Of the solvents listed in Table 1, water, 95% ethanol, and hexane are most commonly used. Each is transparent in the regions of the ultraviolet spectrum in which interesting absorption peaks from sample molecules are likely to occur.

✓ Table 1 Solvent used

Solvents	Wavelength	Solvent	Wavelength
Acetonitrile	190 nm	n-Hexane	201 nm
Chloroform	240nm	methanol	205nm
Cyclohexane	195nm	Iso-octane	195nm
1,4-Dioxane	215nm	Water	190nm
95% Ethanol	205nm	Trimrthyl phosphate	210nm

Woodward- Fieser Rule

- ✓ Woodward (1941) predicted λ_{max} values .
- ✓ Woodward–Fieser rules for dienes is either homoannular with both double bonds contained in one ring or heteroannular with two double bonds distributed between two rings.

Structural feature	$\begin{array}{c} \lambda_{max} & effect \\ (in nanometers) \end{array}$		
Base value for heteroannular diene	214		
Base value for homoannular diene	253		
Increments			
Double bond extending conjugation	+ 30		
Alkyl substituent or ring residue	+ 5		
Exocyclic double bond	+ 5		
acetate group	+ 0		
Ether group	+ 6		
Thioether group	+ 30		
bromine, chlorine	+ 5		
secondary amine group	+ 60		

- ✓ With the aid of these rules the UV absorption maximum can be predicted, for example in these two compounds:
- ✓ In the compound on the left, the base value is 214 nm (a heteroannular diene). This diene group has 4 alkyl substituents (labeled 1,2,3,4) and the double bond in one ring is exocyclic to the other (adding 5 nm for an exocyclic double bond). In the compound on the right, the diene is homoannular with 4 alkyl substituents. Both double bonds in the central B ring are exocyclic with respect to rings A and C.

Absorption maximum : 214 + 20 + 5 = 239 nm



heteroannular diene : 214 alkyl substitutents 4 x 5 = 20 exocy clic double bond : 5



homoannular diene : 253 alkyl substituents : 4 x 5 exocyclic double bond : 2 x 5 Absorption maximum : 253 + 20 + 10 = 283 nm

Thank you