CHAPTER

1 UV-Visible Spectroscopy

Introduction

UV-Vis spectroscopy refers to an analytical method that assesses the amount of continuous wavelengths of UV or visible light absorbed or transmitted by a sample. The sample composition has an impact on this feature, which might reveal information about what's in the sample and at what concentration. Let us look at the qualities of light first because this spectroscopic technique is dependent on the utilization of light.

Light has an inversely proportional amount of energy to its wavelength. As a result, light with shorter wavelengths carries more energy, whereas light with longer wavelengths carries less. A specific amount of energy is necessary to raise electrons in a substance to a higher energy state, which we can detect as absorption. To be promoted to a higher energy state, electrons in various bonding sites in a substance require a varying quantity of energy. That is why various substances absorb light at different wavelengths. Humans can see a visible light spectrum that spans approximately 380 nanometres (nm), which we perceive as violet, to 780 nanometres, which we observe as red. UV light has shorter wavelengths than visible light, up to around 100 nanometres. The wavelength of light can be utilised in UV-Visible spectroscopy to examine or identify distinct chemicals by finding the exact wavelengths that correlate to peak absorption.

Principle

Basically, spectroscopy is related to the interaction of light with matter. As light is absorbed by matter, it results in an increase in the energy content of the atoms or molecules. When ultraviolet radiations are absorbed, this results in the excitation of the electrons from the ground state towards a higher energy state. In analytical chemistry, UV-visible spectroscopy is a useful UV-visible spectroscopy is a useful technique. In both clinical and chemical laboratories, this is one of the most regularly utilised techniques. This method is utilised for both qualitative and chemical analysis. However, the quantitative determination of various chemical and inorganic substances in solution is its primary use. Electrons are accelerated from their ground state to a higher energy state when

UV light is absorbed. According to the hypothesis that underpins this phrase, the energy difference between the higher energy level and the ground state is equal to the energy received from UV radiation.

The wavelength of light entering the detector is measured when a light beam passes through an item. The measured wavelength reveals important details about the chemical structure and number of molecules (present in the intensity of the measured signal). As a consequence, both quantitative and qualitative information may be acquired. Photons with wavelengths ranging from 160 to 3500 nm can be used to collect information as transmittance, absorbance, or reflectance. Electrons are boosted to excited states and anti-bonding orbitals as a response of incident energy absorption. Photon energy must match the energy required by the electron to go to the next higher energy state for this transfer to take place. The fundamental principle of operation of absorption spectroscopy is this mechanism. There are three types of ground state orbitals that might be involved:

1. σ molecular orbital (bonding)
2. π molecular orbital (bonding)
3. n atomic orbital (non-bonding)

Furthermore, the anti-bonding orbitals are (i) σ* (sigma star) orbitals. (ii) π* orbital (pi star). A σ to σ* transition occurs when an electron is excited from s bonding orbital to an anti-bonding orbital. Similarly, π to π* denotes the excitation of an electron from p bonding orbital to an antibonding orbital. The following electronic transitions occur as a result of UV and visible light absorption: σ to σ*; n to σ*; n to π*; π to π* as shown in Fig 1.1. Because the transitions σ to σ* and n to σ* involve higher energy, they typically occur in the far UV area or only faintly in the 180 to 240nm region. As a result, saturated groups exhibit less UV absorption. Molecules with unsaturated centres go via n to π* and π to π* transitions, which entail less energy and so occur at longer wavelengths than transitions to σ* anti-bonding orbitals.

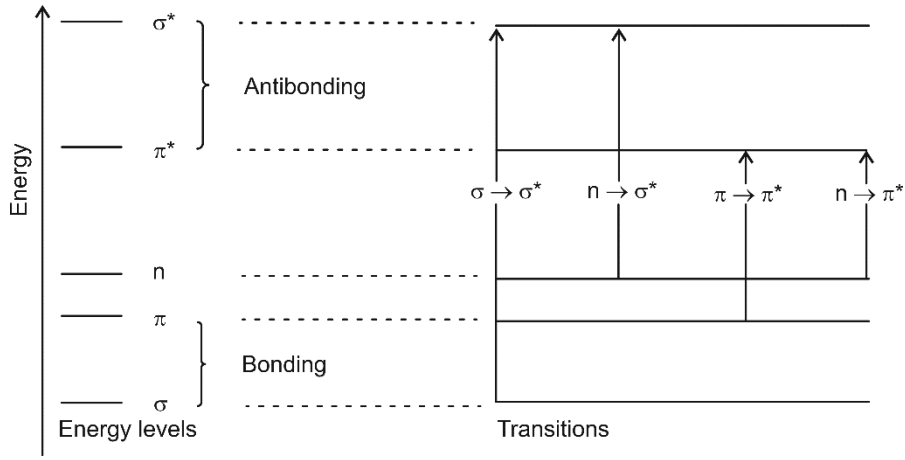


Figure 1.1 Electron transition in UV-Vis spectroscopy.

The Basic Principle of UV Spectroscopy: It complies with the Beer-Lambert Law. This law indicates that when a monochromatic laser beam passes through an absorbing solution, the rate at which the intensity of the incident radiation decreases, as well as the thickness of the absorbing solution, is proportional to the solution's concentration and the incident radiation. The following is a summary of the law:

$$A = \log (I_0/I) = \varepsilon cl$$

Where

A = stand for the absorbance,

I_0 refers to the intensity of light upon a sample cell

I = refers to the intensity of light departing the sample cell

c = stands for the concentration of the solute

l = stands for the length of the sample cell

ε = refers to the molar absorptivity

According to the Beer-Lambert rule, the greater the number of molecules capable of absorbing light at a given wavelength, the greater the amount of light absorption.

Limitations of Lambert-Beer Law

The light source chosen must be monochromatic.

This is not ideal for concentrated solutions, but only for dilute solutions (NMT 1µg/mL). The dissociation of weak acids happens as dilution increases. The weak acids and their conjugate bases approach equilibrium. The absorbance of an acid (HA) and a conjugate base (A^-) cannot be the same. As a result, this law does not fully apply to weak acidic solutions.

Instrumentation of UV-Visible Spectroscopy

The UV-Vis spectrum can be recorded via the following types of absorbance instruments:

1. Single beam spectrometer

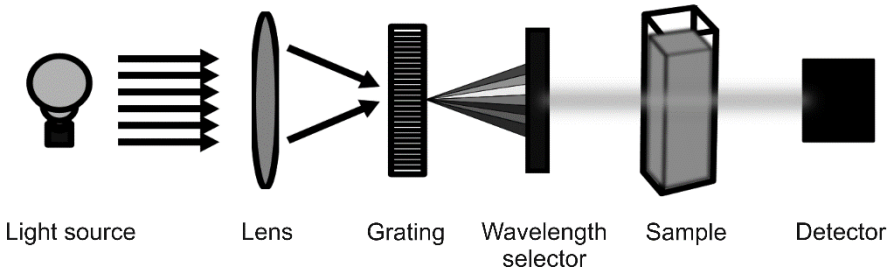


Figure 1.2 Single beam spectrophotometer.

2. Double beam spectrometer

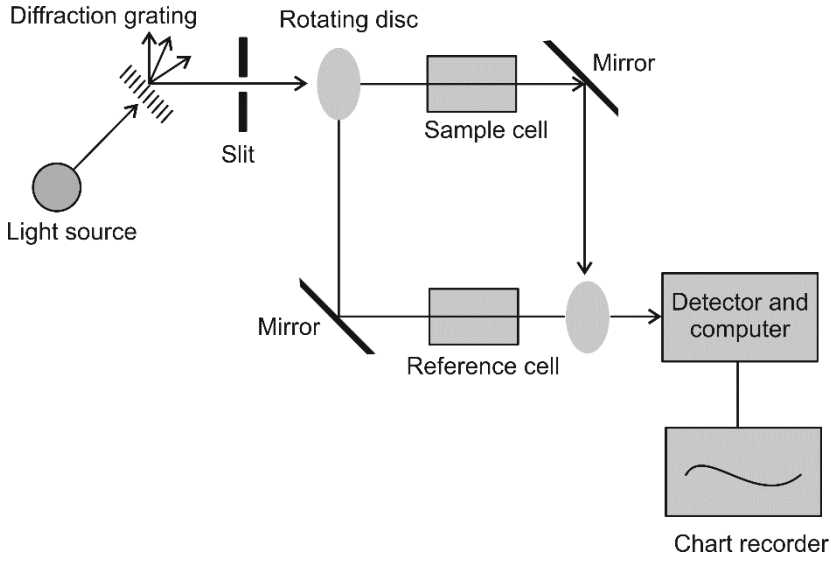


Figure 1.3 Double beam spectrophotometer.

The basic instrumentation of the UV-vis spectrometer comprises of

- Light source
- Diffraction grating
- Wavelength selector
- Sample container or cuvette
- Detector

Instrumentation: A light source, monochromator, sample stage and detector are all necessary components of a spectrometer mentions in fig 1.2 and 1.3. The most common light source is a tungsten filament that is continuous over the UV spectrum. A photodiode or charged couple device (CCD) is widely employed as a detector. Before reaching the detector, photodiodes co-operate with monochromators to filter light of a given wavelength. The visible bulb must be kept off when measuring UV spectrum absorption, and vice versa.

Instrumental components:

1. **UV-Source:** Within its operational wavelength range, the power of a radiating source should not fluctuate. Electrically burning deuterium or hydrogen at low pressures produces a continuous UV spectrum. The production of an excited molecular species, which then disintegrates into two atomic species and a UV photon, produces UV light. Both deuterium and hydrogen lamps emit light with wavelengths ranging from 160 to 375 nm. The substance used to manufacture the cuvettes must not absorb

incoming light, otherwise the absorption spectrum obtained would be skewed. As a result, quartz has a wide range of applications.

2. **Visible Light Source:** The visible light source is a tungsten filament bulb. The wavelengths of light produced by this lamp range from 350 to 2500 nm. The energy output of a tungsten filament lamp is proportional to the fourth power of the operating voltage. As a result, a highly steady voltage must be provided to the lamp in order to produce stable emission. Electronic voltage regulators or constant-voltage transformers are used to assure voltage stability. Small quantities of iodine are put within a quartz 'envelope,' which also contains the tungsten filament in tungsten/halogen lights. WI2 is Iodine combined with gaseous tungsten generated during sublimation to make this substance. When WI2 molecules collide with the filament, they break down and re-deposit tungsten. Tungsten/halogen lights often outlast tungsten filament lamps by two to three times. Tungsten/halogen lamps are utilised in current spectrophotometers because of their excellent efficiency, and their output also extends to the UV area.

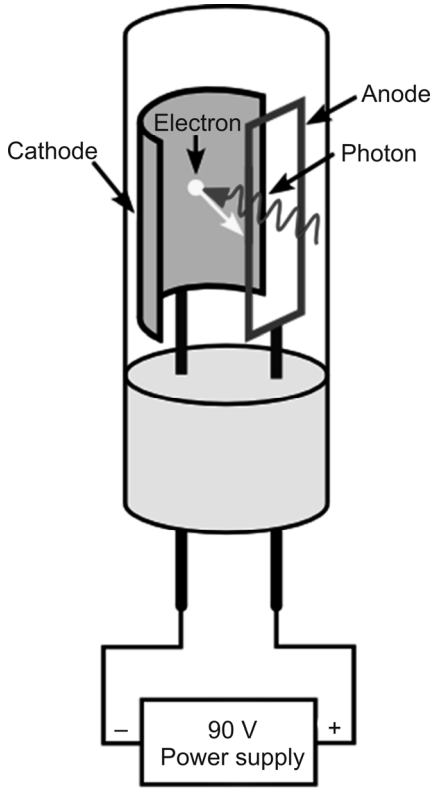


Figure 1.4 Photo Tube.

3. **Cuvettes Monochromator source:** Before reaching the sample, a half-mirror splitter divides light into two halves of equal intensity. One component (or sample beam) passes through a cuvette containing a clear solvent solution of the material under investigation. The second beam, designated the reference beam, travels through a cuvette that is similar but only contains solvent. The passing beam must be able to see through the reference and sample solution containers.
4. **Detectors:** The detector measures the amount of light emitted by cuvettes and transfers the information to a metre, which records and displays the results. The intensities of light beams are calculated and compared using electronic detectors. A UV-Vis spectrophotometer typically has two detectors, one for each wavelength. Both the reference and sample beams

are monitored simultaneously using a phototube (in Fig. 1.4) and a photomultiplier tube (in Fig. 1.5).

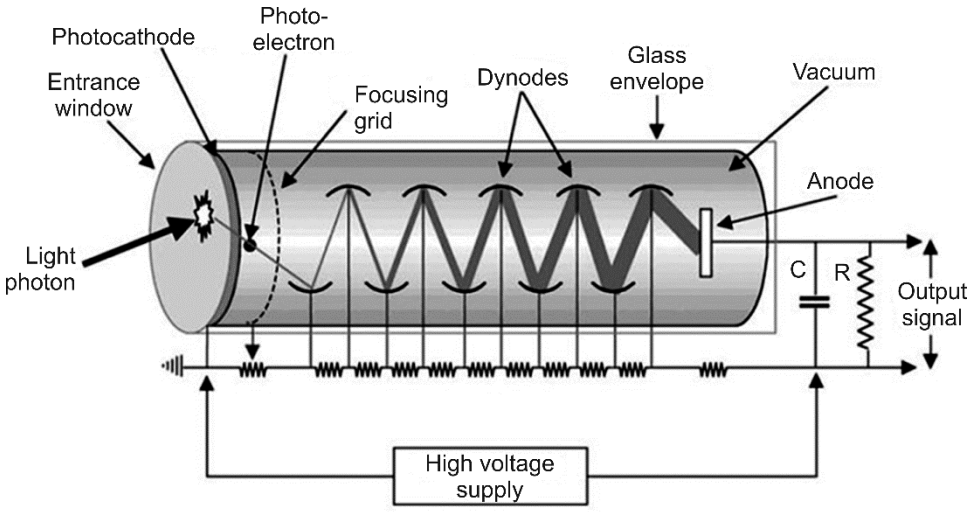


Figure 1.5 Photomultiplier Tube.

The photomultiplier tube is a common detector in UV-Vis instruments. It consists of a photo emissive cathode (which emits electrons when photons strike it), several dynodes (which emit multiple electrons when one electron strikes it), and an anode. After entering the tube, the incident photon strikes the cathode. After then, the cathode produces a significant number of electrons that are propelled towards the first dynode (whose potential is 90V more positive than the cathode). When electrons collide with the first dynode, several electrons are produced for each incident electron. These electrons are then propelled towards the second dynode, which produces additional electrons, which are subsequently accelerated towards the third dynode, and so on. A linear photodiode array is an example of a multichannel photon detector. These detectors can simultaneously monitor all constituents of a scattered radiation beam. A linear photodiode array consists of numerous tiny silicon photodiodes assembled on a single silicon chip. The number of photodiodes on a chip can vary from 64 to 4096, although the most typical amount is 1024 photodiodes. Each diode also has a storage capacitor and a switch. Sequential scanning of diode capacitor circuits is possible.

Charge-Coupled Devices (CCDs): CCDs are similar to diode array detectors in that they use a photo-capacitor array instead of diodes. The intensity of the reference beam should be minimal or zero and is denoted by I_0, whereas the intensity of the sample beam is denoted by I. In a short amount of time, the spectrophotometer analyses all wavelength components automatically. The concentration, molecule structure, and structural changes can all be determined using this method. It can also be used to investigate how the vibrational and

structural energy levels of a substrate or molecule change before and after interactions.

Factors affecting UV-Vis Spectroscopy

A number of factors affect UV spectroscopy that are mentioned below:

- Effect of sample temperature
- Effect of sample concentration
- Effect of sample pH
- Effect of solvent
- Effect of steric hindrance
- Effect of conjugation

Effect of Sample Temperature

The temperature variation of the sample affects the spectrum. As temperature decreases, the sharpness of absorption bands increases and the peak's (absorption maximum) position shifts slightly to the longer wavelength side. However, total absorption intensity is temperature independent. The intensity of the absorption band can be changed by simple thermal expansion of the solution. Rotational and vibrational energy states are affected by temperature. The rotational and vibrational activity levels of the molecules decrease as the temperature decreases. Because the distribution of excited states is reduced at lower temperatures, fine absorption bands are formed. Because the position of the band maximum does not change significantly as temperature decreases, the spectrum must be collected at a constant or specific temperature to give more precise findings.

Effect of Sample Concentration

Rotational and vibrational energy levels are affected by temperature. The rotational and vibrational activity levels of the molecules decrease as the temperature decreases. Because the distribution of excited states is reduced at lower temperatures, fine absorption bands are formed. This influence must be discovered and taken into account in a qualitative study. The quality of the absorption band in the UV spectra is also affected by the type of solvent utilised. Polar solvents have wider bands, but non-polar solvents have higher resolutions. The best resolution is obtained by removing the solvent. All of these effects are caused by solvent-solute interactions. Solvent-solute interactions are higher when the solvent's dielectric constant is high. Water and ethanol, both polar solvents, bind to solutes more strongly via hydrogen bonding or induced dipole-dipole interactions. London interactions in non-polar solvents can modify the ground and excited states, as well as the frequency of absorbed photons. As a result, distinct transition energies in spectra overlap, broadening the absorption band.

Effect of Sample pH

The spectrum acquired by UV-Visible spectroscopy is influenced by changes in the pH of the solution. Aromatic substances absorption spectra such as amines and phenols alter when the pH of the solution changes. Acidic chemicals, such as phenols and substituted phenols, change their absorption spectra when a base is added. When the phenolic proton is removed, the formation of a phenoxide ion promotes the conjugation. As the energy difference between the Lowest unoccupied molecular orbital (LUMO) and Highest occupied molecular orbital (HOMO) orbitals decreases, the wavelength shifts to a longer wavelength and the absorption intensity increases. When an aromatic amine is protonated in an acidic solution, the conjugation mechanism is disrupted. The peak shifts to a shorter wavelength, and the strength decreases as well. Acid-base indicators are useful because of their absorptions in the visible part of the UV-Vis spectrum. A minor change in the chemical structure of the indicator induces a change in the chromophore, which absorbs the maximum wavelength at different pH values, resulting in colour change. Phenolphthalein is one example. It is a weak acid that dissociates in water to form anions, which add a negative charge to the oxygen atom, causing the absorption maximum to shift to a longer wavelength. Phenolphthalein anion is orange, whereas non-ionized phenolphthalein is colourless. At neutral and acidic pH, the equilibrium shifts to the left, resulting in a lower concentration of anions and the absence of pink colour. At basic pH, however, equilibrium moves to the right, resulting in a larger concentration of anions and a pink colour. As a result, to keep pH constant, in a suitable buffer solution, the UV-Vis spectrum should be measured. Over the measuring wavelength range, the buffer must be transparent. The absorbance value rises if the buffer solution absorbs light as well.

Effect of Solvent

To some extent, the absorption spectrum is influenced by the solvent in which the absorption molecule is dissolved. The absorption peak might move to longer or shorter wavelengths when the solvent is changed. It is based on the interaction of the solvent with the chromophore of the target molecule. Ethanol has the most absorption at longer wavelengths when compared to hexane solution. Alcohols and water can form hydrogen bonds with the material, changing the absorption bands of polar molecules. Because the polarities of the ground and excited states of chromophores differ, a change in solvent polarity causes the energy gap between the two states to expand. Highly pure and non-polar solvents do not interact with the solute molecules in either the ground or excited states. Polar solvents, on the other hand, influence the molecular orbitals in the excited state. As a result, the spectra recorded in the non-polar solvent differ from the polar solvent's spectra.

Effect of a Steric Hindrance

The spectrum is also influenced by the arrangement of molecules. Electronic conjugation works well when a molecule is conjugated in a planar state. The position of the absorption peak is determined by the conjugative system's efficacy and length. Autochrome prevents the molecule from being in a planar state, causing it to shift to longer or shorter wavelengths based on the distortion. Because of chromophore distortion, the absorption peak shifts due to conjugation loss. Geometric isomerism exhibits steric hindrance as well. Trans isomers have longer wavelength absorption peaks and higher molar absorptivity than their cis counterpart. Trans-stilbene absorbs more intensely at longer wavelengths due to the steric effect.

Effect of Conjugation

Molecular conjugation plays a big role in determining the spectrum. The absorption peak moves to a lower frequency or a longer wavelength when two or more chromophores are conjugated. Conjugation increases the energy of the most occupied molecular orbital while decreasing the energy of the least occupied molecular orbital. As a result, less energy is required for an electronic transition to occur in a conjugated system. The value of the absorption peak grows as the number of conjugated bands increases. When the number of double bonds in a conjugation increases, the energy required for electronic transition decreases. The conjugation of two chromophores increases molar absorptivity and intensity. As the number of conjugated bonds increases, visible light is absorbed and compounds become coloured. One example is beta carotene, which is a vitamin A precursor molecule. It possesses 11 conjugated bonds and its absorption peak is shifted from the UV to the visible (blue) area, giving it an orange colour.

Choice of the Solvent

UV spectroscopy requires precise solvent selection. The first condition for a suitable solvent is that it does not absorb UV light in almost the same range of wavelength as the substance under investigation. Solvents with their absorbance are mentioned in **table 1.1.** Solvents free of conjugated systems are typically the best choice for this, the minimum wavelength over which they stay UV-transparent varies. The most commonly used solvents are water, 95 percent ethanol, and hexane. Each is transparent in the UV spectrum regions where sample molecules are most likely to exhibit significant absorption peaks. UV spectroscopy requires precise solvent selection. The first condition for a suitable solvent is that it does not absorb UV light in the very same wavelength range as the substance under investigation. Solvents free of conjugated systems are typically the best choice for this, albeit the shortest wavelength at which they remain transparent to ultraviolet radiation varies. Water, 95% ethanol, and hexane are the most often used solvents. Because the polarity of a molecule

changes with an electronic transition, changing the polarity of the solvent can cause the position and intensity of absorption maxima shifts.

Table 1.1 Solvents with their absorbance.

Acetonitrile-190 nm	n-Hexane-201nm
Chloroform-240nm	Methanol-205nm
Cyclohexane-195nm	Isooctane-195nm
1,4-Dioxane-215nm	Water-190nm
Ethanol-205nm	Trimethyl phosphate-210nm

K-Bands

They are also referred as conjugate bands. Because hydrocarbon double bonds are non-polar, changing the solvent polarity does not affect alkene, diene, and polyene π- π* transitions. The polarity of the solution increases as it becomes more polar, the π- π* transitions of polar compounds, such as saturated and α, ß-unsaturated carbonyl compounds, shift to longer wavelengths and, in general, higher intensity. Since the excited state is more polar than the ground state in this transition, dipole-dipole interaction with a polar solvent lowers the excited state's energy more than the ground state. As a result, whether changing from hexane to ethanol as a solvent or altering the polarity of the solvent, there is a bathochromic shift of 10-20 nm.

B-Bands

The B-bands are formed via π -π* transitions, and increasing the solvent polarity has minimal effect on their location or intensity, except for heteroaromatic compounds, which exhibit a dramatic hyperchromic shift as the solvent polarity is increased. These bands are also called as benzenoid bands.

R-Bands

Also termed as radical bands. It has been discovered that raising the solvent's polarity causes n- π* transitions to shift to shorter wavelengths (higher energy). Acetone, for example, has a λ_{max} of 279 nm in hexane and a λ_{max} of 264.5 nm in water. This is because the carbonyl group in the ground state is more polar than the carbonyl group in the excited state. In unconjugated and conjugated carbonyl compounds. The hypsochromic shift occurs when dipole-dipole interaction or hydrogen bonding with a polar solvent lowers the energy of the ground state more than the excited state.

E-Transitions

These bands are also called as ethylene bands. The polarity of solvent especially capable of generating hydrogen bonds, has an impact on these transitions. With protic solvents, alcohols and amines generate hydrogen bonds. These non-bonding electrons of the heteroatom are involved in such interactions. Non-bonded electrons reduce the energy of the n orbital in hydrogen bonding, therefore excitation of these electrons requires more energy, resulting in the hypsochromic shift as polarity increases. The n-π* and n-α* bands of polar compounds migrate to shorter wavelengths as the solvent polarity increases, while the π-π* bands of polar compounds move to longer wavelengths.

Chromophore

A chromophore is a covalently unsaturated group that absorbs UV or visible light. C=C, C=N, N=N, NO_2, and so on. Only when a substance absorbs visible-range light (400-800 nm) does it look coloured. Based on where it absorbs visible or UV photons, a chromophore may or may not give a molecule colour. Those with both bonding and non-bonding electrons, such as C=O, C=N, or N=N, go through π- π *, n-π*, and n-π* transitions, whereas those with both bonding and non-bonding electrons, such as C=O, C=N, or N=N, go through π-π*, n-π* and n-σ* transitions. Because absorption wavelengths and intensities are depending on several variables for a chromophore, there are no defined rules for recognising them.

It is a covalently unsaturated group that absorbs UV or visible rays and may or may not affect the colour of the substance.

- A chromogen is a chemical that contains chromophores.
- In unsaturated linkages like -C=C-,
- The electrons are loosely bonded in -N=N-. The electronic transition required less energy for these loosely connected electrons, and the absorption band occurred in the near UV range.
- For example Acetylene has a -C=C- structure and has a λ_{max} of 175-180 nm.

Auxochrome

Auxochrome is a covalent saturated group that changes both the wavelength and the strength of the absorption maximum when connected to a chromophore such as NH_2, OH, SH, halogens, and so on. By extending the conjugation through resonance, auxochromes often increase the value of λ_{max} as well as ε_{max} . These are also referred to as colour-enhancing groups. Auxochromes do not absorb at wavelengths above 200 nm. Auxochrome and chromophore combine to form a new chromophore with variations λ_{max} and ε_{max}. For example, benzene has a λ_{max}

256 nm, ε_{max} 200, but aniline has a λ_{max} 280 nm, ε_{max} 1430. (both increased). As a result, the NH_2 group is an auxochrome that extends the conjugation involving the nitrogen atom's lone pair of electrons, resulting in the increased values of λmax and εmax.

- It is a saturated and unsaturated group composed of one or more pairs of non-bonded electrons.
- It is attached to the Chromophore and aids in wavelength modification by boosting absorption intensity and increasing max.
- Auxochrome examples include -OH, -NH_2, -OR, and so on.

Absorption and Intensity Shifts

Bathochromic Shift

A bathochromic shift, often known as a red shift, takes place when an absorption maximum moves towards longer wavelength (Fig. 1.7) caused by the presence of an auxochrome or solvent action. For example, benzene has a λ_{max} 256 nm and aniline has a λ_{max} 280 nm. As a result of the presence of the auxochrome NH_2, the bathochromic shift in the max of benzene is 24 nm. Similarly, a bathochromic shift of the n -π * band is observed in carbonyl compounds as the solvent polarity decreases; for example, the λ_{max} of acetone in water is 264.5 nm as opposed to 279 nm in hexane.

Hypsochromic Shift

The term hypsochromic or blue shift refers to the transfer of an absorption maximum towards shorter wavelength (Fig. 1.7). This is due to the elimination of conjugation or a change in the polarity of the solvent. For example, aniline has a λ_{max} 280 nm, whereas anilinium ion (an acidic solution of aniline) has a λ_{max} 254 nm. Because the protonated aniline (anilinium ion) has no lone pair of electrons for conjugation, the hypsochromic shift is caused by the loss of nπ-conjugation of the lone pair of electrons of the nitrogen atom of aniline with the π -bonded system of the benzene ring on protonation. Similarly, when switching from ethanol to hexane as a solvent, there is a hypsochromic shift of 10-20 nm in the λmax of π -π * bands of carbonyl compounds.

Hyperchromic Effect

The hyperchromic effect is an effect that causes an increase in absorption intensity (ε_{max}) (Fig. 1.6). The addition of an auxochrome usually results in a hyperchromic shift. For example, benzene has a B-band at 256 nm with a ε_{max} of 200, whereas aniline has a B-band at 280 nm with a ε_{max} of 1430. The hyperchromic action of the auxochrome NH_2 accounts for the 1230 increase in the value of ε_{max} of aniline over benzene.

Hypochromic Effect

The hypochromic effect is an effect that causes a decrease in absorption intensity max (Fig. 1.6). This is due to the addition of a cluster that alters the chromophore. For example, biphenyl has a λ_{max} of 252 nm and ε_{max} of 19,000, whereas 2,2'-dimethylbiphenyl has a λ_{max} of 270 nm and a maximum of 800. The drop in the value of ε_{max} of 2,2'-dimethylbiphenyl of 18,200 is related to the methyl groups' hypochromic activity, which deforms the chromophore by forcing the rings out of coplanarity causing conjugation loss. Above mentioned chemical shifts are shown in Fig 1.6.

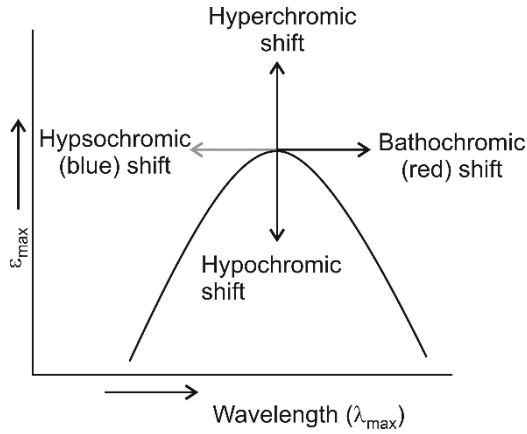


Figure 1.6 Absorption shifts.

Applications of UV Spectroscopy: The UV spectrophotometer principle and theory have a wide range of applications. This is, for example, how a functional group is identified. It can determine whether chromophores are present or absent in a complicated compound.

The degree of conjugation in polyenes can also be determined using this method. The absorption moves to a longer wavelength as the number of double bonds grows. Unknown compounds can also be identified using UV spectroscopy. The spectra of an unknown substance will be compared to that of a reference compound. This unknown substance will be recognised if both spectra coincide.

Geometrical isomers can also be identified via UV spectroscopy. It has been demonstrated that cis-alkenes absorb at a different wavelength than trans-alkenes. If one of the isomers has a non-coplanar structure, UV spectroscopy can still determine it.

Finally, this technology can determine a substance's purity. To do just that, the sample solution's absorption rate will be compared to the reference solution's absorption rate. The strength of absorption can be used to determine the purity of a chemical.

Woodward-Fieser Rule

Woodward and Fieser developed an empirical co-relation of structural changes that allows us to estimate the wavelength at which a conjugation diene will absorb by investigating a large number of dienes of each kind.

Woodward Fieser Rule for Calculating λ_{max} in Dienes

The wavelength of maximum absorption increases with the length of the conjugated system. As the length of the chromophore rises, the absorption strength (E_{max}) increases. The conjugated polyene system appears coloured to the naked eye if there are more than 5 double bonds in conjugation and absorption occurs around or above 400nm.

The presence of an alkyl group on the double bond also induces a bathochromic shift.

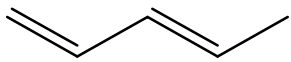
The following are some examples of double bonds in conjugation (Table 1.2).

1. **Dienes contained in an open chain system or Alicyclic dienes**

   The basic unit of Butadiene system.

   Parent value = 214nm (217nm)

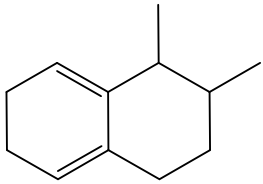
   Example:



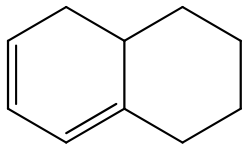
penta-1,3-diene

2. **The homo-annular conjugated double bond** is the conjugated double bond present in the same ring. It is also called Homo diene.

   Example:



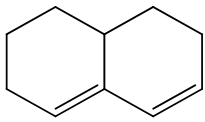
3,4-dimethyl-1,2,3,4,6,7-hexahydronaphthalene



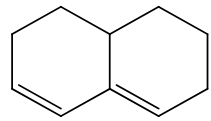
1,2,3,4,4a,5-hexahydronaphthalene

3. **Hetero annular conjugated double bonds** are the conjugated double bonds which are not present in the same ring.

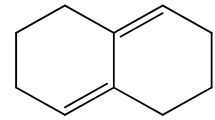
Example:



1,2,3,7,8,8a-hexahydronaphthalene

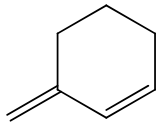


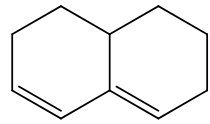
1,2,3,7,8,8a-hexahydronaphthalene



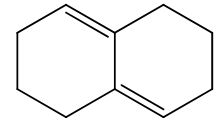
1,2,3,5,6,7-hexahydronaphthalene

4. **Exocyclic double bond** Base value = 5nm





1,2,3,7,8,8a-hexahydronaphthalene



1,2,3,5,6,7-hexahydronaphthalene

According to Woodward- Fieser Rules, each type of diene has a certain fixed basic value and the value of absorption maximum (λ_{max}) depends upon (Table 1.1):

The presence of polar groups such as -Cl, -Br, -OR, -SR etc.

The number of alkyl substituent or ring residues on the double bond.

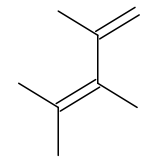
The number of double bonds which extend conjugation.

Table 1.2 Transition involved π-π*.

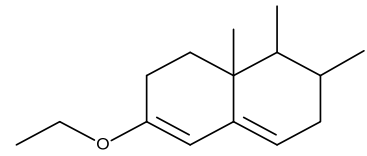
Parent value for Butadiene = 214nm	Homoannular conjugated diene = 253nm
Hetroannular conjugated diene = 214nm	**Increment for each substituent**
Alkyl substituent or ring residue = 5nm	Exocyclic double bond = 5nm
Double bond extending conjugation = 30nm	**Auxochrome**
R = +6nm	-SR = +30nm
-Cl*, -Br* = +5nm	$-NR_2$ = +60nm
$OCOCH_3$ = 0nm	

Examples

1. Acyclic diene = 214nm
   5- alkyl substituent =15nm
   Total = 229nm
   Observed value = 228nm

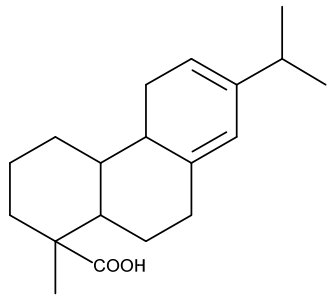


2. Heteroannular = 214nm
   3- Ring residue (3x5) =15nm
   1 Exocyclic double bond = 5nm
   -OR = 6nm

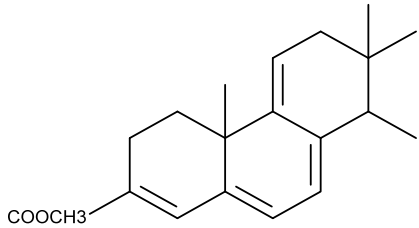


Total = 240nm
Observed = 241nm

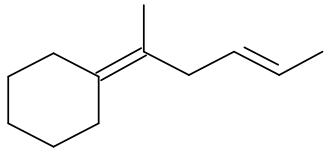
3. Homoannular = 253nm
Alkyl sub = 5nm
3 Ring residue = 15nm
Exocyclic double bond = 5nm
Total = 278nm
Observed = 275nm



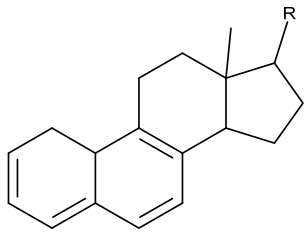
4. Homoannular = 253nm
5 Ring residues = 25nm
3 Exo double bond = 15nm
Double bond extending conjugation = 30nm
-$OCOCH_3$ = 0nm
Total = 353nm
Observed = 355nm



5. Base value = 214nm
2 Alkyl sub = 10nm
2 Ring Residue = 10nm
1 Exo double bond = 5nm
Total = 239nm
Observed = 242nm



6. Basic value = 253nm
1 Exo double bond = 5nm
2 double bond extending conjugation = 60nm
5 Ring Residue = 25nm
Total = 343nm
Observed value= 345nm



Woodward Kuhn rule for polyenes (conjugated system having more than 4 double bonds)

This equation is used for the calculation of λ_{max} and E_{max}.

For,

$$\lambda_{max} = 114 + 5M + n\,(48\text{-}1.7n) - 16.5R_{endo} - 10R_{exo}$$

Where,

n = number of the conjugated double bond.

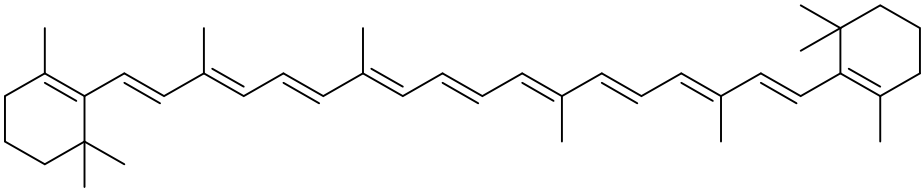
M = number of alkyl or alkyl substances in the conjugated system.

R_{endo} = number of the ring with an endocyclic double bond in a conjugated system.

R_{exo} = number of rings with exocyclic double bonds.

$$E_{max} = (1.74 \times 10^4)\, n$$

β-carotene,



Base value = 114nm

CH_3 = 10

n = 11

R_{endo} = 2

R_{exo} = 0

Hence

λ_{max} = 453.30nm

Observed = 452nm

$E_{max} = 19.14 \times 10^4$

Observed $E_{max} = 15.2 \times 10^4$

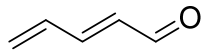
UV absorption in α, β- unsaturated carbonyl compound: In α-β- unsaturated carbonyl compound, the double bond and the carbonyl group are in conjugation.

The spectra for such compounds are the simple summation of ethylene and carbonyl chromophores.

A bathochromic shift is observed if two chromophores' groups are conjugated as a π electron cloud is spread over at least 4 carbon compounds.

There is a π-π* transition due to the ethylene unit which is in conjugation with the carbonyl group.

Woodward Fieser Rules for calculating λ_{max} of carbonyl compound:



penta-2,4-dienal

Base value,

For α, β- unsaturated ketone =215nm

For α, β unsaturated aldehyde =210nm

For acid and ester=193nm

Five membered ring parent enone = 202nm

Acyclic dienone = 245nm

For unsaturated carboxylic acid or ester= 195 nm

Increments (table 1.3)

For each exocyclic double bond = +5nm

For each double bond endocyclic in seven membered rings =+5nm

For each alkyl substituent or ring residue at the

α – position = +10nm

β – position = +12nm

γ or higher = +18nm

For each double bond extending conjugation = +30nm

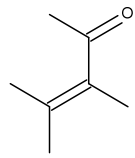
For a homoannular conjugation diene =+39nm

Table 1.3 Value of groups according to there position.

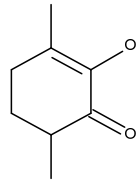
Group	α	β	γ	δ or higher
OH	+35nm	+30nm	-	+50nm
OAc	+6nm	+6nm	+6nm	+6nm
Cl	+15nm	+12nm	-	-
Br	+25nm	+35nm	-	-
OR	+35nm	+30nm	+17nm	+31nm
SR	-	+85nm	-	-
NR_2	-	+95nm	-	-

Examples

1. Acyclic enone = 215nm
   α $-CH_3$ = +10nm
   [2X] β $-CH_3$= 24nm
   Total = 249nm
   Observed = 249nm



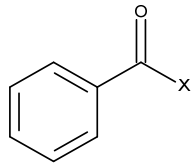
2. Base value = 215nm
   OH, at α = +35nm
   2β substitution
   One alkyl and one ring residue = +24nm
   Total = 274nm
   Observed = 275nm



Calculation of λ_{max} value for substituted aromatic aldehydes, ketone, carboxylic acids and esters.

Devised by Scott for the derivation of acyl benzenes

For a compound of the type



The base value (when X= alkyl or ring residue) = 246nm

When X= H (ArCHO) = 250nm

When X = OH, OR (ArCOOH or ArCOOR) = 230nm

Table 1.4 Increments due to auxochrome.

Auxochrome	Ortho	Meta	Para
Alkyl	+3nm	+3nm	+10nm
OH, OR	+7nm	+7nm	+25nm
Cl	0nm	0nm	+10nm
Br	+2nm	+2nm	+15nm
NH_2	+13nm	+13nm	+58nm
NHAc	+20nm	+20nm	+45nm
NR_2	+20nm	+20nm	+85nm
O	+11nm	+20nm	+75nm

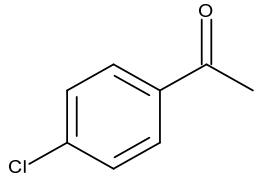
Examples

1. Base value = 246nm

   Cl at Para = 10nm

   Total = 256nm

   Observed = 254nm



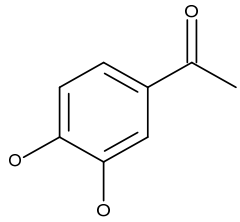
2. Base value = 246nm

   OH, at meta = +7nm

   OH, at para = +25nm

   Total = 278nm

   Observed = 281nm



Short Questions

1. Give an account of qualitative and quantitative analysis using UV spectroscopy?
2. Write notes on Applications of UV Visible Spectroscopy.
3. How do you calculate the absorption maximum wavelength for Dienes with Woodward Fieser Rule?
4. Discuss the application of Woodward-Fieser Rules taking α, β – Unsaturated ketones as example.
5. Write a note on Woodward's rule and its application.
6. Explain the Woodward - Fieser rule in Cyclic dienes.
7. Write down the Solvent effect on absorption spectra.
8. Define bathochromic shift?
9. Define red shift?
10. What is the range of UV-Spectroscopy?

Long Questions

1. State and explain Beer-Lambert Law. Write briefly about the deviations of the absorption laws.
2. With a neat labelled diagram, explain the construction and working of double beam UV-Vis Spectrophotometer.
3. Explain the theory of U.V absorption and add a note on effect of Auxochromes on Chromophores.
4. What are spectral shifts? Define various types of shifts which affect the absorption spectra with suitable examples?