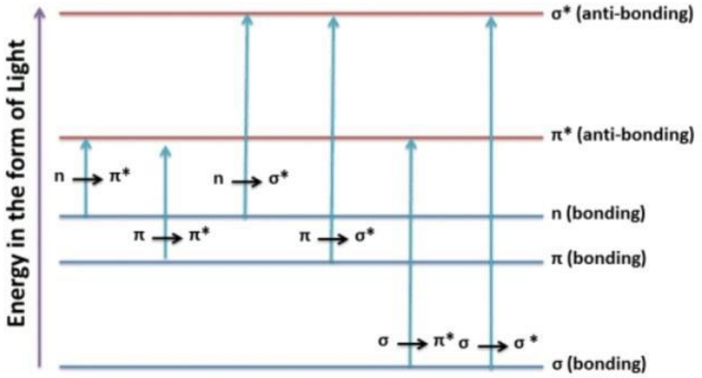
UV VISIBLE SPECTROSCOPY

Introduction To Spectroscopy

UV visible spectroscopy involves. The measurement. Of absorption of energy when electromagnetic radiation of the proper energy is provided .An reactions in promoted from the HOMO to the LUMO. As conjugation increases the HOMO-LUMO gap decreases the absorption position of the , to longer wavelength UV / visible spectroscopy requires electromagnetic radiation of high energy The visible regions correspond to 800-400 nm. and UV regions to 200-400.0m

Electronic Transitions



(I) $\sigma \rightarrow \sigma *$ transition: A transition of an electron from a bonding sigma orbital to the higher energy anti-bonding sigma orbital is designated) $\sigma \rightarrow \sigma *$ transition e.g. In alkanes e.g. this is only transition is available. Sigma bonds are general very strong this. Therefore is a high energy process and these transition requires very short wavelength.

(II) $n \rightarrow \sigma *$ transition :This transition involves saturated compound with one hetero atom with unshared pair electrons. These transition requires less energy as compared to $n \rightarrow \sigma *$ transition. In saturated alkyl halides the energy required for transition decreases with the increase in the size of halogen atom.

(III))$\pi \rightarrow \pi *$ transition: This transition is available in compounds with unsaturated centres e.g. simple alkenes, aromatics, carbonyl compound etc. This transition requires lesser energy than) $\rightarrow \pi *$ transition: In simple alkenes, through several transition are available. e.g. saturated ketones, alkynes, a2o compounds.

(IV) $n \rightarrow \pi *$ transition: In this transition, an electron of unshared electron pair on a hetero atom is excited to $\pi *$ antibonding orbital. This transition involves least amount of energy than all transition and therefore this transition give rise to an absorption band at longer wavelength. e.g. In carbonyl compound

Chromophore. :The term chromophore was previously used to denote a functional group or so other structural feature the presence of which gives a colour to a compound. For example, nitro group violet Spectroscopy because its presence in a compound gives yellow colour to the compound may be defined as any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region

Auxochrome. :It is a group which itself does not act as a chromophore but when attached chromophore it shifts the adsorption maximum towards longer wavelength along with an increase in intensity of absorption. Some commonly known auxochromic groups are-OH-NH_2-OR-NHR

The extended conjugation has been responsible for bathochromic effect of auxochrome Absorption and Intensity Shifts

1. Bathochromic shift/effect (Red shift)

2. Hypsochromic shift/effect (Blue shift)

3. Hyperchromic effect

4. Hypochromic effect

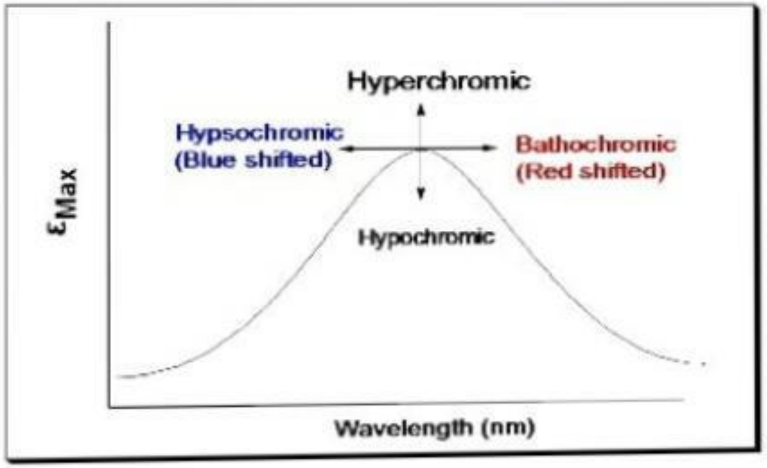


Figure: Absorption and intensity shifts

Bathochromic Shift It is an effect due to which the absorption maximum is shifted towards longer wavelength for the presence of an auxochrome or by the change of polarity of solvent. The n→ π* transition for carbonyl compounds experiences red shift when the polarity of solvent decreased.

Hypsochromic Shift/: It is an effect due to which the absorption maximum is shifted towards shorter wavelength for the removal of conjugation (auxochrome) or by the change of polarity of solvent.

Hyperchromic Shift: It is an effect due to which the intensity of absorption maximum (E) increases. For example, the B-band for pyridine at 257 mu , 2750 is shifted to 262 mu

Hypochromic Effect: It is defined as an effect due to which the intensity of absorption maximum decreases, i.e., extinction coefficient, E. For example, biphenyl absorbs at 250 mu max 19000 whereas 2-methyl biphenyl absorbs at 237 mu, & 10250 (Em decreases).

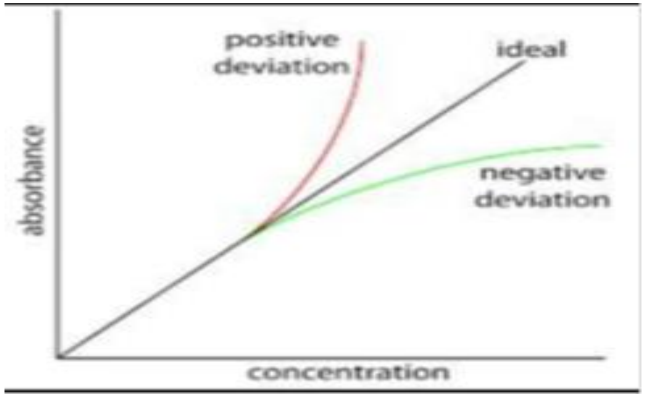
SOLVENT EFFECT

The position and intensity of an absorption band may shift when the spectrum is recorded in different solvents. A dilute sample solution is prefered for analysis. Most commonly used solvent is 95% ethanol. It is best solvent as it is cheap, transparent down to 210nm.Position as well as intensity of absorption maxima get shifted for a particular chromophore by changing the polarity of solvent

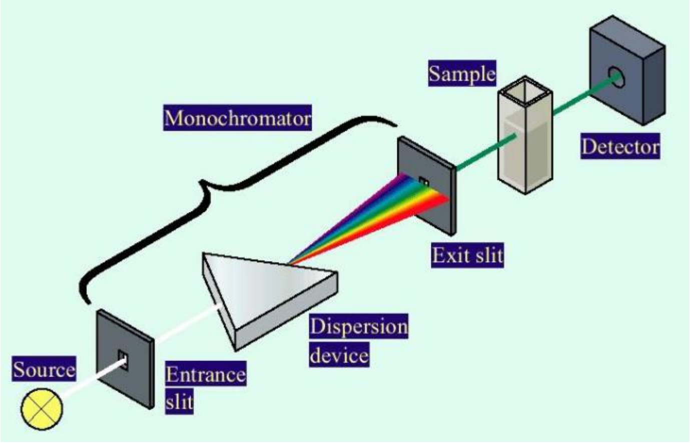
K- Band Due to conjugated enes & enones are affected differently by changing the polarity of the solvent. K bands due to conjugated dienes are not affected by changing the polarity of the solvent, while these bands due to enones shows a red shift by increasing the polarity of solvent.

R- Band The absorption shifts to shorter wavelength (blue shift) with increasing polarity of solvent. B band The position as well as the intensity of the band is not shifted by increasing the polarity of the solvent.But the heterocyclic aromatic compound, a marked hyperchromic shift is observed by increasing the polarity of the solvent.

Beer's Law And Lambert's Law shows that there exists a logarithmic relationship between the transmittance and the length of the optical path through the sample. Beer observed that a similar relationship holds between transmittance and the concentration of a solution, ie, the intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.



Instrumentation



SOURCE OF RADIANT ENERGY

Tungstun Halogen Lamp : 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 Tungsten starts sublimating. 3000 k, beyond this It is used when polychromatic light is required. To prevent this along with inert gas some amount of halogen is introduced(usually iodine). Sublimated form of tungsten reacts with iodine to form Tungsten-Iodine complex. Which migrates back to the hot filament where it decomposes and Tungsten get deposited.

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.They are stable and robust.

Xenon Discharge Lamp : It possesses two tungsten electrodes separated by some distance. These are enclosed in a glass tube (for visible) 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.

Mercury Arch Lamp : In mercury are lamp, mercury vapour is stored under high pressure and excitation of mercury atoms is done by electric. discharge.

MONOCHROMATORS

1.Filters

2. Prisms

3.Grating

FILTERS

Absorption Filters- works by selective absorption of unwanted radiation and transmits the radiation which is required. Examples- Glass and Gelatine filters.

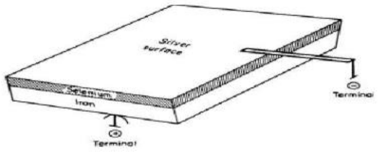
Interference Filters Works on the interference phenomenon, causes rejection of unwanted wavelength by selective reflection It is constructed by using two parallel glass plates, which are silvered internally and separated by thin film of dielectric material of different (CaF_2, SiO, MgF_2) refractive index

Prism: Prism is made from glass, fused silica. Quartz or fused silica is the choice of material of UV spectrum..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.

DETECTORS

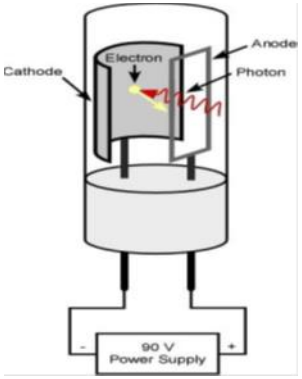
Barrier Cell Detector : There are three common types of detectors which are widely used in UV spectrophotometer Barrier layer cell. This cell is also known as photovoltaic cell The barrier cell consists of a semiconductor, such as selenium, which is deposited on a strong metal base, such as iron. Then a very thin layer of silver or gold is sputtered over the surface of the semiconductor to act as a second collector electrode. The radiation falling on the surface produces electrons at the selenium silver interface.. The electrons are before accumulated on the silver surface. The accumulation of electrons on the silver surface produces electrical voltage difference between the silver surface and the base of cell. If the external circuit has a low resistance, a photocurrent will flow which is directly proportional to the intensity of incident radiation

Detectors (Barrier layer cell)

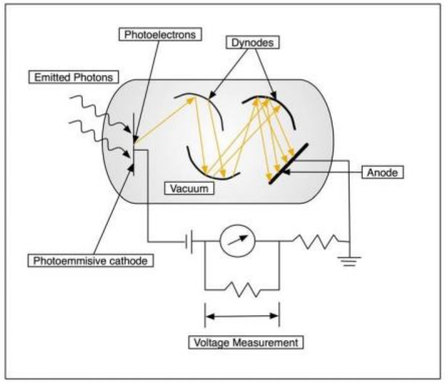


Phototubes Phototube consists of An evacuated glass envelope (with a quartz window for use in ultraviolet region) , A semi cylindrical cathode which has an inner surface coated with a compound with relatively loosely bound electrons, such as an alkali or alkaline earth oxide A central metal wire anode A potential difference of approximately 90 volts is applied across the electrodes. The radiation enters through the quartz window and strikes the photo emissive surface of the cathode. The photons are absorbed and transfer their energy to the loosely bound electrons of the surface material. The electrons escape from the surface and are collected at the anode causing the current to flow through the circuit

Photomultiplier Tube. A photomultiplier tube is generally used as a detector in UV spectrophotometers It is a combination of a photodiode and an electron multiplying amplifier. A photomultiplier tube consists of an evacuated tube which contains one photo-cathode and 9-16 electrodes known as dynodes. The surface of each dynode is of Be-Cu, Cs-Sb or similar material.When radiation falls on a metal surface of the photocathode, it emits electrons. The electrons are attracted towards the first dynode which is kept at a positive voltage. When the electrons strike the first dynode, more electrons are emitted by the surface of dynode; these emitted electrons are then attracted by a second dynode where similar type of electron emission takes place.



The process is repeated over all the dynodes present in the photomultiplier tube until a shower electrons reaches the collector. The number of electrons reaching the collector is a measure of the intensity of light falling on the detector. The dynodes are operated at an optimum voltage that gives a steady signal.



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Recording system. The signal from the photomultiplier tube is finally received by the recording system. The recording is done by recorder pen. The type of arrangement is only done in recording UV spectrophotometers.

Sample cells. The cells that are to contain samples for analysis should fulfil three main conditions

(1) They must be uniform in construction; the thickness must be constant and surfaces facing incident light must be optically flat.

(i) The material of construction should be inert to solvents.

ii) They must transmit light of the wavelength used.

The most commonly used cells are made of quartz or fused silica. These are readily available ever

in matched pairs where sample cell is almost identical to the reference cell.

.**Matched cells**. When double-beam instrumentation is used, two cells are needed, one for the reference and one of the sample. It is normal for the absorption by these cells to differ slightly. This causes a small error in the measurement of the sample absorption and d to analytical e work, matched cells are used. These are cell- in which the absorption of each one is equal to or very near equal to the absorption of the other. A large number of these cells are manufactured at one time and the respective absorptivity measured. Those with very similar absorptivities are put together and designated

APPLICATIONS OF U.V. SPECTROSCOPY:

1. Detection of Impurities
2. Structure elucidation of organic compounds.
3. Quantitative Analysis
4. Qualitative Analysis
5. Chemical Analysis
6. Detection of Functional Groups
7. Quantitative Analysis Of Pharmaceutical Substances
8. Examination Of Polynuclear Hydrocarbons
9. Determination Of Molecular weights
10. HPLC Detector

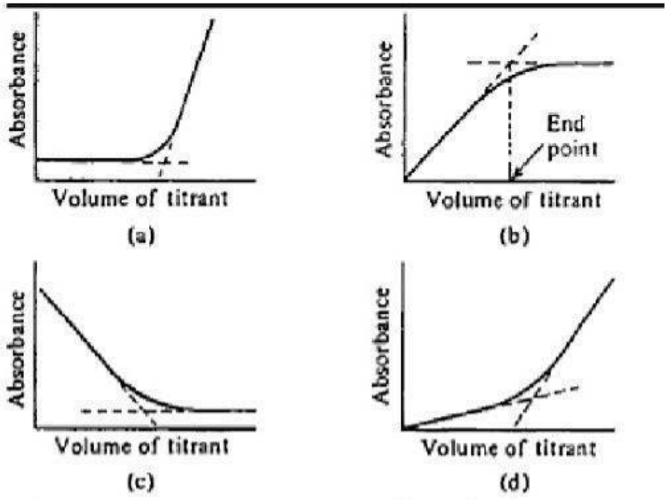
Spectrophotometric Titrations

Curve A is characteristics of case where. Only titrant absorb for e.g.. arsenic 3 with bromide where bromide absorbance reading are taken at wavelength where bromine absorb so long & arsenic will be remain as it is as so as arsenic is consumed by titrant the absorbance will increase due to color of titrant.

Curve B is characteristics of case where only the product of reaction absorb for eg In titration of copper with edta it will carried at 745 nm it is selected because at this position only etdA copper complex will show absorbance.

Curve C is characterized by only the substance is titrated & product do not absorb eg. paratoludience in butanol with perchloric acid at 290 nm at this wavelength is selected paratoludine. Sharpe absorb at this wavelength whereas titrant perchloric acid has not absorbance at this region.

Curve D: Is obtain in such case when a colored analyte is converted into colourless product by a color titrant when titrant is added the color of analyte starts feeling due to formation of colourless product but often equivalence point absorbance suddenly rises due to the color of the titrant alone.



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Acedemic Year : 2021- 2022