BS Chemistry IV SS Class Notes

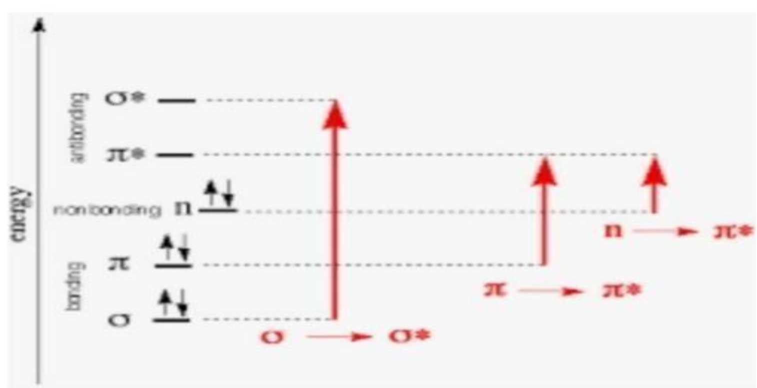
UV SPECTROSCOPY

Why π-π* is the most concenient and useful transition in UV-Vis spectroscopy?

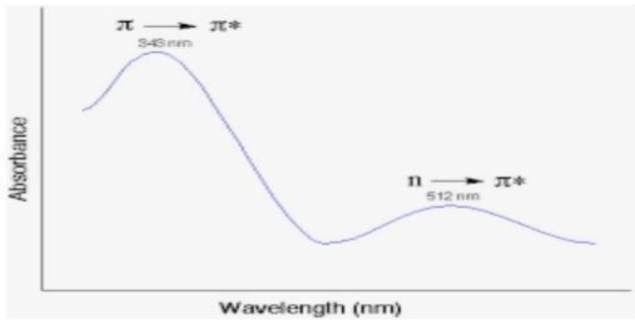
Answer: π-π* transition:

This transition is very important in the UV-Vis spectroscopy because it consists of commonly conjugated π system and the π system is usually intense ($€_{max} > 10000$) and it usually fall in the region of k-band. The compounds that are included in this region appears as k-band for- example conjugated dienes, trienes, butadiene and aromatic rings. The aromatic compounds like benzene displays three absorption bands at 184, 204 and 256nm and of these the band at 204nm is referred to as k-band and this k-band of bnzene is used in other aromatic compounds as well. This transition is available in compounds in unsaturated centers e.g simple alkenes and carbonyl compounds etc. This type of transition required low amount of energy then transition in a simple alkenes. However several transition are available ,π-π* transition has the lowest transition energy and absorption band occurs around 170nm-190nm in unconjugated alkenes is due to this transition in the case of e.g saturated ketones , the most intense band occurs around 150nm is due to π-π* transition **ππ*; =C=C**

or triple bond(alkenes, alkynes)



So from the above graph it is obvious that this transition require low amount of energy as compared to other transitions also the compounds included in this transition are used in our daily life different alkenes use in our daily life such as alkenes such as ethane used for manufacture of polythene, artificial ripening of fruits as general anesthetic and it also used to prepare mustard gas and alkenes used in the preparation alcohols and acetic acid for the manufacture polymers etc.



- This transition has low energy.
- Also have low wavelength.
- Include alkenes or alkynes in UV-Vis spectre.

<u>What are chromophores?</u>

Answer: Chromophores:

<u>Definition:</u>

"A chromophores has a functional group present in a molecule that is capable of electronic transitions in the UV – VIS spectral range resulting in colour of a compound."

<u>Explanation:</u>

Chromophores are those molecules which absorb UV radiation in the range of 180-390nm mostly unsaturated compounds absorb these radiations. Also some heteroatoms also absorb UV radiations in this region and show colours. Many other groups such as organic and inorganic also absorb these radiation and show colours. These are colour bearing groups and show colours so these are called as colour loving groups. Some compounds are colourless whereas some are coloured. The answer lies in the presence or absence of chromophores. If chromophores character is present in the compound then compounds show colours. If chromophores characteristics are not present in the compound then this compound not show colours. And all this occurs when different compounds absorb UV radiation in the range of 180-390nm.

<u>*Chromophores Types*</u>

and complex forming compounds resulting from charge transfer between metals and ligands. Mostly it is considered that there are three types of chromophores. Commonly three types of compounds show colour characteristics, namely, organic, inorganic

<u>Organic molecules:</u>

An organic molecule absorbs light in the UV VIS region depending on its molecular structure. Electronic transitions take place between the ground state and the excited electronic states of molecules having some degree of unsaturation or a heteroatom. Those in lower Transitions in the UV region are generally not accompanied by colour changes whereas energy visible region are capable of producing colour changes

Nitro 

Azo 

Azoxy 

Carbonyl 

Inorganic

Inorganic compounds containing atoms with electrons in dorbital give weak absorptions in the visible region. Metals in transition series are often coloured on account of such transitions, e.g., blue colour of aqueous copper sulphate solution Inorganic compounds containing atoms with electrons in dorbital give weak absorptions in the visible region. Metals in transition series are often coloured on account of such transitions, e.g., blue colour of aqueous copper sulphate solution.

Charge Transfer Complexes:

In some cases a compound is colourless naturally but in presence of a complex forming agent becomes coloured. In such cases one species is an electronic donor group and the other is an electron acceptor. On interaction the charge transfer complex formed is intensely coloured, e.g., a blood red complex is formed when a Fe^{3+} combines with SCN^{-2}. The complex formed absorbs light resulting in transfer of an electron from SCN^{-1} to Fe^{3+}.

Chromophoric Shifts:

we have often observed that the colour of a compound deepens or fades when either the environmental conditions are changed or on reaction with other species. In such situations chromophoric shifts take place.

Bathochromic Shift:

This type of shift (red shift) results in shift to longer wavelengths i.e. colourless to the colour or deepening of colour. Examples increase in conjugation or increase in number of aromatic rings can result in colouration or deepening of colour. The increase in intensity is referred to as hyper chromic eff ect

Hypochromic shift:

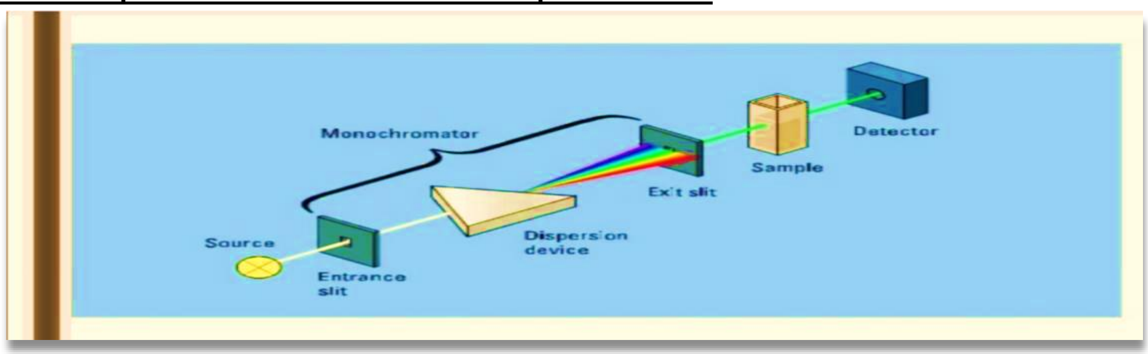
This type of shift (blue shift) is a shift of absorption to shorter wavelengths resulting in a coloured solution becoming colourless or a deep colour to become lighter. The fading of colours is also referred to hypsochromic effect.

<u>What are the main components of a UV-Vis absorption instrument?</u>

Answer:

The ultraviolet and visible regions of the electromagnetic spectrum include the wavelength range that is about 100 nm upto the 800 nm. The vacuum ultraviolet regions has the shortest wavelength and due to this short wavelength this region has the highest energies (100-200 nm), thus it is difficult to make measurement in this region and is little used in analytic techniques most analytical procedures in the ultraviolet regions are made between 200 and 400 nm.The absorption of radiation in the ultraviolet and visible regions of the electromagnetic spectrum results in electronic transition between molecular.

<u>Main components of ultraviolet –visible spectrometer:</u>



Following are the main components of ultraviolet visible spectrometer:

- **Light source**
- **Monochromator**
- **Sample and reference cells**
- **Detecter**
- **Amplifer**
- **Recording devices**

<u>Light source:</u>

The main component of ultraviolet visible spectrometer is the light source in this tungsten filament lamps and hydrogen-deuterium lamps are most widely used and suitable light source and they cover the whole ultraviolet tungsten filament lamps contain large amount of red radiation they emit the radiation of about 375 nm specially. While the intensity of hydrogen deuterium lamps falls below the range of 375 nm.

Monochromator:

Monochromators generally composed of prisms and slits .In ultraviolet visible absorption spectrometer consists of:

- ***Entrance slit***
- ***Dispersion device***
- ***Exit slit***

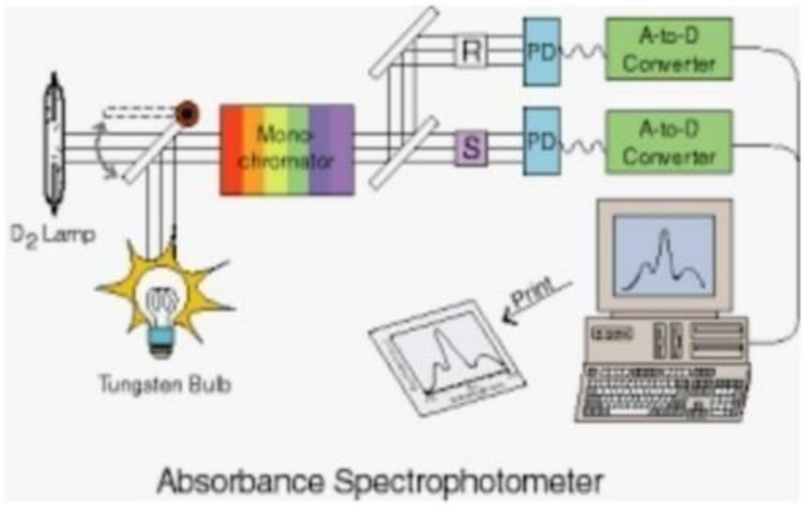
The most of the spectrometers are double beam spectrophotometers the radiaton emited from the light source is dispersed with the aid of rotatng prism the various wavelength of the light source which are separated by the prism are then selected by the slits such as the rotaton of the prism result in a series of contnuously increasing wavelength in order to pass through the slits for recording purpose the beam selected by the slit is monochromatc and is further divided into two beams with the aid of another prism.

Sample and reference cells:

The beams that are expended from the light source and is selected by monochromators then one of the two divided beams is passed through the sample soluton and second beam is passed through the reference soluton or reference cells. Both sample soluton and reference soluton are contained in the cells these cells are made of either silica or quartz. Glass cannot be used for the cells as it also absorbs light in ultraviolet regions.

Dtectore:

Generally in ultraviolet visible spectroscopy two photo cells perform the purpose of detector one of the photo cell receive the beam from sample cell and second photo cell receive the beam from the reference cell. The intensity of the radiaton from the reference cell is stronger than the beam of sample cell. This will produce pulsatng or alternatng currents in the photo cells that play the role of detector in ultraviolet spectroscopy. Simply we can say that detectors detect the light source and produce alternatng currents in order to detect the pulsatng current.



Amplifier:

The alternating current generated in the photo cells both in the reference and samples and reference cells. This current is transferred to the amplifier. The amplifier is attached to a small servomotor. Generally current generated in the photo cell is of very low intensity, the main purpose of amplifier is to amplifier the signal many times so we can get clear and recordable signals, so we can say that amplifier only enhance the quality of the image, so we can see it very clear only due to the help of the amplifier.

Recording devices:

We have read that amplifier increase the quality of recordable signals most of the time amplifier is coupled to a pen recorder which is connected to computer. Computer stores all the data that is generated and produces the spectrum of the desired compound.

The construction of a traditional ultraviolet visible spectrometer is very similar to IR spectrometer such as sample handling, detection and output are required. Spectrum is plotted automatically on most ultraviolet/visible spectrophotometers. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. Quantitative analysis can be done with the help of ultraviolet and visible spectroscopy most of the substances such as inorganic and biochemical substances can be quantitatively estimated either directly or after the formation of a complex.