

Solutions of the Tutorial Sheet: UV-Vis spectroscopy

Q.1. What is meant by electronic, vibrational and rotational transitions? Which of these transitions require more and the lesser energy?

Ans. Electronic transition: An electronic transition occurs when the valence electrons namely, s, p, and n electrons, of a molecule are excited from one electronic state to a higher energy electronic state. Typically, it involves the absorption of UV-Visible radiation.

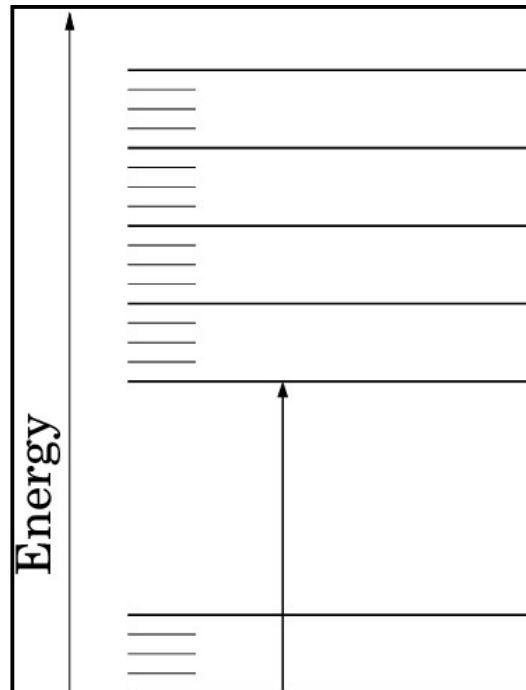
Electronic transitions take place when absorb UV-visible light (photon energy is associated) and the electrons in a molecule/atom are excited from lower energy level (E_0) to a higher energy level (E_n), where $n=1,2,3,\dots$. The spacing between energy levels (ΔE) in electronic transitions is ~ 35 to 71 kcal/mole (UV-Vis region).

Vibrational transition: Each electronic state contains several vibrational energy levels. The transition between vibrational levels having different energy is known as vibrational transition which requires absorption of an Infra-Red (IR) radiation.

Transitions between the lower vibrational energy level (v_0) to higher vibrational energy level (v_n) is known as vibrational transitions, where $n=1,2,3,\dots$. These transitions require less energy (IR region) than the transitions within electronic energy levels. The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.

Rotational transition: Each vibrational state contains several rotational energy levels. The transition between rotational levels having different energy is known as rotational transition which requires absorption of a microwave radiation. The spacing between energy levels in rotational energy levels is even smaller than vibrational energy levels.

Among these, the electronic transition requires a maximum amount of energy whereas rotational transition requires a minimum amount of energy. $\Delta E_{\text{Rotational}} < \Delta E_{\text{Vibrational}} < \Delta E_{\text{Electronic}}$

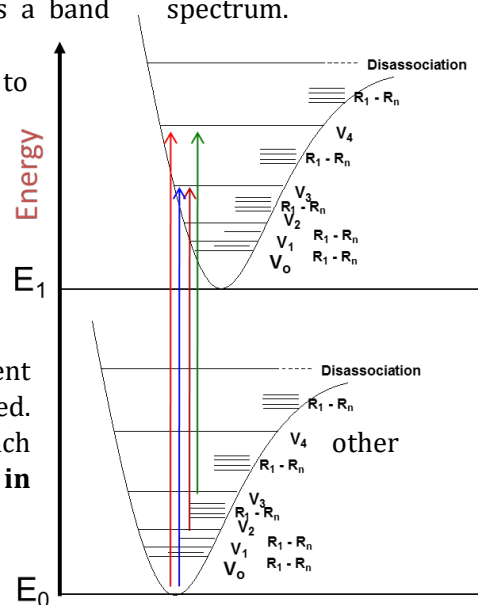


Q.2. What is the difference between an atomic absorption and a molecular absorption spectrum and why does this difference exist?

Ans. Atomic spectrum is a line spectrum whereas molecular spectrum is a band spectrum.

Atoms don't possess any vibrational or rotational energy levels due to absence of vibrational and rotational motions. So, they undergo only electronic transitions. Hence, a line spectrum is produced.

On the other hand, molecules possess both vibrational and rotational energy levels in addition to electronic levels as these can vibrate and rotate as well. For any electronic excitation, various vibrational and rotational energy levels are available and molecule can assume any one of these levels. On the average, various molecules occupy various different vibrational and rotational excited states and these levels are closely spaced. Hence, the various lines obtained in the molecular spectrum are so close to each other that it appears as a band. (Figure shows various possible transition in molecule leading to band spectrum)



Q.3. What is the range of UV and visible region in EMR spectrum?

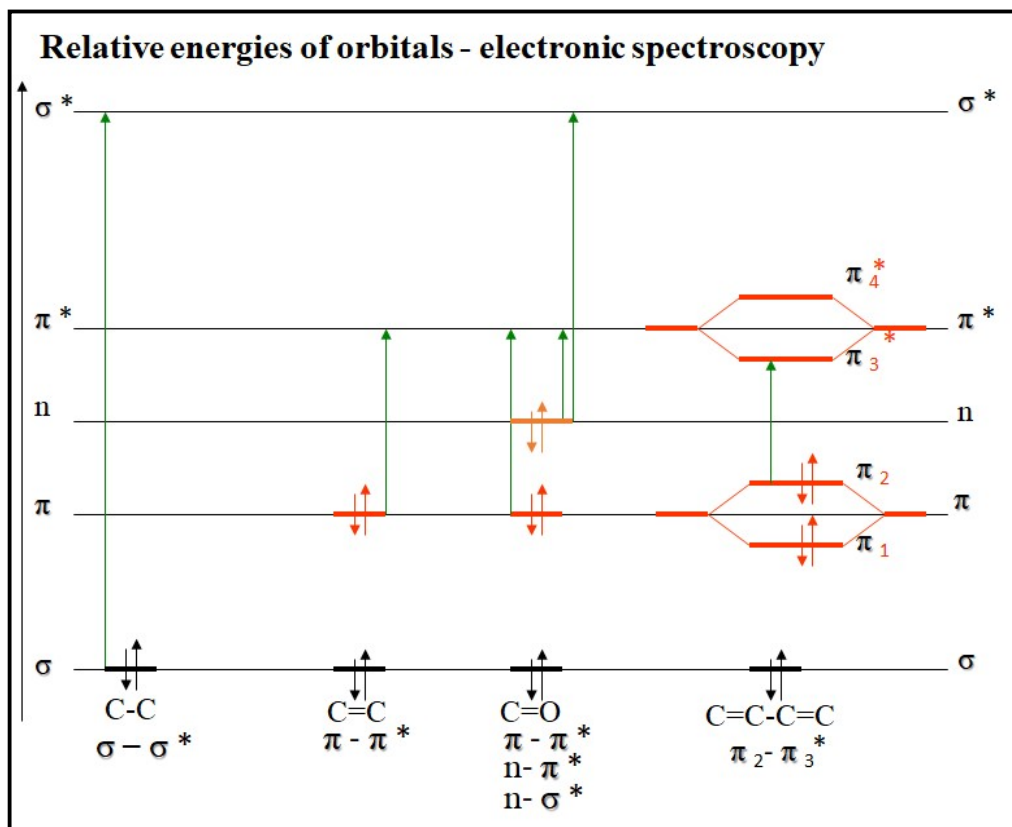
Ans. The UV radiation region extends from 10 nm to 400 nm and the visible radiation region extends from 400 nm to 800 nm. Near UV Region: 200 nm to 400 nm. Far UV Region: below 200 nm.

Q.4. What happens on absorption of UV and infrared radiation by a molecule?

Ans. Absorption of UV radiation causes electronic transitions in a molecule whereas absorption of infrared radiation results in vibrational transitions in a molecule.

Q5. Draw relative energies of various types of molecular orbitals. Show various transitions in case of alkanes (C-C), alkenes (C=C), carbonyl (C=O) and conjugated alkenes (C=C-C=C).

Ans.



Q.6. What do you understand by the terms: chromophore, auxochrome, bathochromic shift, hypsochromic shift, hyperchromic shift and hypochromic shift?

Ans. Chromophore: Chromophore may be defined as the functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions. e.g. $-\text{NO}_2$, $\text{N}=\text{O}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$, $\text{C}=\text{S}$, etc

Auxochrome: It is a substituent or a functional group, which by itself does not absorb in the UV-visible region but upon attachment on a chromophore, increases the wavelength of absorption (λ_{max}) and also alters the intensity of absorption. e.g. $-\text{OH}$, $-\text{Br}$, $-\text{OR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{SH}$ etc.

Bathochromic shift: When the wavelength of maximum absorption shifts towards a longer wavelength or towards the red end of a spectrum, it is known as red-shift or bathochromic shift.

Hypsochromic Shift: When the wavelength of maximum absorption shifts towards a shorter wavelength or towards the blue end of a spectrum, it is known as blue-shift or hypsochromic shift.

Hyperchromic shift: It is defined as an increase in the intensity of absorption.

Hypochromic shift: It is defined as a decrease in the intensity of absorption.

Q.7. Give the possible transitions in the following molecules: (a) Methanol (b) Benzoic acid (c) Pyridine (d) Ethane.

Ans. (a) Methanol: Possible transition: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$

(b) Benzoic acid: Possible transition: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

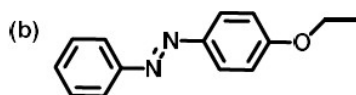
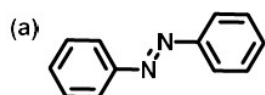
(c) Pyridine: Possible transition: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

(d) Ethane: Possible transition: $\sigma \rightarrow \sigma^*$

Q.8. State the importance of the wavelength of maximum absorption λ_{\max} . Arrange the following molecules in order of increasing λ_{\max} .

(i) (a) C_6H_6 (b) $\text{CH}_2=\text{CH}_2\text{-CH}_2\text{-CH}_2=\text{CH}_2$ (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{C}_6\text{H}_5\text{CH=CH-CH=CH}_2$

(ii)



Ans. λ_{\max} is the wavelength at which absorbance (absorption) for the molecule is maximum.

Following is the order:

(i) $\text{CH}_2=\text{CH}_2\text{-CH}_2\text{-CH}_2=\text{CH}_2 < \text{C}_6\text{H}_6 < \text{C}_6\text{H}_5\text{CHO} < \text{C}_6\text{H}_5\text{CH=CH-CH=CH}_2$

(ii) $b > a$

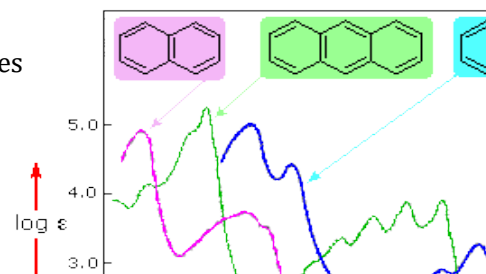
Q.9. (i) Naphthalene and anthracene are colorless, but tetracene is orange. Why?

(ii) β -carotene is orange. Why?

Ans. More the no. of double bonds in conjugation, lesser energy is required for $\pi\text{-}\pi^*$ transitions as HOMO and LUMO gap decreases. This leads to increase in the magnitude of λ_{\max} . Compounds having 8 or more than 8 double bonds in conjugation will appear coloured to human eye.

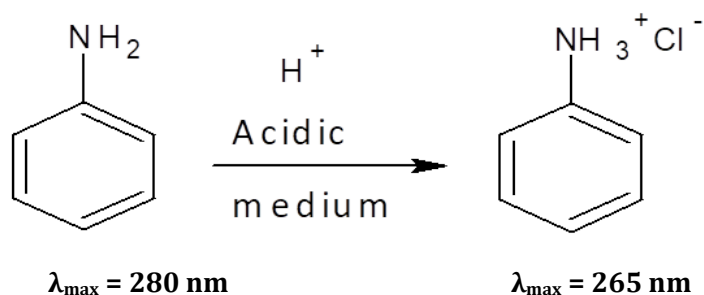
(i) The added conjugation in naphthalene, anthracene and tetracene causes bathochromic shifts of the absorption bands. So more than >8 double bond will shift the absorption in visible region. Naphthalene and anthracene absorb radiation in the UV region so they are colorless, while tetracene absorbs in the visible region so it is orange.

(ii) Carotene has 11 conjugated double bond, so it will absorb radiation in visible region that's why color is orange.

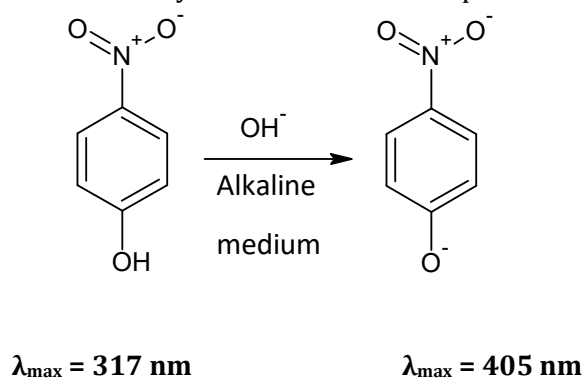


Q.10. (i) Aniline shows blue shift in acidic medium. Explain.
(ii) p-Nitrophenol shows red shift in alkaline medium. Explain.

Ans. (i) Aniline shows blue shift in acidic medium, as the lone pair of electrons on nitrogen is no longer in conjugation due to protonation.

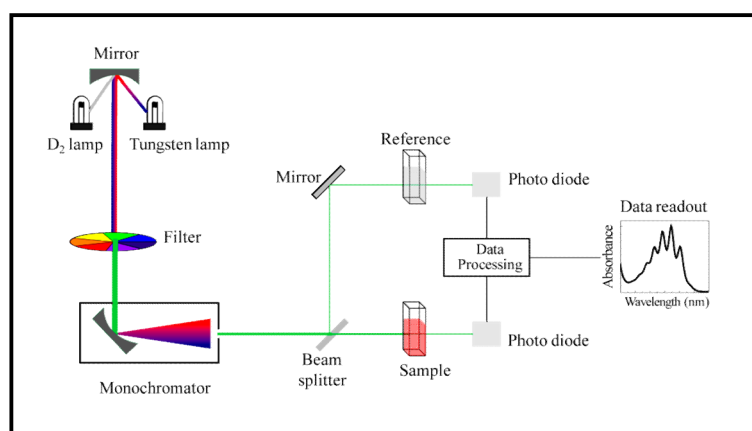


(ii) In alkaline medium, p-nitrophenol shows red shift. Because lone pairs on negatively charged oxygen (phenolate ion) delocalizes more effectively than the unshared pair of electron in parent p-nitrophenol molecule.



Q.11. Draw the diagram for UV-Vis spectrophotometer. Name the light source used for visible and UV radiations. Compare the materials from which cuvettes must be made for UV and visible work. What is the role of photomultiplier tube?

Ans. Diagram of a UV-Vis spectrophotometer:



Light sources:

For UV radiation: Deuterium lamp;

For Visible radiation: Tungsten lamp

Cuvette materials:

For UV radiation: Quartz;

For Visible radiation: Quartz or Glass

A photomultiplier tube, useful for light detection of very weak signals, is a photoemissive device in which the absorption of a photon results in the emission of an electron resulting into photocurrent. The photocurrent generated is amplified by the amplifier and is then measured by detector.

Q.12. Why σ to σ^* transition is not observed by general UV-Vis spectrophotometer?

Ans. The energy gap between $\sigma - \sigma^*$ is high and comes below 200 nm wavelength. The general UV-Vis spectrophotometer provides radiations from 200 nm to 800 nm only not below 200 nm. That's why this transition from σ to σ^* is not observed (even though it is allowed) by general UV-Vis spectrophotometer.

Q.13. Why with change in the concentration of H^+ ions in an aqueous solution there is a change in the colour of phenolphthalein and methyl orange indicators.

Ans. Phenolphthalein and methyl orange are a class of acid-base indicators whereby the chemical structures and conjugation changes depending on the H^+ concentration. Here are the structural changes:

