**Spectroscopy**

Spectroscopy is interaction of light with matter. Matter is the chemical substance which is subjected to interaction with light. Light is electromagnetic radiation.

**The electromagnetic spectrum:**

The energy which travels in the form of waves is called as electromagnetic radiation. It can propagate without any medium. It consists of an electrical and a magnetic component which oscillate in planes perpendicular to each other and also to the direction of propagation. All electromagnetic radiations travel with the same velocity in vacuum ($3 \times 10^8$ ms$^{-1}$). But these radiations differ in frequency and wavelengths.

The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*
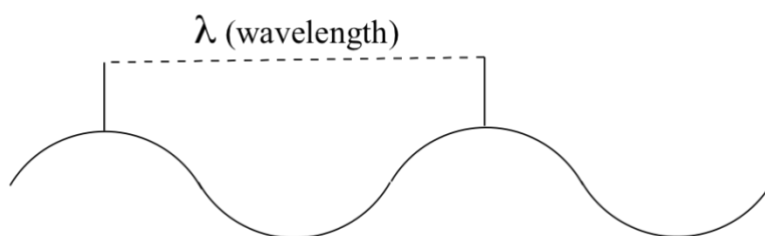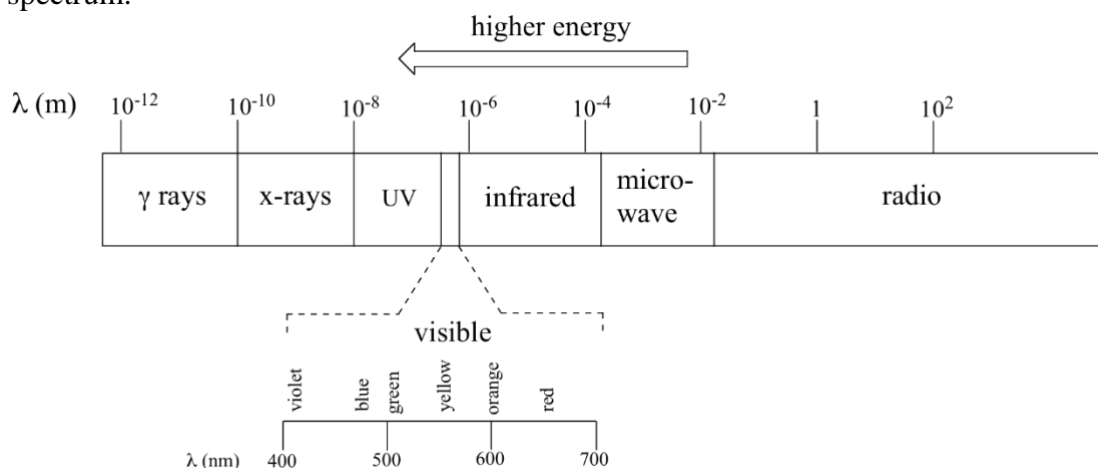


High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as $10^{-16}$ meter from crest to crest.

The energy of a particular wavelength can be expressed as:

$$E = hc\lambda$$

where E is energy in kcal/mol, $\lambda$ (the Greek letter lambda) is wavelength in meters, c is 3.00 x $10^8$ m/s (the speed of light), and h is 9.537 x 10-14 kcal•s•mol$^{-1}$, a number known as Planck's constant. Because electromagnetic radiations travel at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s$^{-1}$.

The full range of electromagnetic radiation wavelengths is referred to as the electromagnetic spectrum.

higher energy

λ (m)   $10^{-12}$   $10^{-10}$   $10^{-8}$   $10^{-6}$   $10^{-4}$   $10^{-2}$   1   $10^2$

| γ rays | x-rays | UV | infrared | micro-wave | radio |

visible

violet  blue  green  yellow  orange  red

λ (nm)   400   500   600   700

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy 'ground state' to some higher energy 'excited state'. Other wavelengths are not absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.
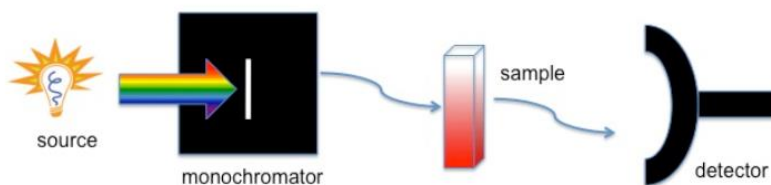
source    monochromator    sample    detector

Figure 4.4.1 Illustration of a single beam UV-vis instrument.

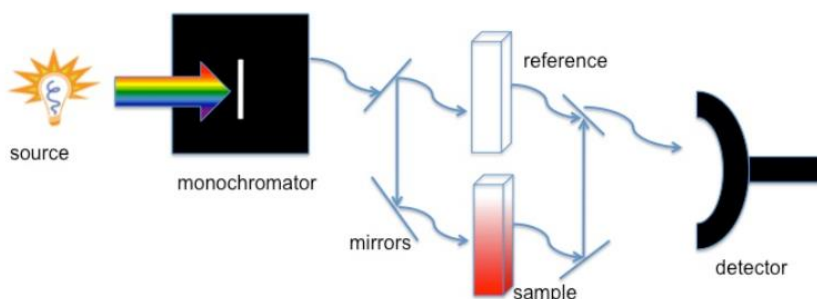source    monochromator    mirrors    reference    sample    detector

Figure 4.4.2 Illustration of a double beam UV-vis instrument.

A given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring. Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of ΔE, the molecule will specifically absorb radiation with wavelength that corresponds to ΔE, while allowing other wavelengths to pass through unabsorbed.
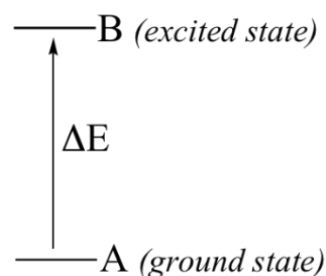
By observing which wavelengths, a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.
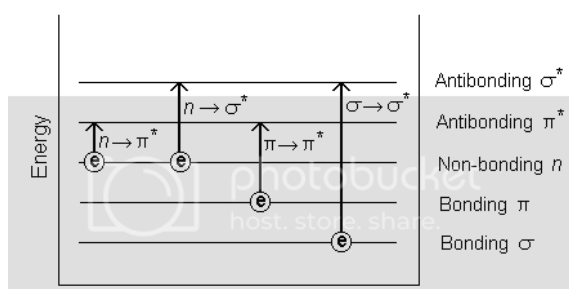


Various types of transitions

Figure-1

Visible or ultraviolet – is absorbed by valence (outer) electrons. These electrons are promoted from their normal (ground) states to higher energy (excited) states. The energies of the orbitals involved in electronic transitions have fixed values , and as energy is quantised, it would be expected that absorption peaks in ultraviolet/ visible spectroscopy should be sharp peaks.. The spectrum has broad peaks .This is because there are also vibrational and rotational energy levels available to absorbing materials. This results in peak broadening.
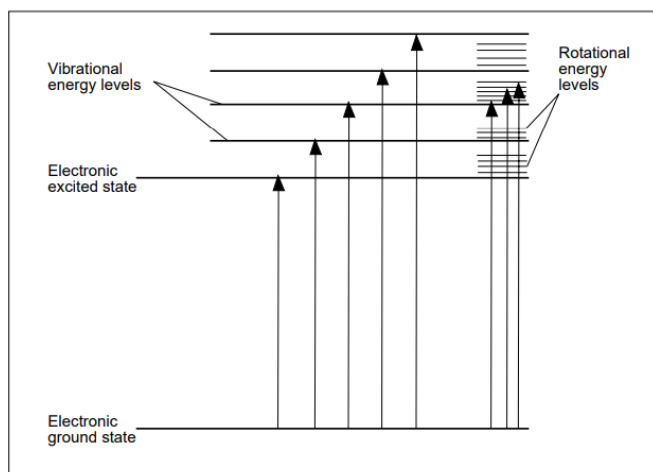


**Transition probability**
It is not essential that exposure of a compound to ultraviolet or visible light must always give rise to an electronic transition. The probability of a particular electronic transition has been found to depend upon the value of molar extinction coefficient and certain other factors. According transitions can be divided into two categories.

(i) Allowed transitions
(ii) Forbidden transitions

(i) **Allowed transitions** – these are transitions having molar coefficient 104 or more. These are generally designated as $\pi \to \pi^*$ transitions. For example, in 1,3-butadiene which exhibits absorption at 217nm has $\varepsilon$ value 21000 represents an allowed transition. These transitions are mainly favoured due to symmetry relationship. For e.g., 1,3- butadiene absorbs at 217nm and has molar absorptivity of 21000.

(ii) **Forbidden transitions** – these are transitions for which € is generally less than $10^4$. for example, transition of saturated aldehyde showing weak absorption near 290 nm and having $\varepsilon$ 100 has been a forbidden transition. For e.g., Carbonyl group absorbs at 300nm and has a molar absorptivity of 10-100.

## TRANSITIONS IN ULTRAVIOLET SPECTROSCCOPY
Electronic transitions in UV-visible spectroscopy which are important are
$n \to \pi^*$ & $\pi \to \pi^*$ transitions.

### a) σ → σ* transitions

A transition of an electron from bonding sigma orbital to higher energy antibonding sigma orbital is designated $\sigma \to \sigma^*$ transition in ultraviolet visible spectroscopy. In alkanes, there are only sigma bonds are available. Therefore, alkanes are showing this type of transition. In general, sigma bonds are very strong. Therefore, high energy is required for $\sigma \to \sigma^*$ transition. This transition is allowed by symmetry considerations

The ultraviolet radiation with wavelengths below 200 nm, named "vacuum UV" because it is strongly absorbed by the oxygen in air. Hence a vacuum apparatus is often used with the UV spectrophotometer.

Hence UV spectroscopy is not used for study of saturated compounds.

b) **$\pi \to \pi^*$ transitions** - This transition is available in compounds with unsaturated centres, e.g., simple alkenes, aromatics, carbonyl compounds, etc. The $\pi \to \pi^*$ transition shows absorption band around 170nm-190 nm in unconjugated alkenes. This transition is allowed by symmetry considerations and hence the probability of transitions is high. They tend to have molar absorptivities on the order of 10,000 and undergo a red shift with solvent interactions (a shift to lower energy and longer). The intensity of the band due to this transition is high.

c) **$n \to \pi^*$ transitions** - 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 the transitions and therefore, this transition gives rise to an absorption band at longer wavelengthsIn saturated aliphatic ketones, e.g., the $n \to \pi^*$ transitions around 280 nm is the lowest energy transitions. This $n \to \pi^*$ transition is "forbidden" by symmetry considerations, thus the intensity of the band due to this transition is low, although the wavelength is long (lower energy). They tend to have molar absorbtivities less than 2000.

## DESIGNATION OF BANDS

One may designate the UV absorption bands by using electronic transitions or the letter designation.

**K-** **Band**

The band due to $\pi \rightarrow \pi^*$ transitions in a compound with conjugated $\pi$ system is usually intense ($\varepsilon . > 10000$) and is frequently referred to as the k-band german- konjugierte). The examples of the compounds in which k-band appears are conjugated dienes trienes, enones and aromatic rings. Benzene itself displays three absorption bands at 184, 204 and 256nm and of these the band at 204nm is often designated as k-band.

**R-** **Band**

The $n \rightarrow \pi^*$ transition (R-band German radikalartig) in compounds with single chromatographic groups i.e., carbonyl or nitro are forbidden with € value less than 100. In $n \rightarrow \pi^*$ transition the energy separation between the ground and excited states is reduced. hence the system absorbs at longer wavelength. Due to the presence of the heteroatom and lone pair i.e. the R-band also undergoes a red shift with little change in intensity. Eg. Acetone, acrolein, methyl vinyl ketone, acetaldehyde, acetophenone, crotonaldehyde

**B-Band**

These bands are observed in aromatic compounds and hetero aromatic compounds. Here B refers to Benzenoid bands Eg. Benzene, toluene, acetophenone, benzoic acid, naphthalene, styrene. The band at 256 nm is often designated as B-band.

**E-Band** : ( Ethylenic bands ) due to oscillation of electrons in aromatic ring eg; benzene 184 nm E-Band

**DIFFERENT EFFECTS**

1**. Effect of solvent**

The transitions of polar bonds, like C=O but not ethylene, are affected by solvent polarity as solvent polarity is increased, $\pi \rightarrow \pi^*$ bands undergo red shifts. This is so since excited state is more polar than the ground state and hence stabilization is greater relative to the ground state with two n electrons receives greater stabilization than the excited state with only one n electron.

2. **Effect of conjugation**

Absorption in near UV that is above 200 nm is invariably associated with the presence of unsaturated groups or atoms with unshared pairs of electrons the saturated hydrocarbon which do not have these structural elements observe below 200nm reason, not of much significance for structural study of organic compounds.

As the number of conjugated pi bonds increases, the $\lambda_{max}$ also increases.

Because longer frequency = smaller energy, this means that the **energy gap $\Delta E$** between the highest-occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) **decreases** as the number of conjugated pi bonds **increases.**

| Ethene | Butadiene | Hexatriene |
|--------|-----------|------------|
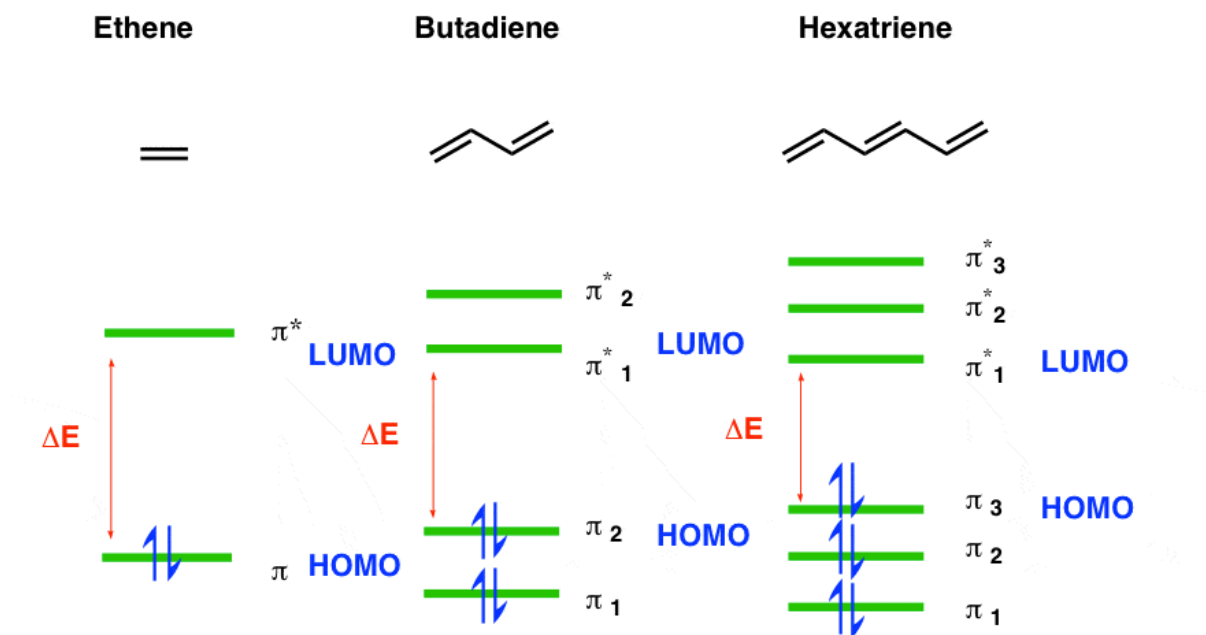


Note that the energy gap ΔE (HOMO-LUMO gap) **decreases**
(becomes smaller) as the number of conjugated pi orbitals increases

| Chromophore | Example | Excitation | $\lambda_{max}$, nm | ε | Solvent |
|-------------|---------|------------|---------------------|---|---------|
| C=C | Ethene | π → π* | 171 | 15,000 | hexane |
| C≡C | 1-Hexyne | π → π* | 180 | 10,000 | hexane hexane |
| C=O | Ethanal | n → π* <br> π → π* | 290 <br> 180 | 15 <br> 10,000 | hexane |
| N=O | Nitromethane | n → π* <br> π → π* | 275 <br> 200 | 17 <br> 5,000 | ethanol <br> ethanol |
| C-X X=Br, I | Methyl bromide <br> Methyl iodide | n → σ* <br> n → σ* | 205 <br> 255 | 200 <br> 360 | hexane <br> hexane |

**Applications of UV-Visible Spectroscopy**

1. **Detection of Impurities**

- It is one of the best methods for determination of impurities in organic molecules.
- Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
- By also measuring the absorbance at specific wavelength, the impurities can be detected.

2. **Structure elucidation of organic compounds**
- It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of unsaturation, the presence of hetero atoms.

3. UV absorption spectroscopy can be used for the **quantitative determination of compounds** that absorb UV radiation (by using Calibration curve method).

4. UV absorption spectroscopy can characterize those types of compounds which absorbs UV radiation thus used in qualitative determination of compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

5. Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

6. Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

7. Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

8. UV spectrophotometer may be used as a detector for HPLC.