(i) Optical Absorption Spectroscopy

UV-visible spectroscopy

This technique involves the absorption of near-UV or visible light.Absorption spectroscopy is employed to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present [3]. When organic compounds absorb UV or visible light,energy from the light is used to promote an electron from a bonding or non-bonding orbital into one of the empty anti-bonding orbitals. In each possible case, an electron is excited from a full orbital into an empty anti-bonding orbital. Each jump takes energy from the light, and a big jump needs more energy than a small one. Figure 4.1 showing the possible electron jumps that light may cause.

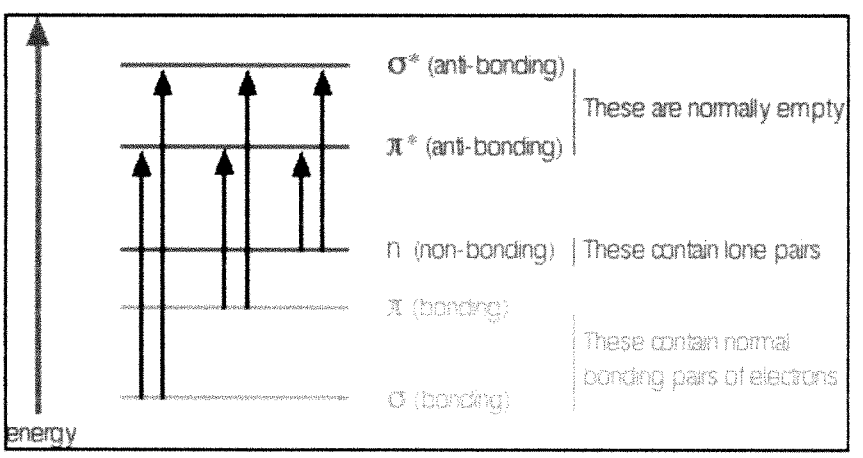

Figure 4.1 Possible electron jumps [http://www.chemguide.co.uk/analysis/uvvisible/theory.html]

Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making one of these energy jumps,

then that wavelength will be absorbed its energy will have been used in promoting an electron.

The relationship between the frequency of light absorbed and its energy

$$E=hv \tag{4.1}$$

Where, E is the energy of each quanta of light, h is the Planck's constant and v is the frequency of light. For higher energy jump, light of a higher frequency is to be absorbed.

UV-visible spectrophotometer measures both intensity and wavelength. It is usually applied to molecules and inorganic ions in solution.For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as I_o .The intensity of the light, I passing through the sample cell is also measured for that wavelength. If I is less than I_o, then obviously the sample has absorbed some of the light.

The Beer-Lambert Law gives, the relationship between A (the absorbance) and the two intensities is given by:

$$A=\log_{10}\frac{I_o}{I} \tag{4.2}$$

An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. An absorbance of 1 happens when 90% of the light at that wavelength has been absorbed that means that the intensity is 10%

of what it would otherwise be. A spectrophotometer can be either single beam or double beam.

Shown in the figure 4.2, a single beam UV-visible spectrophotometer.

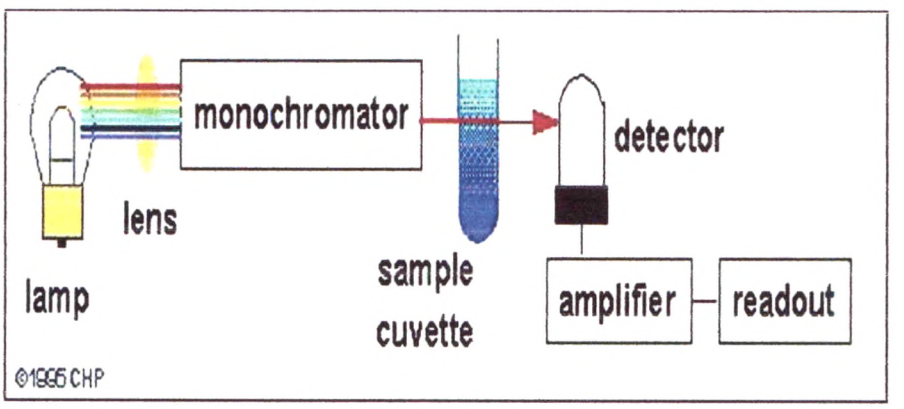

Figure 4.2 Schematic of single beam UV-visible Spectrophotometer [http://n elchem. kaist. ac kr/vt/chem-ed/spec/uv-vis/uv-vis.htm].

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament (300-2500 nm), a deuterium arc lamp, continuous over the ultraviolet region (190-400 nm), xenon arc lamps, continuous from 160-2,000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths [4]. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD).Single photodiode detectors and photomultiplier tubes are used with scanning monochromators, which filter the light so that only light of a single wavelength reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode

arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels or groups of pixels simultaneously.

In a single beam spectrophotometer the light passes through the sample cell. I_o must be measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time shown in figure 4.3. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

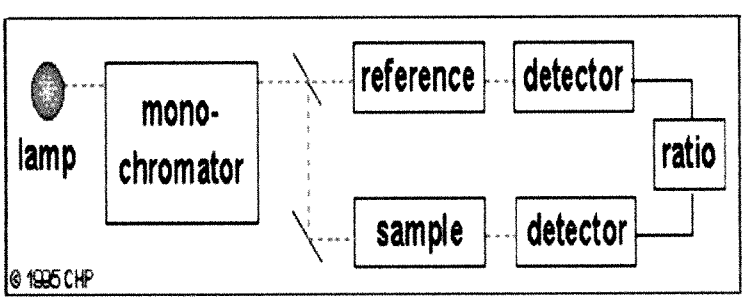

Figure 4.3 Schematic of a dual-beam UV-visible spectrophotometer[Available at http://www.files.chem.vt.edu/chem-ed/spec/uv-vis/dualbeam.html]

The Tauc's plot is used to determine optical bandgap. Tauc plot shows the quantity hv (the photon energy) on the abscissa and the quantity $(\alpha hv)^r$ on the ordinate, where α is the absorption coefficient of the material [5]. The value of the exponent r denotes the nature of the transition; for example, r = ½ for indirect transitions [5]. The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical bandgap of the material. However, if the material does not have a single phase, it will likely not have a single distinct absorption onset, which corresponds to a more gradually sloping curve in the Tauc's plot.

(ii) Photoluminescence Spectroscopy:

Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon.

If a light particle (photon) has an energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap. In this process of photoexcitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron energy eventually falls back down to the valence band. As this