

# INTRODUCTION TO SPECTROSCOPY

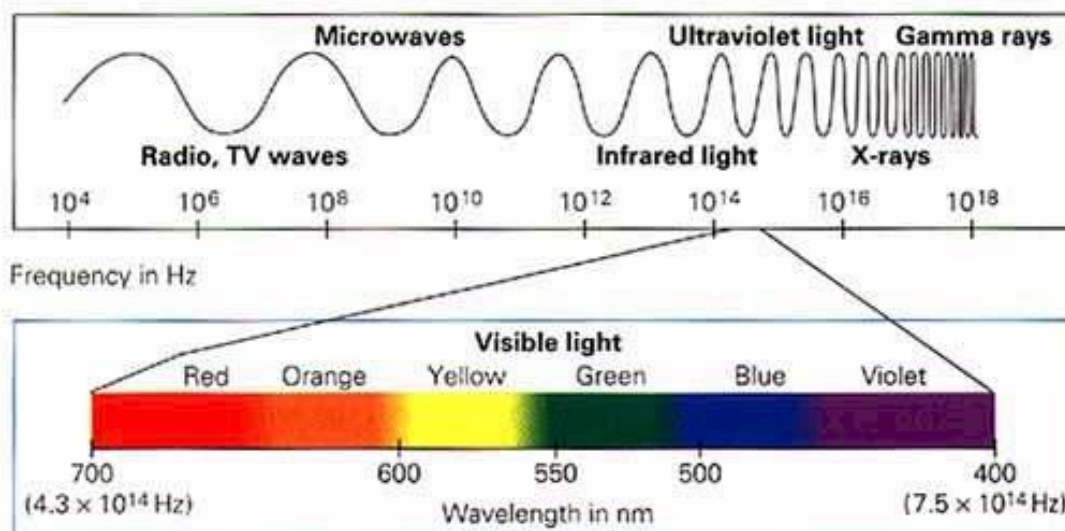
## I Spectroscopy and the Electromagnetic Spectrum

***Spectroscopy is the study of the interaction of matter and electromagnetic radiation.***

***Electromagnetic radiation is radiant energy having the properties of both particles and waves.*** An electromagnetic spectrum consists of a range of all different types of electromagnetic radiation—each type associated with a particular energy range.

***The arrangement of all types of electromagnetic radiations in order of their wavelength or frequencies is known as electromagnetic spectrum.***

Visible light is the type of electromagnetic radiation with which we are most familiar, but it represents only a fraction of the range of the entire electromagnetic spectrum. X-rays and radio waves are other types of familiar electromagnetic radiation.



The electromagnetic spectrum is made up of the following components: (High energy (Frequency) to low energy (Frequency)).

- ***Cosmic rays***, which consist of radiation discharged by the sun, have the highest energy, the highest frequencies, and the shortest wavelengths.

- **(gamma rays)** are emitted from the nuclei of certain radioactive elements and, because of their high energy, can severely damage biological organisms.
- **X-rays**, somewhat lower in energy than are less harmful, except in high doses. Low-dose X-rays are used to examine the internal structure of organisms. The denser the tissue, the more it blocks X-rays.
- **Ultraviolet (UV)** light is responsible for sunburns, and repeated exposure can cause skin cancer by damaging DNA molecules in skin cells.
- **Visible light** is the electromagnetic radiation we see.
- **Infra Red (IR)**. We feel infrared radiation as heat.
- **Micro waves**. We cook with microwaves and use them in radar.
- **Radio waves** have the lowest energy (lowest frequency). We use them for radio and television communication, digital imaging, remote controls, and wireless linkages for laptop computers. Radio waves are also used in NMR spectroscopy and in magnetic resonance imaging (MRI)

**II Both Particle and Wave nature:** A particle of electromagnetic radiation is called a photon. We may think of electromagnetic radiation as photons traveling at the speed of light. Because electromagnetic radiation has both particle-like and wave-like properties, it can be characterized by either its frequency or its wavelength

**III Frequency:** Frequency is defined as the number of wave crests that pass by a given point in one second. Frequency has units of hertz (Hz).

**IV Wavelength:** Wavelength is the distance between two successive crests or troughs. Wavelength is generally measured in micrometers or nanometers. One micrometer is  $10^{-6}$  of a meter; one nanometer (nm) is  $10^{-9}$  of a meter.

The frequency of electromagnetic radiation, therefore, is equal to the speed of light (c) divided by the radiation's wavelength:

$$v(\text{Neu}) = C/\lambda$$

So **wavelength has invers relation with frequency and energy**. Short wavelengths have high frequencies and high energy, and long wavelengths have low frequencies and low energy.

The relationship between the energy (E) of a photon and the frequency (or the wavelength) of the electromagnetic radiation is described by the equation

$$E = h\nu = hc/\lambda$$

where h is the proportionality constant called Planck's constant, named after the German physicist who discovered the relationship.

**V Wavenumber** is another way to describe the frequency of electromagnetic radiation, and the one most often used in infrared spectroscopy. ***It is the number of waves in one centimeter, so it has units of reciprocal centimeters.*** Scientists use wavenumbers in preference to wavelengths because, ***unlike wavelengths, wavenumbers are directly proportional to energy.*** The relationship between wavenumber and wavelength is given by the equation:

$$\bar{\nu} \quad (\text{cm}^{-1}) = 1/\lambda$$

So high frequencies, large wavenumbers, and short wavelengths are associated with high energy.

## **VI Absorption and Emission Spectra**

### **VIA Absorption Spectra:**

When electromagnetic radiations are passed through an organic compound, these induce electronic, vibrational and rotational transitions in the molecule. The energy required for each of these transitions is quantized.

Thus only the radiation supplying the required quantum (Photon) of energy is absorbed and the remaining portion of the incident radiation is transmitted. The wavelength or the frequencies of the absorbed radiations are measured with the help of spectrophotometer. Generally a spectrometer records an absorption spectrum as a plot of intensity versus their wave length or frequency. Such spectra which are obtained by absorption of electromagnetic radiations are called as absorption spectra. UV, Visible, IR and NMR all are examples of absorption spectra. Absorption band in absorption spectrum can be characterized by the wave length at which max absorption occurs.

## **VIB Emission spectra**

The spectra which are obtained by the emission of electromagnetic radiations from the excited substances are known as **Emission spectra**, like atomic emission spectra. The excitation is caused by heating the substance to a high temperature either thermally or electrically. The excited substance emits certain radiations when it comes to the ground state and a spectrometer records these radiations as an emission spectrum.

# CHAPTER NO. 1 UV & VISIBLE SPECTROSCOPY

## 1. UV and visible spectroscopy

**UV and visible spectroscopy deals with the recording of the absorption of radiations in the ultraviolet visible regions of the electromagnetic spectrum.**

Ultraviolet light (10-400 nm) and visible light (400-800 nm) have just the right energy to cause an electronic transition—the promotion of an electron from one orbital of lower energy to another of higher energy. ***Due to these electronic transitions, this spectroscopy is usually termed as electronic spectroscopy.***

### 1.1 Vacuum UV Region:

The UV region below 200 nm cannot be used by conventional UV spectrophotometer because oxygen (200-150 nm) and nitrogen (below 150 nm) absorb strongly in this region. However, by creating a vacuum, it is possible to study the whole range of UV below 200 nm. That's why the region below 200nm is called vacuum Ultraviolet Region. However, this requires a special spectrophotometer with special conditions, so we are only confined to 200-400 nm in daily routine.

Depending on the energy needed for the electronic transition, a molecule will absorb either ultraviolet or visible light. If it absorbs ultraviolet light, a UV spectrum is obtained; if it absorbs visible light, a visible spectrum is obtained. Wavelength is inversely related to the energy: The shorter the wavelength, the greater is the energy. ***Ultraviolet light, therefore, has greater energy than visible light.***

### 1.2 Absorption of radiation and electronic transitions

The normal electronic configuration of a molecule is known as its **ground state** and all the electrons are in the lowest-energy molecular orbitals. When a molecule absorbs light of an appropriate wavelength and an electron is promoted

to a higher energy molecular orbital, the molecule is then in an **excited state**. Thus, an **electronic transition is the promotion of an electron to a higher energy MO**.

The electromagnetic radiation that is absorbed has energy exactly equal to the energy difference between the excited and the ground state. Similarly, when a molecule absorbs UV/visible radiation, its valency electrons are excited from ground state (highest occupied molecular orbital (HOMO) to higher energy state (Lowest Unoccupied Molecular Orbital (LUMO)). The wavelength of absorbed radiation depends upon the energy difference between ground state orbital and excited state orbital.

***A difference of more than about 4 eV (about  $7 \times 10^{-19}$  J) between HOMO and LUMO means that  $\lambda_{max}$  will be in the ultraviolet region (wavelength,  $\lambda$ , < 300 nm). If the energy difference is between about 3 eV (about  $4 \times 10^{-19}$  J) and 1.5 eV (about  $3 \times 10^{-19}$  J) then  $\lambda_{max}$  will be in the visible part of the spectrum.***

### **1.3 Absorption of radiation and electronic transitions**

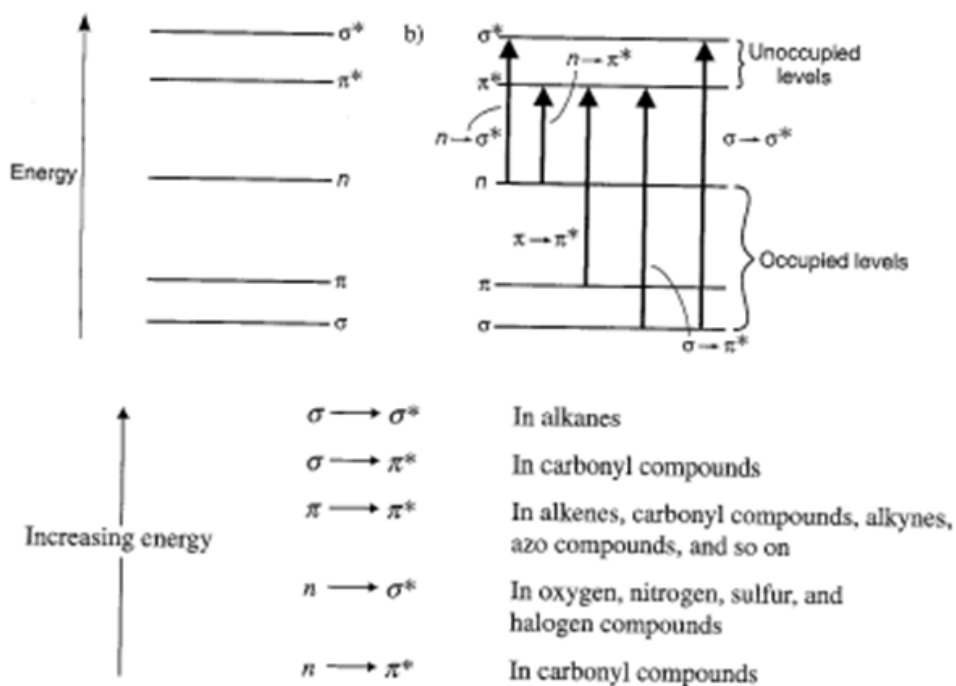
When continuous radiation passes through a transparent material, a portion of the radiation may be absorbed. If that occurs, the residual radiation, when it is passed through a prism, yields a spectrum with gaps in it, called an absorption spectrum. As a result of energy absorption, atoms or molecules pass from a state of low energy (the initial, or ground state) to a state of higher energy (the excited state). This excitation process must be quantized.

Electrons can be promoted from any filled orbital to any empty orbital. The smallest energy difference between a full and empty molecular orbital is between the HOMO and the LUMO. The smaller this difference, the less energy will be needed to promote an electron from the HOMO to the LUMO: the smaller the amount of energy needed, the longer the wavelength of light needed since  $\Delta E = h\nu$ . Therefore, an important measurement is the wavelength at which a compound shows maximum absorbance,  $\lambda_{max}$ . ***A difference of more than about 4 eV (about  $7 \times 10^{-19}$  J) between HOMO and LUMO means that  $\lambda_{max}$***

*will be in the ultraviolet region (wavelength,  $\lambda$ , < 300 nm). If the energy difference is between about 3 eV (about  $4 \times 10^{-19}$  J) and 1.5 eV (about  $3 \times 10^{-19}$  J) then  $\lambda_{max}$  will be in the visible part of the spectrum.*

### 1.4 Types of Electronic Transitions:

There are four types of electronic transitions which are associated with the absorption of UV/Visible radiations from a bonding or non-bonding orbital to anti bonding orbital. There are  $\delta$  and  $\pi$  bonding orbitals having  $\delta^*$  and  $\pi^*$  antibonding orbitals respectively. Non-bonding (n) orbitals are not associated with any antibonding orbitals because lone pair electrons in non bonding orbitals do not make bonds.



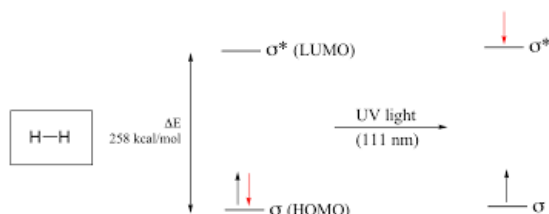
Following four types of transitions are involved in UV-Visible spectroscopy.

- 1)  $\delta \rightarrow \delta^*$  (sigma to sigma star)
- 2)  $n \rightarrow \delta^*$  (nonbonding to sigma star)
- 3)  $\pi \rightarrow \pi^*$  and last

4)  $n-\pi^*$ .

#### 1.4.1) $\delta-\delta^*$ (sigma to sigma star) Transition

The transition or promotion of an electron from bonding sigma orbital to the associated non-bonding sigma star orbital is called as  **$\delta-\delta^*$  (sigma to sigma star) Transition**. This transition occurs in saturated hydrocarbons, such as  $\text{CH}_3-\text{CH}_3$  (135 nm) which contain only sigma bonds. This transition requires high energy due to large distance between  $\delta$  and  $\delta^*$ . Due to this reason this transition takes place at shorter wave length (less than 150 nm) which falls in vacuum UV region. So, this transition is not useful for routine UV/Visible spectroscopy. It means that UV-Visible spectroscopy is not very informative for alkanes.



#### 1.4.2 $n-\delta^*$ (nonbonding to sigma star)

Second transition  $n-\delta^*$  occur in saturated molecules containing heteroatoms, such as oxygen, nitrogen, sulphur and halogens for example  $\text{CH}_3\text{OH}$ . This transition also requires high energy (shorter wavelength) as it involves the excitation of electrons from nonbonding  $n$  orbital of heteroatom to antibonding sigma electron of the molecule. Energy required for this transition is less than  $\delta-\delta^*$  transition, still it is large enough to occur in vacuum UV region and are not commonly useful in routine spectroscopy. Some organic compounds undergoing this transition are halides, alcohols, ethers, aldehydes, ketones etc. e.g.,  $\text{CH}_3\text{Cl}$  173 nm,  $\text{CH}_3\text{I}$  258,  $\text{CH}_3\text{OH}$  183 water 167.

In alkyl halides, the energy required for  **$n-\delta^*$**  transition increases, wave length decreases as the electronegativity of the halogen is increased, because it increases the excitation of the non-bonding electrons. Similarly, amines show excitation at higher wave length than alcohols due to Nitrogen having less electronegativity than oxygen. e.g., trimethyl amine show max at 227 nm while



methyl alcohol at 183 nm. Protonated trimethyl amine does not show any absorbance due to  $n-\delta^*$  transition because it has no non bonded electrons.

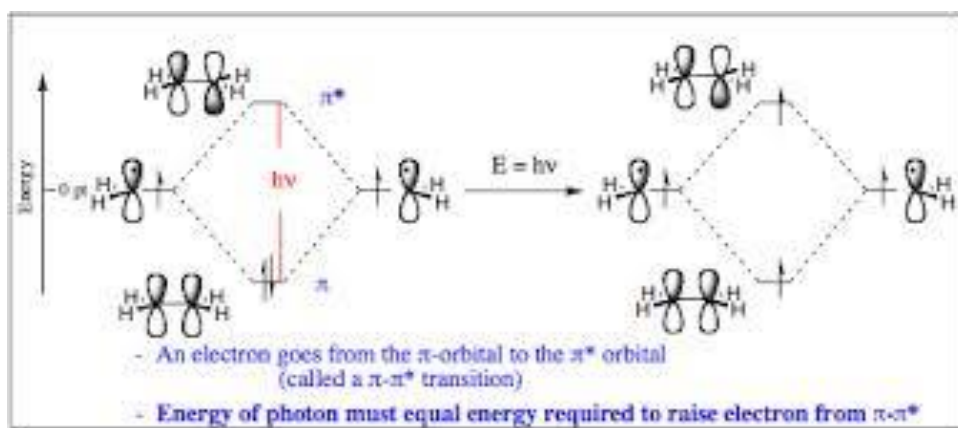
This transition is also less informative and less useful.

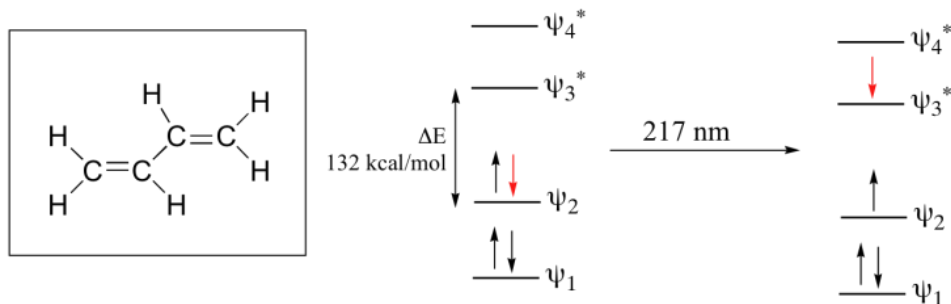
### 1.4.3. $\pi-\pi^*$ transition

Remaining these two transitions are more useful for practical purposes.  $\pi-\pi^*$  transition occur in molecules containing double and triple bonds or aromatic rings. This type of transition is common in compounds having one or more covalently unsaturated group like C=C, C=O, NO<sub>2</sub> etc. **This involves the transition of an electron from (pi)  $\pi$  orbital to  $\pi^*$  (pi star) orbital.**

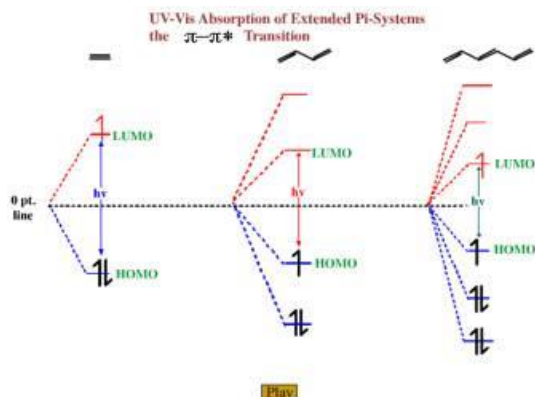
These transitions require less energy than above two transitions and generally absorb at longer wave length 160-190 nm range.

**However, a conjugated system of unsaturated bonds absorbs at much longer wave length, for example butadiene absorbs at 215 nm.** Reason is that the energy difference between the HOMO and LUMO for butadiene is less than that for ethene. Therefore, we would expect butadiene to absorb at a longer wavelength than ethene (the longer the wavelength the lower the energy,  $\Delta E = hc/\lambda$ ). This is found to be the case: butadiene absorbs at 215 nm compared to 185 nm for ethene.

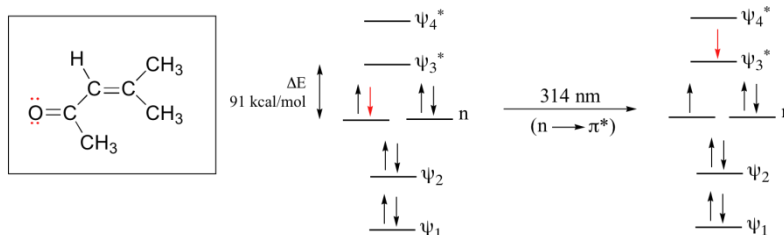




It means that the more conjugated a compound is, the smaller the energy transition between its HOMO and LUMO and hence the longer the wavelength of light it can absorb. Hence UV-visible spectroscopy can tell us about the conjugation present in a molecule. The conjugation in butadiene means it absorbs light of a longer wavelength than ethene.



Still low energy (longer wave length) transitions occur in molecules that contain double or triple bonds involving hetero atom, e.g., C=O, C=N, etc. In this case excitation can take place from nonbonding atomic orbital of a hetero atom to antibonding pi star orbital of double or triple bond. This transition occurs at the longest wave lengths as it requires least energy due to less distance between orbitals. For example saturated aldehydes and ketones show absorption at 275-295 nm. These transitions are most useful for analysis. This means that only organic compounds with Pi electrons are most useful for UV Vis spectra.

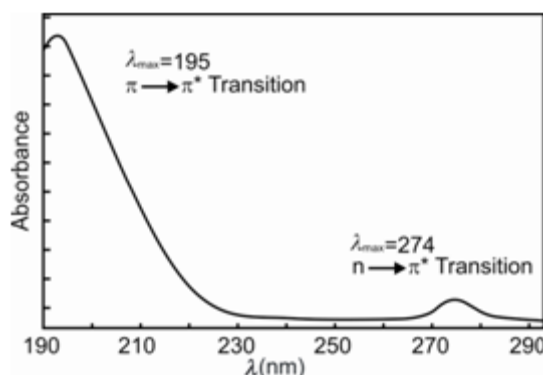


#### 1.4.4 Forbidden transitions:

Not all of the transitions that at first sight appear possible are observed. Certain restrictions, called **selection rules**, must be considered. One important selection rule states that transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place; they are called “**forbidden**” transitions. Other selection rules deal with other factors that need not to be discussed here. Transitions that are formally forbidden by the selection rules are observed, However, their intensity of the absorption is much lower than the allowed transitions. The  $n$  to  $\pi^*$  transition is the most common type of forbidden transition.

#### 1.4.5 The UV spectrum of acetone

Acetone has both electrons and lone-pair electrons. Thus, there are two absorption bands: one for the  $\pi:\pi^*$  transition and one for the  $n:\pi^*$  transition. The  $\lambda_{\max}$  (stated as “lambda max”) is the wavelength corresponding to the highest point (maximum absorbance) of the absorption band. For the  $\pi-\pi^*$  transition  $\lambda_{\max}$  is 195 nm, for  $n-\pi^*$  transition  $\lambda_{\max}$  is 274 nm. AS we know that the transition corresponds to  $\pi-\pi^*$  is at the shorter wavelength because that transition requires more energy than the transition from  $n-\pi^*$ .



## 1.5 INSTRUMENTATION

The typical ultraviolet-visible spectrophotometer consists of a light source, a monochromator, and a detector.

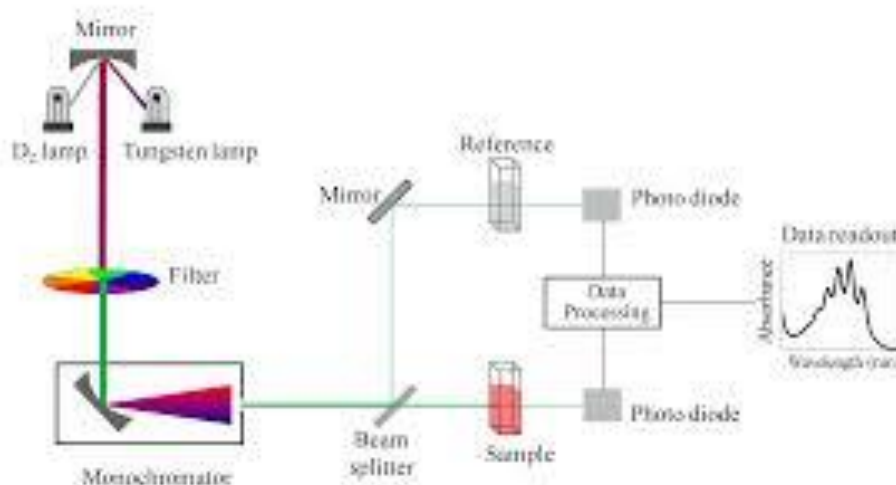
1-The light source can be two types.

1.1-For Ultraviolet radiation, usually a deuterium lamp is used.

1.2- For radiation in visible region of spectrum, a second light source, tungsten lamp is used.

2-The monochromator spread the beam of light into its component wavelengths. A system of slits then focuses the desired wavelength on the sample cell. The light that passes through the sample cell reaches the detector, which records the intensity of the transmitted light  $I$ .

3- The detector is generally a photomultiplier tube, although in modern instruments photodiodes are also used.



4- In a typical double-beam instrument, the light emitting from the light source is split into two beams, the sample beam and the reference beam. When there is no sample cell in the reference beam, the detected light is taken to be equal to the intensity of light entering the sample  $I_0$ .

5- The sample cell must be constructed of a material that is transparent to the electromagnetic radiation being used in the experiment. For spectra in the **visible range of the spectrum**, cells composed of glass or plastic are generally

suitable. For measurements in the **ultraviolet region of the spectrum**, however, **glass and plastic cannot be used** because they absorb ultraviolet radiation. Instead, cells made **of quartz must be used since** quartz does not absorb radiation in this region. The instrument design just described is quite suitable for measurement at only one wavelength.

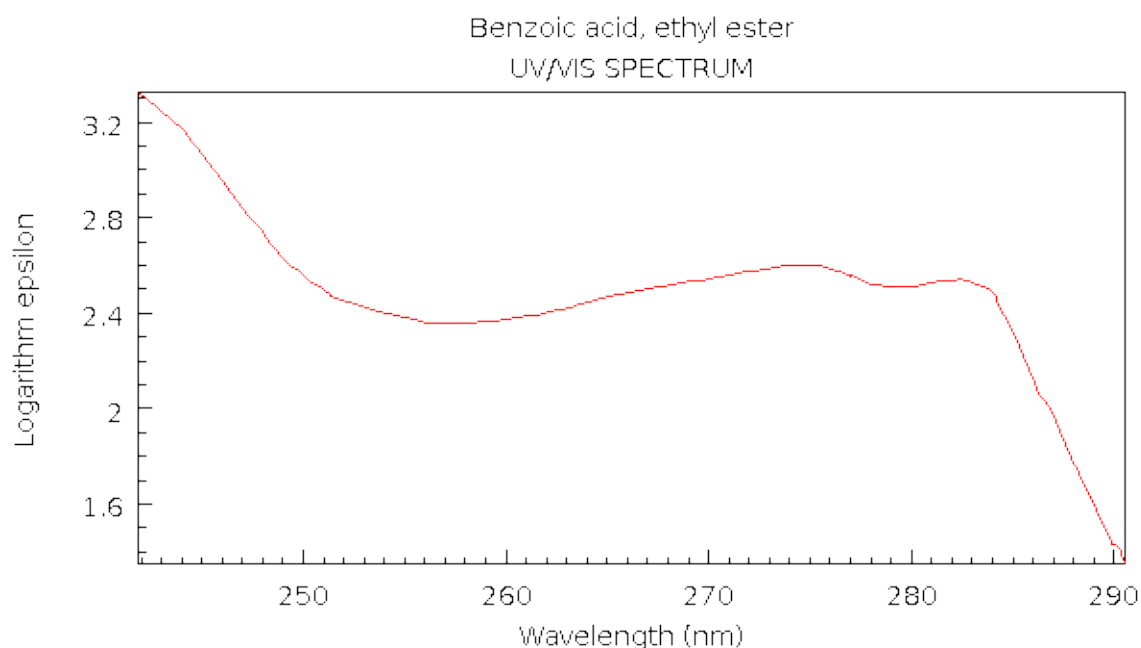
**6-** If a complete spectrum is desired, this type of instrument has some deficiencies. A mechanical system is required to rotate the monochromator and provide a scan of all desired wavelengths. This type of system operates slowly, and therefore considerable time is required to record a spectrum.

***A modern improvement on the traditional spectrophotometer is the diode-array spectrophotometer. A diode array consists of a series of photodiode detectors positioned side by side on a silicon crystal. Each diode is designed to record a narrow band of the spectrum. The diodes are connected so that the entire spectrum is recorded at once. This type of detector has no moving parts and can record spectra very quickly. Furthermore, its output can be passed to a computer, which can process the information and provide a variety of useful output formats. Since the number of photodiodes is limited, the speed and convenience described here are obtained at some small cost in resolution. For many applications, however, the advantages of this type of instrument outweigh the loss of resolution.***

## **1.6 PRESENTATION OF SPECTRA**

**The ultraviolet-visible spectrum is generally recorded as a plot of absorbance versus wavelength.** It is customary to then replot the data with either  **$\epsilon$  or  $\log \epsilon$  plotted on the y-axis** and **wavelength plotted on the x-axis.** Figure below, the spectrum of benzoic acid, is typical of the manner in which spectra are displayed. However, very few electronic spectra are reproduced in the scientific literature; most are described by indications of the wavelength maxima

and absorptivity of the principal absorption peaks. For benzoic acid, a typical description might be



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

$\lambda_{\text{max}} =$	230 nm	$\log \epsilon = 4.2$
	272	3.1
	282	2.9

## 1.7 The Beer–Lambert Law

Wilhelm Beer and Johann Lambert independently proposed that *at a given wavelength, the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a solution of the sample.* In other words, **absorbance depends on both the concentration of the sample and the length of the light path through the sample. The relationship among absorbance, concentration, and length of the light path is known as the Beer–Lambert law and is given by**

$$A = c l \epsilon$$

Where

**$A =$  Absorbance of the sample  $= \log I_0/I$**

**$\epsilon =$  molar absorptivity (liter mol<sup>-1</sup> cm<sup>-1</sup>)**

**$l =$  length of the light path through the sample, in centimeters**

***c*** = concentration of the sample, in moles/liter

***I*** = intensity of the radiation emerging from the sample

***I*<sub>0</sub>** = intensity of the radiation entering the sample

**The molar absorptivity (formerly called the extinction coefficient)** of a compound is a constant that is characteristic of the compound at a particular wavelength. **It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00-cm path length.** The molar absorptivity of acetone, for example, is 9000 at 195 nm and 13.6 at 274nm.

1-**The solvent** in which the sample is dissolved when the spectrum is taken is reported because molar absorptivity is not exactly the same in all solvents. So the UV spectrum of acetone in hexane would be reported as 195 nm (hexane); 274 nm (hexane).

2-**Because absorbance is proportional to concentration**, the concentration of a solution can be determined if the absorbance and molar absorptivity at a particular wavelength are known.

## **1.8 THE ORIGIN OF UV BAND STRUCTURE**

For an **atom** that absorbs in the ultraviolet, the absorption spectrum sometimes consists of **very sharp lines**, as would be expected for a quantized process occurring between two discrete energy levels. **For molecules**, however, the UV absorption usually occurs **over a wide range of wavelengths** because molecules (as opposed to atoms) normally have many excited modes of vibration and rotation at room temperature. In fact, the vibration of molecules cannot be completely “frozen out” even at absolute zero. Consequently, a collection of molecules generally has its members in many states of vibrational and rotational excitation. The energy levels for these states are quite closely spaced, corresponding to energy differences considerably smaller than those of electronic levels. **The rotational and vibrational levels are thus “superimposed” on the electronic levels. A molecule may therefore undergo electronic and**

**vibrational-rotational excitation simultaneously, as shown in Figure 7.3.** Because there are so many possible transitions, each differing from the others by only a slight amount, each electronic transition consists of a vast number of lines spaced so closely that the spectrophotometer cannot resolve them. **Rather, the instrument traces an “envelope” over the entire pattern.** What is observed from these types of combined transitions is that the UV spectrum of a molecule usually consists of a broad band of absorption centered near the wavelength of the major transition.

## 1.9 SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important.

1-The first criterion for a good solvent is that it **should not absorb ultraviolet radiation in the same region as the substance** whose spectrum is being determined. *Usually solvents that do not contain conjugated systems are most suitable for this purpose,* although they vary regarding the shortest wavelength at which they remain transparent to ultraviolet radiation. Some of the important solvents like **water, 95% ethanol, and hexane are most commonly** used. Each is transparent in the regions of the ultraviolet spectrum in which interesting absorption peaks from sample molecules are likely to occur.

2-A second criterion for a good solvent is its **effect on the fine structure of an absorption band.** Figure 7.5 illustrates the effects of polar and nonpolar solvents on an absorption band. **A non-polar solvent does not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, in which fine structure is often observed.**

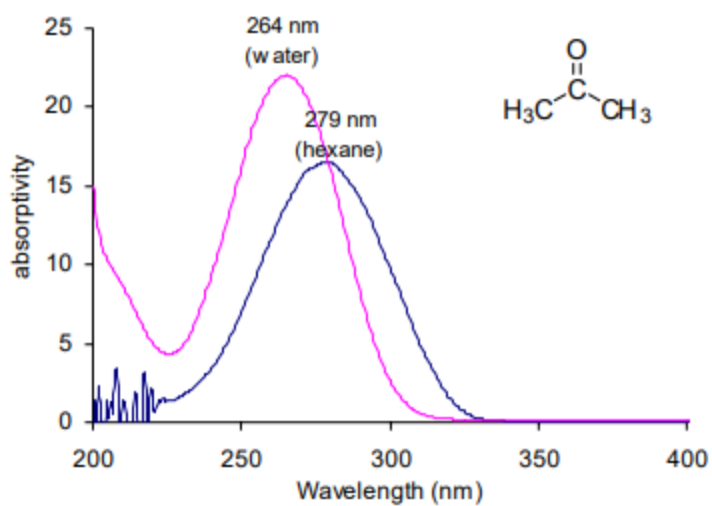
**In a polar solvent, the hydrogen bonding forms a solute-solvent complex, and the fine structure may disappear.**



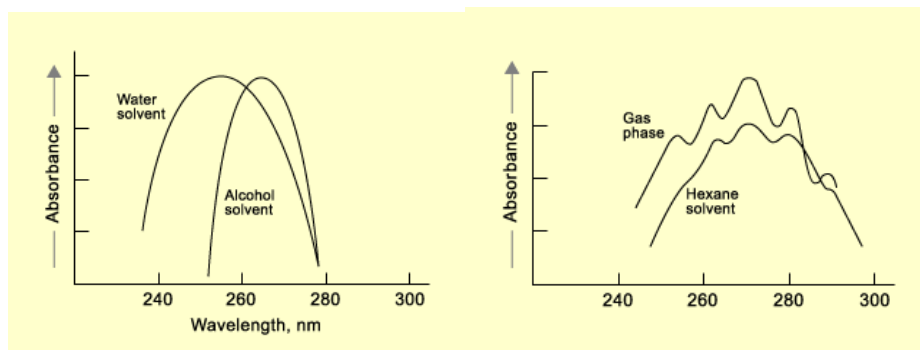
3-A third criterion for a good solvent is its ability to influence the wavelength of ultraviolet light that will be absorbed via stabilization of either the ground or the excited state.

In case of  $\pi - \pi^*$  transitions, the excited states are more polar than the ground state and the polar solvent molecules make bond with excited states and lower the energy of the excited state more than that of the ground state. Therefore, a polar solvent decreases the energy of  $\pi - \pi^*$  transition and absorption maximum appears  $\sim 10-20$  nm red shifted in going from hexane to ethanol solvent.

In case of  $n - \pi^*$  transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. For example, the figure 5 shows that the absorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.



*Figure 5 : UV-spectra of acetone in hexane and in water*



## 1.10 Chromophore

***A chromophore is that part of a molecule that absorbs UV or visible light.***

The carbonyl group is the chromophore of acetone.

1-Although the absorption of ultraviolet radiation results from the excitation of electrons from ground to excited states, the **nuclei that the electrons hold together in bonds play an important role** in determining which wavelengths of radiation are absorbed. The **nuclei** determine the strength with which the electrons are bound and thus **influence the energy spacing between ground and excited states**. Hence, the characteristic energy of a transition and the wavelength of radiation absorbed depend upon the properties of a group of atoms rather than of electrons themselves. **The group of atoms producing such an absorption is called a chromophore.**

2-As structural changes occur in a chromophore, the exact energy and intensity of the absorption are expected to change accordingly. Very often, it is extremely difficult to predict from theory how the absorption will change as the structure of the chromophore is modified, and it is necessary to apply empirical working guides to predict such relationships.

**Alkanes.** For molecules, such as alkanes, that have only single bonds and no hetero atom with no lone pairs of electrons, the only electronic transitions possible are of the  $\delta - \delta^*$  type. These transitions are of such a high energy that they absorb ultraviolet energy at very short wavelengths—shorter than the wavelengths that are experimentally accessible using typical spectrophotometers.

**Alcohols, Ethers, Amines and Sulfur Compounds.** In saturated molecules that contain hetero atoms bearing nonbonding pairs of electrons, transitions of the  $n - \delta^*$  type become important. They are also rather high-energy transitions, but they do absorb radiation that lies within an experimentally accessible range. Alcohols and amines absorb in the range from 175 to 200 nm, **while organic thiols and sulfides absorb between 200 and 220 nm**. Most of the absorptions

are below the cutoff points for the common solvents, so they are not observed in solution spectra.

**Alkenes and Alkynes.** With unsaturated molecules,  $\pi$ - $\pi^*$  transitions become possible. These transitions are of rather high energy as well, but their positions are sensitive to the presence of substitution, as will be clear later. Alkenes absorb around 175 nm, and alkynes absorb around 170 nm.

**Carbonyl Compounds.** Unsaturated molecules that contain atoms such as oxygen or nitrogen may also undergo  $n$ - $\pi^*$  transitions. **These are perhaps the most interesting and most studied transitions**, particularly among carbonyl compounds. These transitions are also rather sensitive to substitution on the chromophoric structure. The typical carbonyl compound undergoes an  $n$ - $\pi^*$  transition around 280 to 290 nm ( $\epsilon = 15$ ). Most  $n$ - $\pi^*$  transitions are forbidden and hence are of low intensity. Carbonyl compounds also have a  $\pi$ - $\pi^*$  transition at about 188 nm ( $\epsilon = 900$ ).

### **1.11 (Auxochromes) Attachment of substituent groups:**

Simple chromophores nearly all absorb at approximately the same wavelength (160 to 210 nm). **The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position and intensity of an absorption band of the chromophore.** The substituent groups may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal chromophore. **Substituents that change the intensity of the absorption, and possibly the wavelength, are called auxochromes.** Typical auxochromes include methyl, hydroxyl, alkoxy, halogen, and amino groups.

**Other substituents may have any of four kinds of effects on the absorption:**

1. Bathochromic shift (red shift)—a shift to lower energy or longer wavelength.
2. Hypsochromic shift (blue shift)—a shift to higher energy or shorter wavelength.
3. Hyperchromic effect—an increase in intensity.
4. Hypochromic effect—a decrease in intensity.

## 1.12 Complimentary Colour

If a compound appears yellow, it means it absorbs all the radiation from a white light except yellow. Similarly, a blue body absorbs all radiations of white light and reflects blue so it looks blue. **This reflected colour is called complimentary colour of the absorbed colour.** So, it can be said that no colour is absorbed by a white body. Similarly, no light is reflected by a black body. So, it means a compound looks coloured because it absorbs certain radiations from the UV/Visible region and reflects the remaining.

***Saturate hydrocarbons only absorb in Vacuum UV region so they appear transparent in UV/Visible region so they are used solvents in for practical studies. Saturated compounds containing heteroatoms involve  $n\text{-}\pi^*$  transitions and mostly appear in vacuum UV region. So, they also can be used as a solvent.***

***All the compounds having chromophore groups in their molecules generally contain  $\pi$  electrons and some of them contain nonbonding electrons.***

## 1.13 THE EFFECT OF CONJUGATION

One of the best ways to bring about a **bathochromic shift is to increase the extent of conjugation in a double-bonded system.** In the presence of conjugated double bonds, the electronic energy levels of a chromophore move closer together. As a result, the energy required to produce a transition from an occupied electronic energy level to an unoccupied level decreases, and the wavelength of the light absorbed becomes longer.

**Conjugation of two chromophores not only results in a bathochromic shift but increases the intensity of the absorption.** These two effects are of prime importance in the use and interpretation of electronic spectra of organic molecules because conjugation shifts the selective light absorption of isolated chromophores from a region of the spectrum that is not readily accessible to a region that is easily studied with commercially available spectrophotometers.

The exact position and intensity of the absorption band of the conjugated system can be correlated with the extent of conjugation in the system.

### 1.14 AROMATIC COMPOUNDS

The ultraviolet spectrum of benzene **contains three absorption bands**, which sometimes contain a great deal of fine structure. The electronic transitions are basically of the **pi-pi\*** type, but their details are not as simple as in other compounds. Figure 7.17a shows the molecular orbitals of benzene.

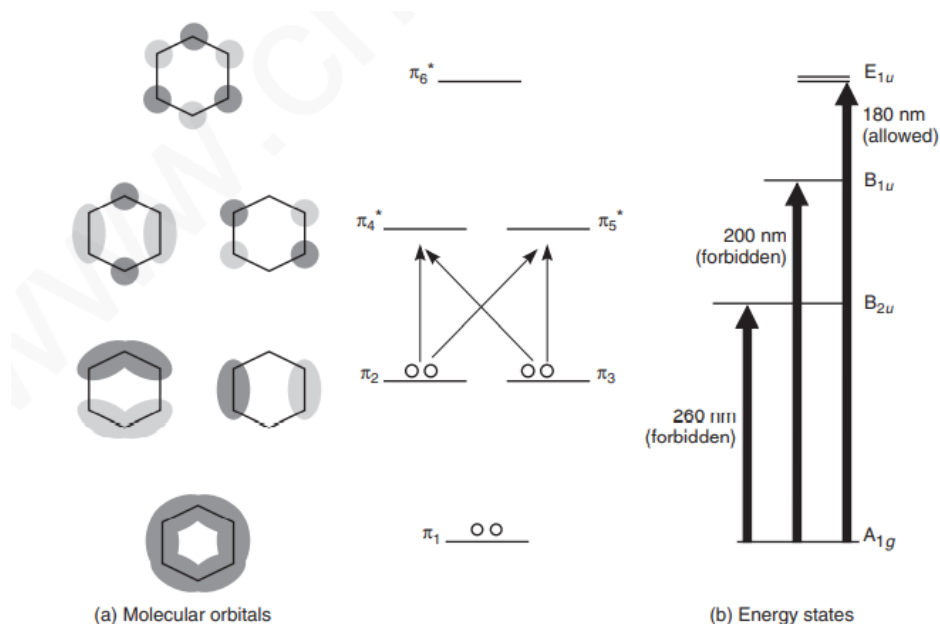
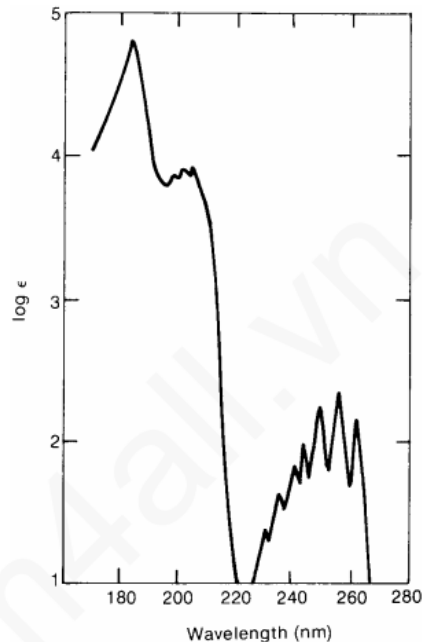


FIGURE 7.17 Molecular orbitals and energy states for benzene.

Figure 7.17b shows the energy-state levels of benzene. Three electronic transitions take place to these excited states. Those transitions, which are indicated in Figure 7.17b, are the so-called primary bands at 184 and 202 nm and the secondary (fine-structure) band at 255 nm. Figure 7.18 is the spectrum of benzene.



**FIGURE 7.18** Ultraviolet spectrum of benzene.  
 (From Petruska, J., *Journal of Chemical Physics*, 34  
 (1961): 1121. Reprinted by permission.)

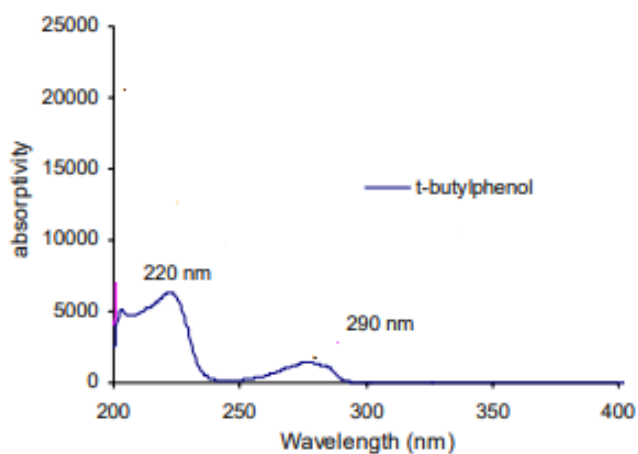
Of the primary bands, the **184-nm band (the second primary band)** has a molar absorptivity of 47,000. It is an allowed transition. Nevertheless, ***this transition is not observed under usual experimental conditions because absorptions at this wavelength are in the vacuum ultraviolet region of the spectrum, beyond the range of most commercial instruments.***

In polycyclic aromatic compounds, the second primary band is often shifted to longer wavelengths, in which case it can be observed under ordinary conditions. **The 202-nm band (primary band) is much less intense ( $\epsilon = 7400$ ), and it corresponds to a forbidden transition.**

The secondary band is the least intense of the benzene bands ( $\epsilon = 230$ ). It also corresponds to a symmetry-forbidden electronic transition. The secondary band, appears with a great deal of fine structure. **This fine structure is lost if the spectrum of benzene is determined in a polar solvent or if a single functional group is substituted onto the benzene ring.** In such cases, the secondary band appears as a broad peak, lacking in any interesting detail. Substitution on the benzene ring can cause bathochromic and hyperchromic shifts. Unfortunately, these shifts are difficult to predict. Consequently, it is

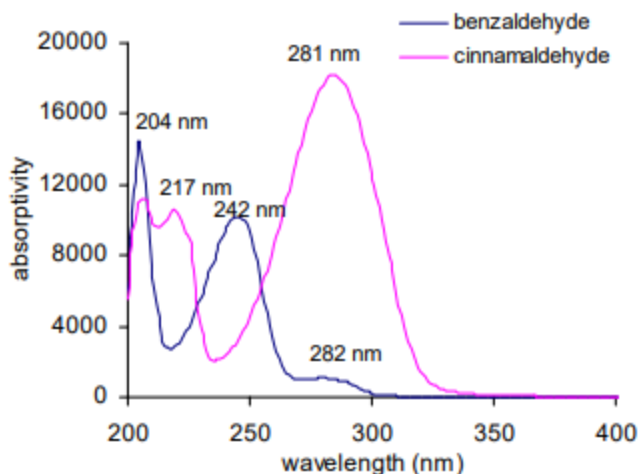
impossible to formulate empirical rules to predict the spectra of aromatic substances as was done for dienes, enones, and the other classes of compounds.

**1.14.1 Effect of Substituents with Unshared Electrons:** The non-bonding electrons shift the primary and secondary absorption bands to longer wavelength. E.g., In going from benzene to t-butylphenol, the primary absorption band at 203.5 nm shifts to 220 nm and secondary absorption band at 254 nm shifts to 275 nm. Both bands show hyperchromic effect.



**Figure 8 :** UV-spectra of t-butyl phenol

**1.14.2 Effect of  $\pi$  Conjugation:** Conjugation of the benzene ring also shifts the primary band at 203.5 nm more effectively to longer wavelength and secondary band at 254 nm is shifted to longer wavelength to lesser extent. In some cases, the primary band overtakes the secondary band. For example, benzoic acid shows primary band at 250 nm and secondary band at 273 nm, but cinnamic acid that has longer chromophore exhibits primary band at 273 nm and secondary band remains merged with it. (figure 10). The hyperchromic effect arising due to extended conjugation is also visible.



**Figure 10** : UV-spectra of benzaldehyde and cinnamaldehyde in methanol

### 1.14.3 Effect of Electron-withdrawing and Electron-releasing Groups:

**Electron-withdrawing substituents** viz.  $\text{NH}_3^+$ ,  $\text{SO}_2\text{NH}_2$ ,  $\text{CN}$ ,  $\text{COOH}$ ,  $\text{COCH}_3$ ,  $\text{CHO}$  and  $\text{NO}_2$  etc. have **no effect** on the position of secondary absorption band of benzene ring. But their conjugation effects with  $\pi$  electrons of the aromatic ring are observed.

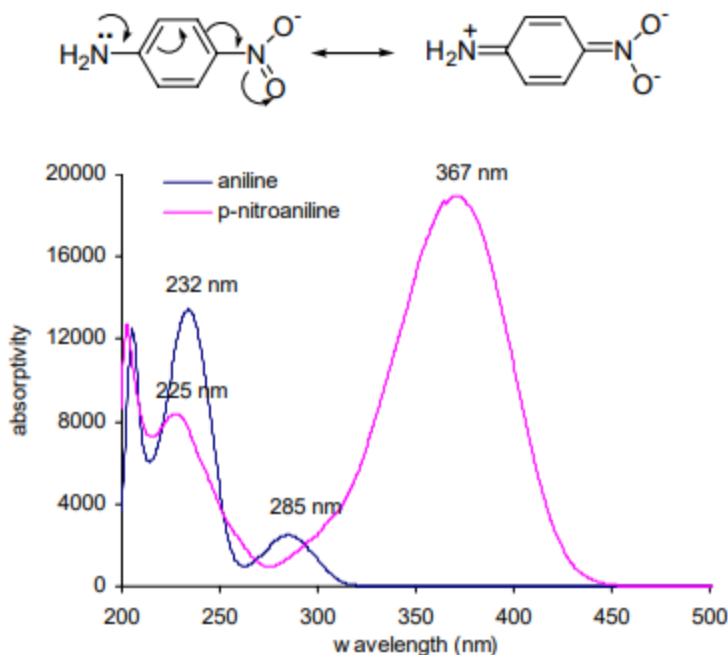
**1.14.4 Electron-donating groups** such as  $-\text{CH}_3$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$ ,  $-\text{NH}_2$  etc **increase** both  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values of the secondary band.

In case of disubstituted benzene derivatives, it is essential to consider the effect of both the substituents.

**1.14.4.1 In para-substituted benzenes, two possibilities exist.** If **both the groups are electron-donating** then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band.

**1.14.4.2 If one group is electron-releasing and other is electron-withdrawing**, the magnitude of red shift is greater compared to the effect of single substituent individually. For example, aniline shows secondary band at 285 nm which due to presence of electron-withdrawing p-nitro substituent is shifted to 367 nm with a significant increase in absorbptivity (figure 11)





**Figure 11** : UV-spectra of aniline and p-nitroaniline in methanol

**1.14.5 Polycyclic Aromatic Compounds:** In case of polycyclic aromatic hydrocarbons, due to extended conjugation, both primary and secondary bands are shifted to longer wavelength. The primary band at 184 nm in benzene shifts to 220 nm in case of naphthalene and 260 nm in case of anthracene. Similarly, the structured secondary band which appears as broad band around 255 nm in benzene is shifted to 270 nm and 340 nm respectively in case of naphthalene and anthracene molecules.

### 1.16 THE WOODWARD-FIESER RULES FOR DIENES

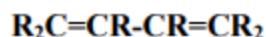
Absorption of a particular wavelength of light depends upon the  $\pi$ -electron system of the molecule. The more the conjugation of the  $\pi$ -electron system within the molecule, the higher the wavelength of light it can absorb.

Following are a few sample applications of these rules.

## UV-Vis - Woodward-Fieser Rules

As you look over the rules below, you will notice a striking feature. Making the chromophore more conjugated significantly increases the value of  $\lambda_{\max}$ . **Greater conjugation leads to a longer  $\lambda_{\max}$ .**

### CONJUGATED DIENE CORRELATIONS



Base: (choose the highest appropriate base value)

for acyclic 214, or

for heteroannular 214, or

for homoannular 253

Auxochrome Corrections:

+60 for each dialkylamino

+30 for each alkylthio

+5 for each exocyclic olefin

+30 for each extending olefin

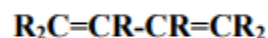
+5 for each Cl, Br, or alkoxy

+5 for each alkyl (cyclic or acyclic)

## UV-Vis Lesson 3 - Woodward-Fieser Rules

As you look over the rules below, you will notice a striking feature. Making the chromophore more conjugated significantly increases the value of  $\lambda_{\max}$ . **Greater conjugation leads to a longer  $\lambda_{\max}$ .**

### CONJUGATED DIENE CORRELATIONS



Base: (choose the highest appropriate base value)

for acyclic 214, or

for heteroannular 214, or

for homoannular 253

Auxochrome Corrections:

+60 for each dialkylamino

+30 for each alkylthio

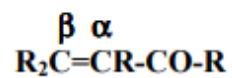
+5 for each exocyclic olefin

+30 for each extending olefin

+5 for each Cl, Br, or alkoxy

+5 for each alkyl (cyclic or acyclic)

---

**ENONE CORRELATIONS****Base:**

for acyclic or cyclohexenone 215, or  
for cyclopentenone 202

**Auxochromes:**

+30 for each extending olefin

+5 for each exocyclic olefin

$\alpha$	Auxochrome	$\beta$	$\gamma, \delta, \text{etc.}$
+35	-OH or -OR	+30	
+25	-Br	+30	
+15	-Cl	+12	
+10	aliphatic	+12	+18
+6	-OCOR	+6	+6

## BENZOYL CORRELATIONS

### X-C<sub>6</sub>H<sub>4</sub>-CO-Z

#### Base:

where Z = H, 250; or

where Z = aliphatic, 246; or

where Z = O-H / O-R, 230

X-C<sub>6</sub>H<sub>4</sub>-COH (benzaldehydes)

X-C<sub>6</sub>H<sub>4</sub>-COR (acetophenones, α-tetralones, etc.)

X-C<sub>6</sub>H<sub>4</sub>-COOH / X-C<sub>6</sub>H<sub>4</sub>-COOR (acids / esters)

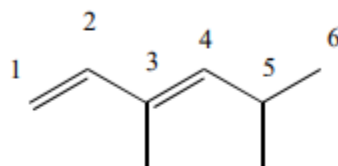
#### Auxochromes:

R	<i>o</i> -, <i>m</i> -	<i>p</i> -
NR <sub>2</sub>	20	85
O-H, O-R	7	25
aliphatic	3	10
Br	2	15
Cl	0	10

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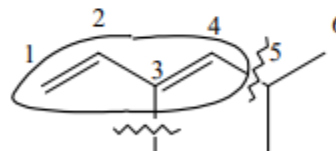
### Application Examples for Woodward's Rules

#### Diene Example #1:

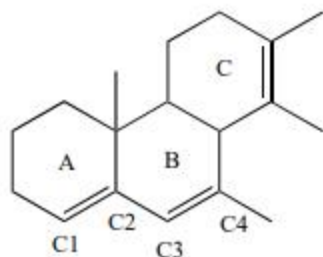


Calc.  $\lambda_{\max} = 214$  (acyclic base) + 5 (alkyl auxochrome at C<sub>3</sub>) + 5 (alkyl auxochrome at C<sub>4</sub>) = 224 nm

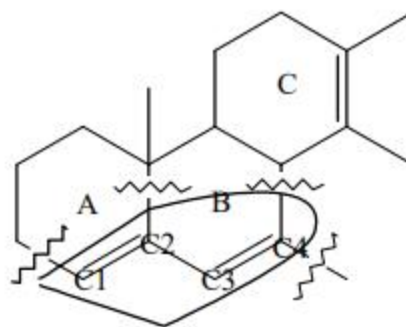
One way to identify an auxochrome is to draw a loop around the entire conjugated system (including extending olefins) and then add hash marks across all bonds attached to the loop. The hash marks define auxochrome attachments.



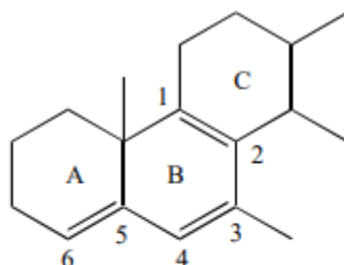
**Diene Example #2:**



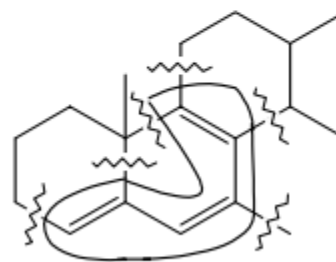
Calc.  $\lambda_{\max}$  = 214 (heteroannular since two pi bonds are not in the same ring) + 20 (5 + 5 + 5 + 5 = 20, for each of the alkyl or ring auxochromes attached to C<sub>1</sub>, C<sub>2</sub>, C<sub>4</sub>, and C<sub>4</sub>) + 5 (pi bond of C<sub>1</sub>-C<sub>2</sub> is exocyclic to ring B)  
= 239 nm



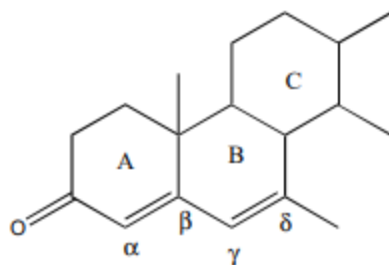
**Diene Example #3:**



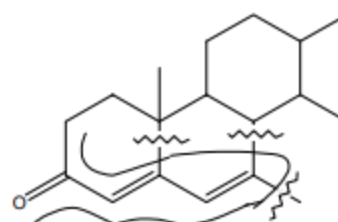
Calc.  $\lambda_{\max}$  = 253 (choose diene with highest base value, pi bonds C<sub>1-2</sub> and C<sub>3-4</sub> are within same ring, so homoannular base should be selected) + 30 (C<sub>5-6</sub> pi bond is conjugated to diene and is therefore an extending diene) + 5 (C<sub>5-6</sub> is exocyclic to ring B) + 30 (5 + 5 + 5 + 5 + 5 + 5 = 30, for the alkyl or ring auxochromes at C<sub>1</sub>, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub>, and C<sub>6</sub>) = 318 nm



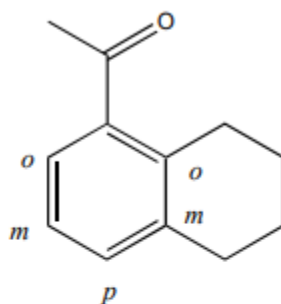
### Enone Example #1:



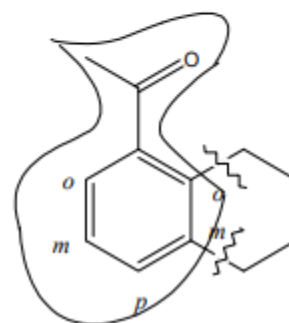
Calc.  $\lambda_{\max}$  = 215 (cyclohexenone base) + 30  
(extending conjugation) + 5  
( $\alpha, \beta$  olefin is exocyclic to ring  
B) + 12 ( $\beta$  auxochrome) + 36  
(2  $\delta$  auxochromes) = 298 nm



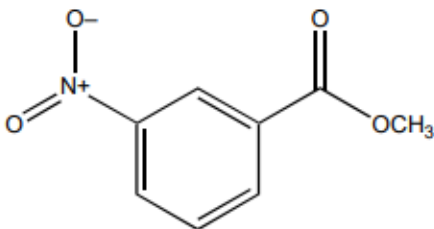
### Benzoyl Example #1:



Calc.  $\lambda_{\max}$  = 246 (Benzoyl Base,  
where Z is the aliphatic methyl group) +  
3 (*o* auxochrome) + 3 (*m* auxochrome)  
= 252 nm

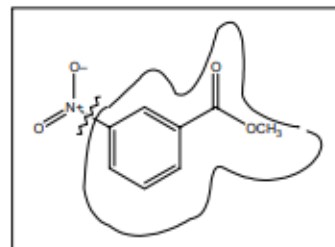


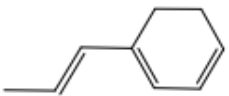
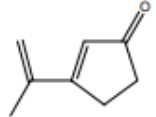
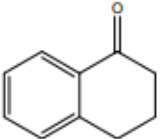
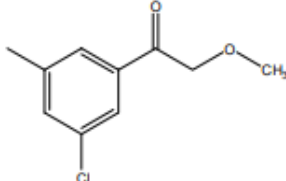
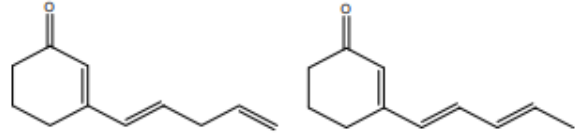
**Benzoyl Example # 2:**



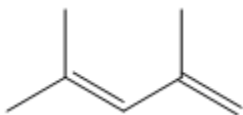
Calc.  $\lambda_{\max} = 230$  (Benzoyl Base, where Z is O-R in this ester functionality) + ?  
(There is no value listed for a *meta* nitro group.)

> **230 nm.** The rules are not perfect. They do not allow you to make predictions for all compounds, not even all the simple ones. The best you can predict in this situation is that the observed  $\lambda_{\max}$  should be greater than 230 nm. After all, the nitro group contains a  $\pi$  bond that extends the length of the conjugated  $\pi$  system. And if nothing else, you know that greater conjugation means longer wavelength  $\lambda_{\max}$ .



<p>QUVVis3-1. What is the predicted <math>\lambda_{\max}</math> for the compound drawn below?</p> 	
<p>QUVVis3-2. Calculate the predicted <math>\lambda_{\max}</math> for the compound drawn below.</p> 	<p>AUVVis3-1. 298 nm</p> <p>298 = 253 (homoannular base) + 30 (extending olefin) + 15 (three alkyl auxochromes on alkene <math>\pi</math> system)</p>
<p>QUVVis3-3. What is the chromophore in the compound drawn below?</p> 	<p>AUVVis3-2. 262 nm.</p> <p>262 = 202 (cyclopentenone base) + 30 (extending olefin) + 12 (<math>\beta</math> alkyl auxochrome) + 18 (<math>\gamma</math> alkyl auxochrome)</p>
<p>QUVVis3-4. What is the predicted <math>\lambda_{\max}</math> for the compound drawn in QUVVis3-3?</p>	<p>AUVVIS3-3. Benzoyl.</p>
<p>QUVVis3-5. What is the predicted <math>\lambda_{\max}</math> for the compound drawn below?</p> 	<p>AUVVIS3-4. 249 nm.</p> <p>246 (Z = aliphatic base) + 3 (<i>ortho</i> alkyl).</p>
<p>QUVVis3-6. Suppose you have the two compounds listed below and a UV-Vis instrument, but no access to tables or rules for calculation of <math>\lambda_{\max}</math> values. How could you use UV-Vis to differentiate between these two compounds?</p>  <p style="text-align: center;">A                      B</p>	<p>AUVVis3-5. 249 nm.</p> <p>246 (benzoyl base, where the aliphatic <i>carbon</i> atom of the group <math>-\text{CH}_2\text{OCH}_3</math>, not the oxygen atom, is directly attached to the benzoyl carbonyl so that Z = aliphatic) + 0 (<i>meta</i> Cl) + 3 (<i>meta</i> alkyl). You could NOT use predicted <math>\lambda_{\max}</math> values to differentiate between the compounds drawn in problems QUVVIS3-4 and QUVVIS3-5!</p>
	<p>AUVVis3-6</p> <p>Record <math>\lambda_{\max}</math> of both compounds. The compound with the longer wavelength (&gt;nm) will be the more conjugated isomer (B).</p>





**Name of Compound**

**Woodward Component**

**Core-** Transoid/Heteroannular Diene

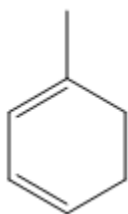
**Substituents-** 3 alkyl groups

**Other Effects**

**Calculated  $\lambda_{\max}$**

**Observed  $\lambda_{\max}$**

### Example/Sample Problem 2



**Name of Compound**

**Woodward Component**

**Core-** Cisoid/Homoannular Diene

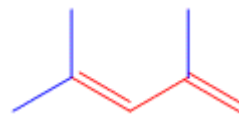
**Substituents-** 3 alkyl groups

**Other Effects**

**Calculated  $\lambda_{\max}$**

**Observed  $\lambda_{\max}$**

### Example/Sample Problem 3



2,4-dimethylpenta-1,3-diene

**Contribution**

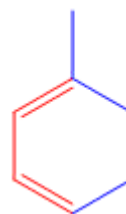
+ 215 nm

3 x 5 = + 15 nm

0

**230 nm**

234 nm



1-methylcyclohexa-1,3-diene

**Contribution**

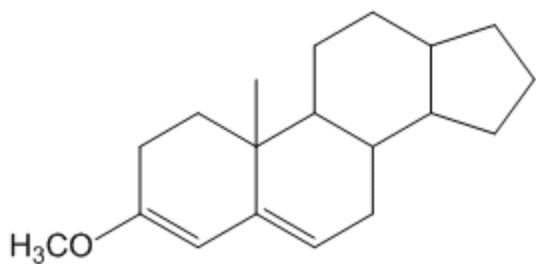
+ 253 nm

3 x 5 = + 15 nm

0

**268 nm**

N/A



**Name of Compound**

**Woodward Component**

**Core-** Transoid/Heteroannular Diene

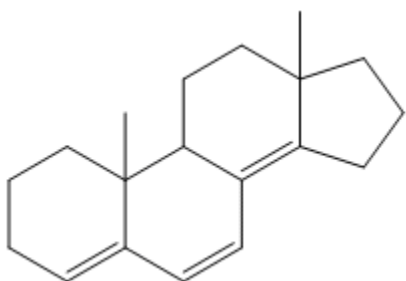
**Substituents-** 3 alkyl groups  
1 alkoxy group

**Other Effects-** Exocyclic Double Bond

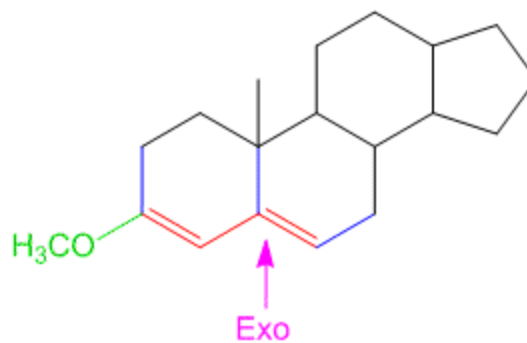
**Calculated  $\lambda_{max}$**

**Observed  $\lambda_{max}$**

#### Example/Sample Problem 4



**Name of Compound**



3-methoxy-10-methyl-  
2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-  
cyclopenta[a]phenanthrene

**Contribution**

+ 215 nm

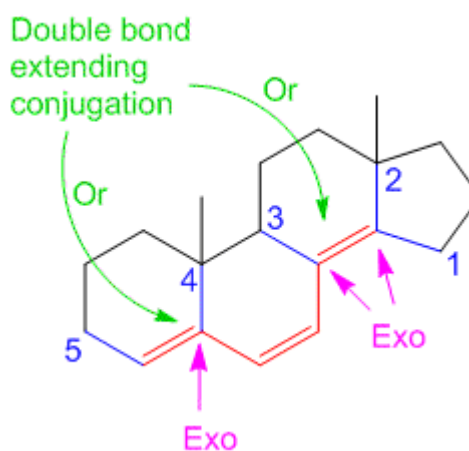
3 x 5 = + 15 nm

+ 6 nm

+ 5 nm

**241 nm**

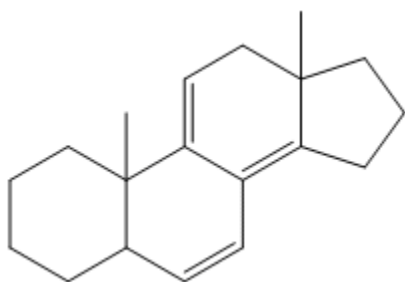
N/A



10,13-dimethyl-2,3,9,10,11,12,13,15,16,17-decahydro-1H-  
cyclopenta[a]phenanthrene

Woodward Component	Contribution
<b>Core- Transoid/Heteroannular</b>	+ 215 nm
<b>Substituents- 5 alkyl groups</b>	5 x 5 = + 25 nm
<b>1 Double bond extending conjugation</b>	+ 30 nm
<b>Other Effects- 3 Exocyclic Double Bond</b>	+ 15 nm
<b>Calculated <math>\lambda_{max}</math></b>	<b>285 nm</b>
<b>Observed <math>\lambda_{max}</math></b>	283 nm

### Example/Sample Problem 5



**Note-** In this example the molecule contains both, a homoannular diene system and a heteroannular diene system. In such a molecule the core chromophore is considered to be the homoannular system and accordingly the calculations are performed.

#### Homoannular system



Component	Contribution
<b>Core- Homoannular/Cisoid diene</b>	+ 253 nm
<b>Substituents- 5 alkyl substituents</b>	5 x 5 = + 25 nm
<b>Double bond extending conjugation</b>	+ 30 nm

**Other Effects- 3 Exocyclic double bonds**

$$3 \times 5 = + 15 \text{ nm}$$

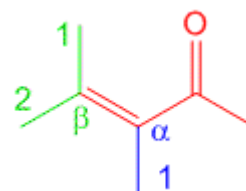
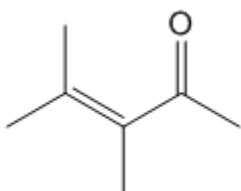
**Calculated  $\lambda_{\text{max}}$**

**323 nm**

**Observed  $\lambda_{\text{max}}$**

n/a

### Example/Sample Problem 6



**Name of Compound**

3,4-dimethylpent-3-en-2-one

**Component**

**Contribution**

**Core-  $\alpha,\beta$ -unsaturated ketone**

+ 215 nm

**Substituents at  $\alpha$ -position- 1 alkyl group**

+ 10 nm

**Substituents at  $\beta$ -position- 2 alkyl groups**

2 x 12 = 24 nm

**Other Effects**

0

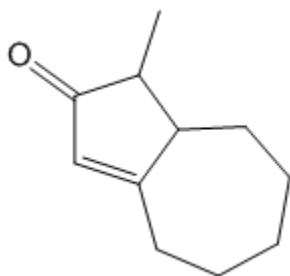
**Calculated  $\lambda_{\text{max}}$**

**249 nm**

**Observed  $\lambda_{\text{max}}$**

249 nm

### Example/Sample Problem 7



**Name of Compound**

1-methyl-4,5,6,7,8,8a-hexahydroazulen-2(1H)-one

**Component**

**Contribution**

**Core- cyclopentenone**

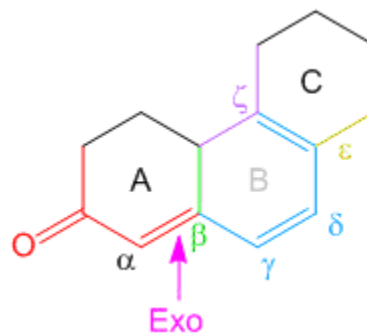
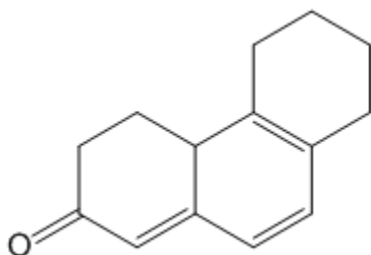
+ 202 nm

**Substituents at  $\alpha$ -position**

0

<b>Substituents at <math>\beta</math>-position-</b> 2 alkyl groups	$2 \times 12 = + 24 \text{ nm}$
<b>Other Effects-</b> 1 Exocyclic Double Bond	+ 5 nm
<b>Calculated <math>\lambda_{\text{max}}</math></b>	<b>231 nm</b>
<b>Observed <math>\lambda_{\text{max}}</math></b>	226 nm

### Example/Sample Problem 8



<b>Name of Compound</b>	4,4a,5,6,7,8-hexahydrophenanthren-2(3H)-one
<b>Component</b>	<b>Contribution</b>
<b>Core-</b> cyclohexenone	+ 215 nm
<b>Substituents at <math>\alpha</math>-position:</b>	0
<b>Substituents at <math>\beta</math>-position:</b> 1 alkyl group	+ 12 nm
<b>Substituents at <math>\gamma</math>-position:</b>	0
<b>Substituents at <math>\delta</math>-position:</b>	0
<b>Substituents at <math>\epsilon</math>-position:</b> 1 alkyl group	+ 18 nm
<b>Substituents at <math>\zeta</math>-position:</b> 2 alkyl group	$2 \times 18 = + 36 \text{ nm}$
<b>Other Effects:</b> 2 Double bonds extending conjugation	$2 \times 30 = + 60 \text{ nm}$
<b>Homoannular Diene system in ring B</b>	+ 35 nm

1 Exocyclic double bond

+ 5 nm

Calculated  $\lambda_{\max}$

381 nm

Observed  $\lambda_{\max}$

388 nm

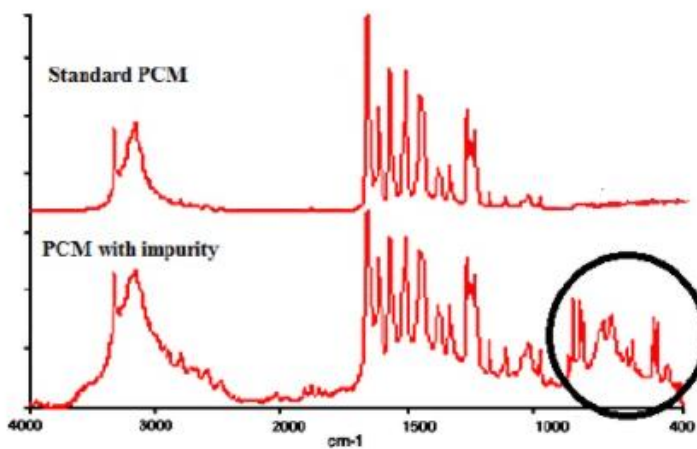
### 1.17 Application of u.v. spectroscopy

#### APPLICATIONS OF U.V. SPECTROSCOPY:

##### 1. Detection of Impurities

- UV absorption spectroscopy 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.

#### U.V. SPECTRA OF PARACETAMOL (PCM)



## 2. Structure elucidation of organic compounds.

- UV spectroscopy is useful in the structure elucidation of organic molecules, the presence or absence of unsaturation, the presence of hetero atoms.
- From the location of peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not etc.

## 3. QUANTITATIVE ANALYSIS

- UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law which is as follows.

$$A = \log I_0 / I_t = \log 1/T = -\log T = abc = \epsilon bc$$

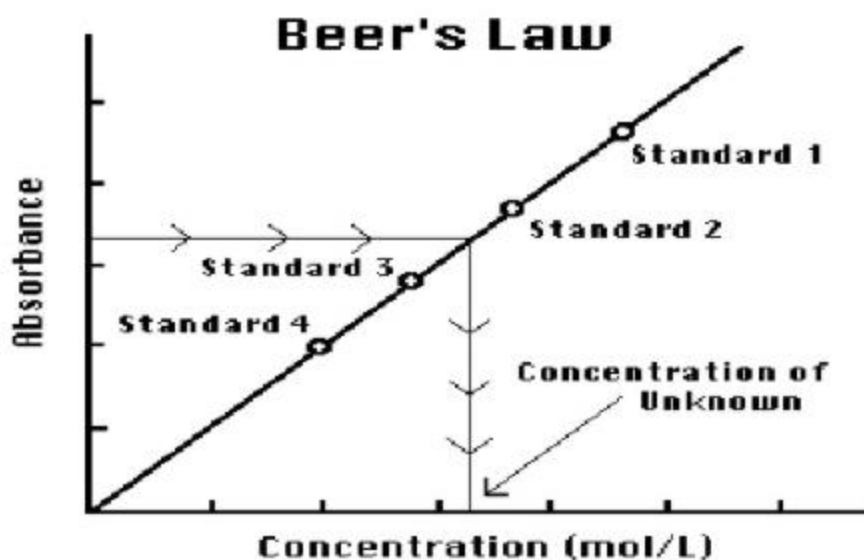
Where :

$\epsilon$  -is extinction co-efficient,

c- is concentration, and

b- is the length of the cell that is used in UV spectrophotometer.

## BEER'S LAW

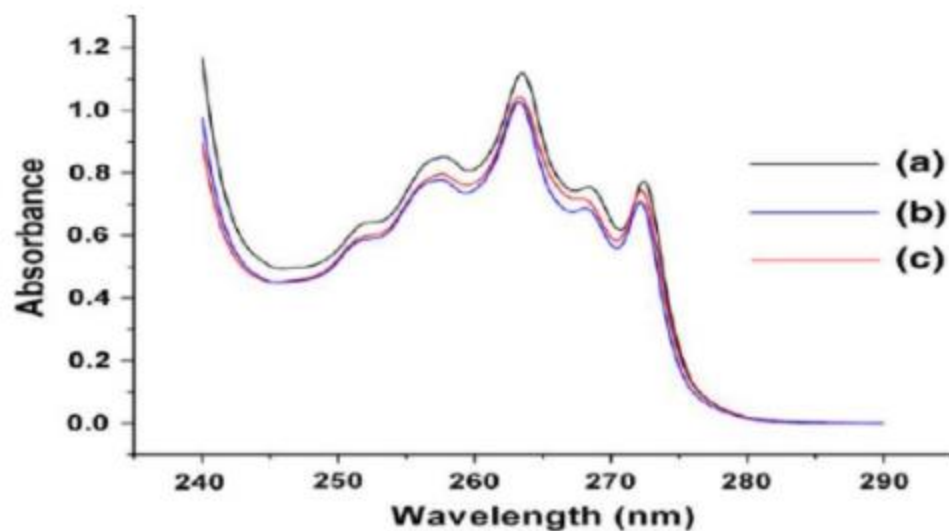


### 4. QUALITATIVE ANALYSIS

- UV absorption spectroscopy can characterize those types of compounds which absorb UV radiation. Identification is done by comparing the absorption spectrum with the spectra of known compounds.



## U.V. SPECTRA'S OF IBUPROFEN



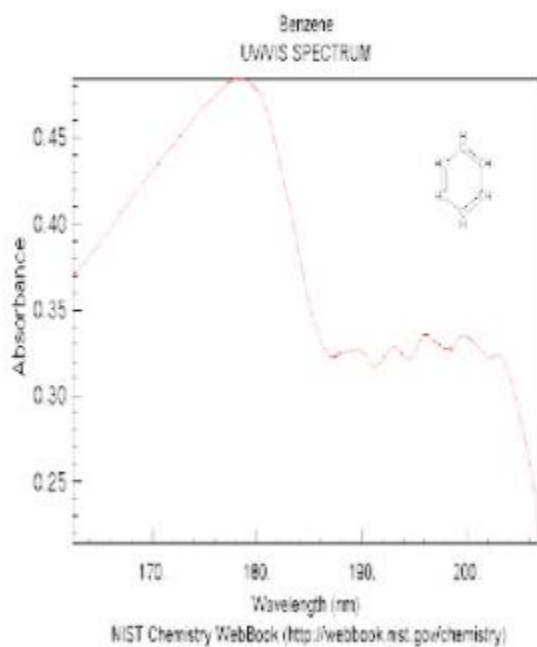
### 5. CHEMICAL KINETICS

- 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.

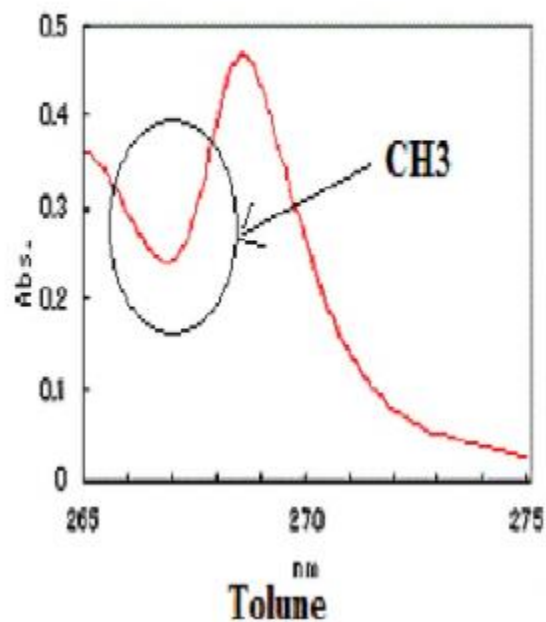
## 6. DETECTION OF FUNCTIONAL GROUPS

- This technique is used to detect the presence or absence of functional group in the compound
- Absence of a band at particular wavelength regarded as an evidence for absence of particular group

BENZENE



TOLUENE



## 9. MOLECULAR WEIGHT DETERMINATION

- Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.
- For example, if we want to determine the molecular weight of amine then it is converted in to *amine picrate*. Then known concentration of amine picrate is dissolved in a litre of solution and its optical density is measured at  $\lambda_{\max}$  380 nm.
- ❖ After this the concentration of the solution in gm moles per litre can be calculated by using the following formula.

$$C = \frac{\log I_0 / I_t}{\epsilon_{\max} \times l}$$

- ❖ "c" can be calculated using above equation, the weight "w" of amine picrate is known. From "c" and "w", molecular weight of amine picrate can be calculated. And the molecular weight of picrate can be calculated using the molecular weight of amine picrate. 