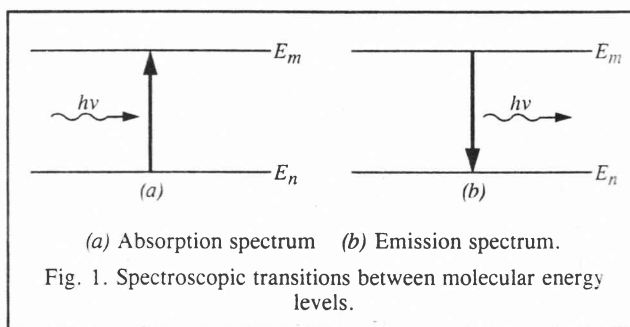


5

Molecular Spectroscopy-I (ROTATIONAL, VIBRATIONAL AND ELECTRONIC SPECTRA)

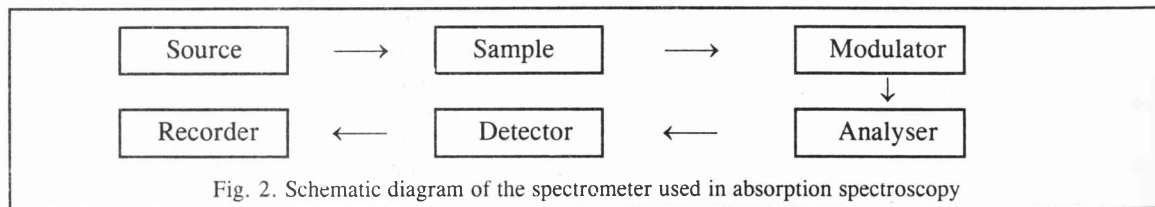
What is Spectroscopy ? Chemists, physicists, biochemists and other scientists are deeply interested in knowing the structure of molecules. If one could actually 'see' a molecule, there would probably be little fun in investigating it further. However, these systems are of so infinitesimal dimensions that it is not possible to see them, though some progress has of late been made in 'photographing' these species. Our knowledge about molecular structure is derived indirectly from the technique known as **spectroscopy** which deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.

Quantum mechanics tells that the energy levels of all systems are *quantized* and are designated by the appropriate quantum numbers. These energy levels are obtained by the solutions of the time-independent Schrödinger equation, the details of which are not really essential to the understanding of spectroscopy. Let us consider how a spectrum arises. Consider two molecular energy levels E_n and E_m , as shown in Fig. 1. If a photon of frequency ν falls on a molecule in the ground state and its energy $h\nu$ is exactly equal to the energy difference $\Delta E (= E_m - E_n)$ between the two molecular energy levels, then the molecule undergoes a **transition** from the lower energy level to the higher energy level with the **absorption** of a photon of energy $h\nu$. The spectrum thus obtained is called the **absorption spectrum**. If the molecule falls from the excited state to the ground state with the **emission** of a photon of energy $h\nu$, the spectrum obtained is called the **emission spectrum**.



Basic Features of Spectrometers

The schematic diagram of the spectrometer used for absorption spectroscopy is given in Fig. 2.



This spectrometer is used when absorption occurs in infrared and ultraviolet regions of the electromagnetic spectrum. The source in a spectrometer produces radiation spanning a range of frequencies, but in a few cases (such as lasers), it is almost a monochromatic radiation. The radiation source in an absorption spectrometer is a heated ceramic filament coated with rare-earth oxides (a Nernst emitter or filament) for the infrared region. The source for the visible region of the spectrum is

a tungsten filament which gives out intense white light ; for the ultraviolet region the source is a hydrogen discharge lamp. A *klystron* (which is also used in radar installations and microwave ovens) or, more commonly, a semiconductor device called *Gunn diode*, is used to generate microwaves. The radiofrequency radiation is generated by causing an electric current to oscillate in a coil of wire.

The variation of absorption with frequency is determined, traditionally, by analyzing the spectral radiation by means of a *dispersing element* which separates different frequencies into rays that travel in different directions. The simplest dispersing element is a glass or quartz prism but a diffraction grating is more widely used. A *diffraction grating* consists of a glass or ceramic plate into which fine grooves have been cut about 1000 nm apart (a spacing comparable to the wave length of visible light) and covered with a reflective aluminium coating. The grating causes interference between waves reflected from its surface and constructive interference occurs at specific angles that depend on the frequency of the radiation being used. Thus, each wave length of light is directed into a specific direction.

The third component of spectrometers is the *detector*, a device that converts the spectral radiation into an electrical signal that is passed on to a recording device operating synchronously with the analyzer, thus producing either a trace on a chart recorder or a computer record of the spectrum. Common detectors are the radiation-sensitive semiconductors. The radiation is chopped by a shutter that rotates in the beam so that an alternating signal is obtained from the detector (an oscillating signal is easier to amplify than a steady signal). A modulator is introduced to convert the signal to an alternating character. This procedure enables more AC electronics to be employed in the recording stages. In the microwave region the source frequency is varied and the analyser is not necessary.

The highest resolution is obtained when the sample is gaseous and at such low pressure that collisions between molecules are infrequent. Gaseous samples are essential for microwave (pure rotational) spectroscopy for molecules can freely rotate only in the gaseous state. In order to achieve sufficient absorption, the path lengths of gaseous samples must be very long, of the order of metres. Long path lengths are achieved by multiple passage of the beam between two parallel mirrors at each end of the sample cavity. For infrared spectroscopy, the sample is typically a liquid held between windows of sodium chloride (which is transparent down to 700 cm^{-1}) or potassium bromide (down to 400 cm^{-1}). Other ways of preparing the sample include grinding it into a paste with 'Nujol', a hydrocarbon oil, or pressing it into a solid disk, with powdered potassium bromide.

Nowadays it is a common practice to use **Fourier-transform technique in spectroscopy**, particularly with infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. In Fourier-transform infrared (FTIR) spectroscopy, a Michelson-type interferometer is used to analyse the spectrum. It functions by producing an interferogram which is the superposition of a series of waves, each of which represents a component in the spectrum in terms of intensity and wave number. A Fourier transformation of the interferogram then produces a well-resolved absorption spectrum of the species, with a good signal-to-noise (S/N) ratio, also abbreviated as SNR.

The molecular spectra are governed by the so-called **selection rules** which specify the changes in the quantum numbers accompanying a particular transition. The chemist is lucky that selection rules exist which determine a spectrum. If there were no selection rules, the resulting spectrum would have been very chaotic, indeed ! The selection rules are, in fact, the 'backbone' of spectroscopy and are obtained from the quantum theory of interaction of radiation with matter. Let us enumerate a few examples which would later be elucidated. For a diatomic molecule, such as H_2 , NO, CO, etc., the selection rule for a pure *rotational transition* is $\Delta J = \pm 1$, where J is the rotational quantum number. The selection rule for a pure *vibrational transition* is $\Delta v = \pm 1$, where v is the vibrational quantum number.

The selection rules, however, are not always obeyed strictly. This is because certain approximations which have been used in the derivation of the selection rules are not valid strictly. The spectral transitions which obey a given selection rule are called **allowed transitions** whereas those which violate a selection rule are called **forbidden transitions**. In general, the allowed transitions are more intense (stronger) than the forbidden transitions which are weak. The selection rules for spectral transitions are derived from time-dependent perturbation theory (TDPT), discussed in Chapter 2.

The **natural linewidth** (or **life-time broadening**) of a spectral line is determined by the Heisenberg uncertainty principle, $\Delta E \Delta t \geq h/4\pi$, where ΔE is the uncertainty in the energy and Δt is the uncertainty in the life-time of the energy level. Since for a photon $E = h\nu$ so that $\Delta E = h\Delta\nu$, hence the natural linewidth, $\Delta\nu$, is given by

$$\Delta\nu \geq (4\pi\Delta t)^{-1} \quad \dots(1)$$

Width and Intensity of Spectral Lines. When we analyse the spectrum of a molecule, the first thing we wish to know is how sharp and how intense (strong) is the spectral line. In other words, we are interested in the width and intensity of a spectral line. These two quantities are common to all branches of spectroscopy. Fig. 3(a) shows a sharp spectral line having no width while Fig. 3(b) shows a spectral line having a width ΔE at half-height. The chemist would, indeed, be a happy person if the spectral lines were all very sharp and very intense. In practice, this is not so.

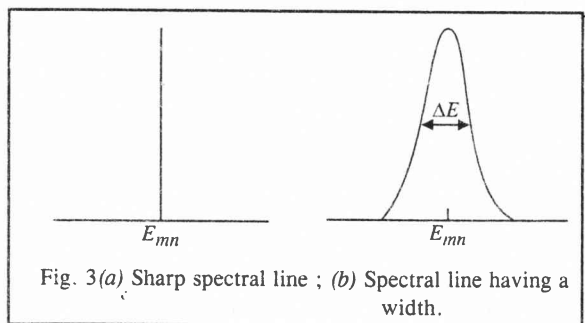


Fig. 3(a) Sharp spectral line ; (b) Spectral line having a width.

Two factors contribute to broadening of a spectral line : (i) The **collision broadening** and (ii) the **Doppler broadening**. The collision broadening is largely responsible for the width of spectral lines in the ultraviolet (UV) and visible regions. These transitions mostly take place between electrons in the outer shells in a molecule. When molecules in the gaseous or liquid phase collide with one another, they deform the charge clouds of the outer electrons thereby slightly perturbing the energy levels of these electrons. Hence, the spectral transitions between these perturbed energy levels are broadened.

The **Doppler broadening** arises when the molecule under investigation has a velocity relative to the observer or observing instrument. This is generally the case with gaseous samples where the molecules are undergoing random motion according to the postulates of the kinetic theory of gases. If the molecule is moving *towards* the measuring instrument with velocity u , then the frequency ν' of radiation 'seen' by the molecule is given by

$$\nu' = \nu (1 + u/c) \quad \dots(2a)$$

where ν is the radiation frequency and c is the velocity of light. If, on the other hand, the molecule is moving *away* from the measuring instrument, the frequency of radiation 'seen' by the molecule is given by

$$\nu' = \nu (1 - u/c) \quad \dots(2b)$$

Rearranging Eq. 2a, we obtain

$$(\nu - \nu') / \nu = \Delta\nu/\nu = -u/c \quad \dots(3a)$$

Similarly, rearranging Eq. 2b, we obtain

$$(\nu - \nu') / \nu = \Delta\nu/\nu = u/c \quad \dots(3b)$$

The quantity $\Delta\nu$ is the **Doppler broadening**. We see that, depending upon the direction of motion of the molecule relative to the instrument, the observed frequency becomes either higher or lower than the actual radiation frequency. From the kinetic theory of gases, it can be shown that the Doppler broadening of the spectral line of a molecule of mass m is given by

$$\Delta\nu/\nu = (2/c) (2kT \ln 2/m)^{1/2} \quad \dots(4)$$

Since $\Delta\nu/\nu$ is directly proportional to $T^{1/2}$, Doppler broadening can be reduced (and spectral lines of maximum sharpness can be obtained) by working with cold gaseous samples.

We now turn to the **intensity of spectral lines**. The intensity of a spectral line is determined by

The shorter the wavelength, the greater is the energy of the radiation.

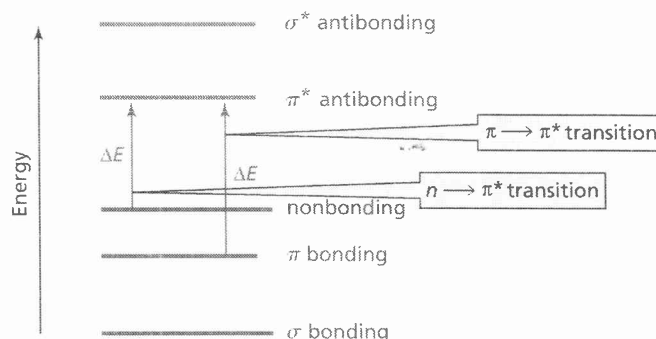
UV/Vis spectroscopy provides information about compounds with conjugated double bonds. Ultraviolet light and visible light have just the right energy to cause an electronic transition—the promotion of an electron from one orbital to another of higher energy. Depending on the energy needed for the electronic 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. Ultraviolet light is electromagnetic radiation with wavelengths ranging from 180 to 400 nm (nanometers); visible light has wavelengths ranging from 400 to 780 nm. (One nanometer is 10^{-9} m, or 10 \AA .) **Wavelength** (λ) is inversely related to the energy: The shorter the wavelength, the greater is the energy. Ultraviolet light, therefore, has greater energy than visible light.

$$E = \frac{hc}{\lambda}$$

h = Planck's constant
 c = velocity of light
 λ = wavelength

The normal electronic configuration of a molecule is known as its **ground state**—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 relative energies of the bonding, nonbonding, and antibonding molecular orbitals are shown in Figure 8.5.

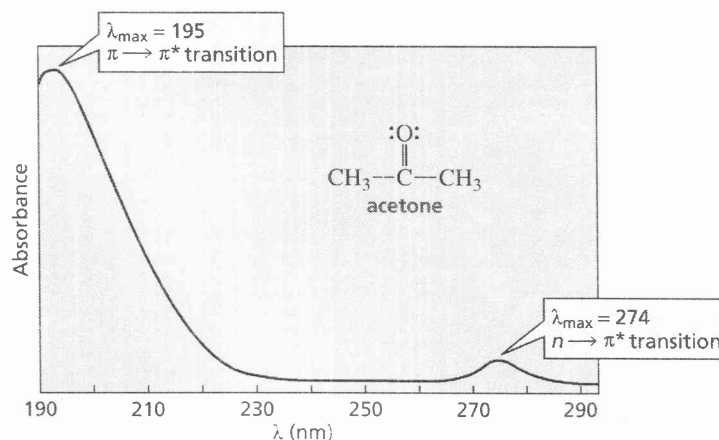
Figure 8.5 ▶
Relative energies of the bonding, nonbonding, and antibonding orbitals.



Ultraviolet and visible light have sufficient energy to cause only the two electronic transitions shown in Figure 8.5. The electronic transition with the lowest energy is the promotion of a nonbonding (lone-pair) electron (n) into a π^* antibonding molecular orbital. This is called an $n \rightarrow \pi^*$ (stated as “ n to π star”) transition. The higher energy electronic transition is the promotion of an electron from a π bonding molecular orbital into a π^* antibonding molecular orbital, known as a $\pi \rightarrow \pi^*$ (stated as “ π to π star”) transition. This means that *only organic compounds with π electrons can produce UV/Vis spectra*.

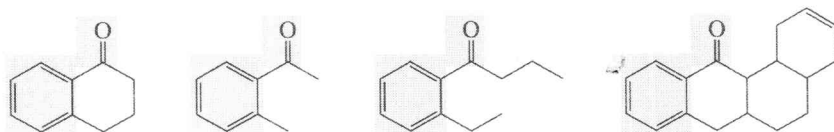
The UV spectrum of acetone is shown in Figure 8.6. Acetone has both π electrons and lone-pair electrons. Thus, there are two **absorption bands**: one for the $\pi \rightarrow \pi^*$

Figure 8.6 ▶
The UV spectrum of acetone.



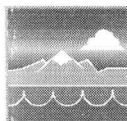
transition and one for the $n \rightarrow \pi^*$ transition. The λ_{\max} (stated as “lambda max”) is the wavelength corresponding to the highest point (maximum absorbance) of the absorption band. For the $\pi \rightarrow \pi^*$ transition, $\lambda_{\max} = 195 \text{ nm}$; for the $n \rightarrow \pi^*$ transition, $\lambda_{\max} = 274 \text{ nm}$. We know that the $\pi \rightarrow \pi^*$ transition in Figure 8.6 corresponds to the λ_{\max} at the shorter wavelength because that transition requires more energy than the $n \rightarrow \pi^*$ transition.

A **chromophore** is that part of a molecule that absorbs UV or visible light. The carbonyl group is the chromophore of acetone. The following four compounds all have the same chromophore, so they all have approximately the same λ_{\max} .



PROBLEM 20

Explain why diethyl ether does not have a UV spectrum, even though it has lone-pair electrons.

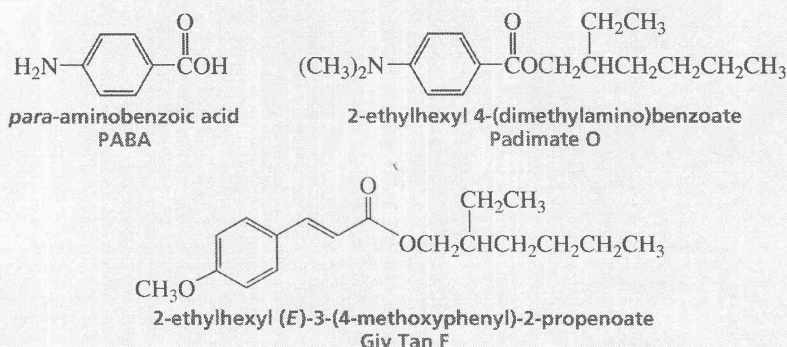


ULTRAVIOLET LIGHT AND SUNSCREENS

Exposure to ultraviolet light stimulates specialized cells in the skin to produce a black pigment known as melanin, which causes the skin to look tan. Melanin absorbs UV light, so it protects our bodies from the harmful effects of the sun. If more UV light reaches the skin than the melanin can absorb, the light will burn the skin and can cause photochemical reactions that can result in skin cancer (Section 29.6). UV-A is the lowest-energy UV light (315 to 400 nm) and does the least biological damage. Fortunately, most of the more dangerous, higher-energy UV light, UV-B (290 to 315 nm) and UV-C (180 to 290 nm), is filtered out by the ozone layer in the stratosphere. That is why there is such great concern about the apparent thinning of the ozone layer (Section 9.9).

Applying a sunscreen can protect skin against UV light. Some sunscreens contain an inorganic component, such as zinc oxide, that reflects the light as it reaches the skin. Others contain a compound that absorbs UV light. PABA was the first commercially available UV-absorbing sunscreen. PABA absorbs UV-B light, but is not very soluble in oily skin lotions. Less polar compounds, such as Padimate O, are now commonly used. Recent research has shown that sunscreens that absorb only UV-B light do not give adequate protection against skin cancer; both UV-A and UV-B protection are needed. Giv Tan F absorbs both UV-B and UV-A light, so it gives better protection.

The amount of protection provided by a particular sunscreen is indicated by its SPF (sun protection factor). The higher the SPF, the greater is the protection.



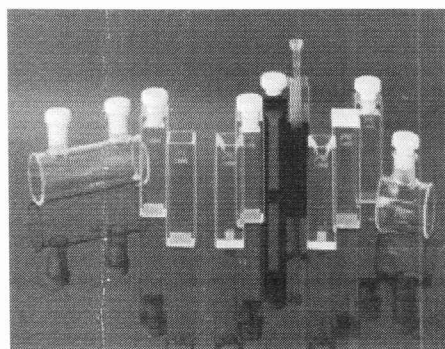
8.10 The Beer–Lambert Law

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

Wilhelm Beer (1797–1850) was born in Germany. He was a banker whose hobby was astronomy. He was the first to make a map of the darker and lighter areas of Mars.

Johann Heinrich Lambert (1728–1777), a German-born mathematician, was the first to make accurate measurements of light intensities and to introduce hyperbolic functions into trigonometry.

Although the equation that relates absorbance, concentration, and light path bears the names of Beer and Lambert, it is believed that **Pierre Bouguer (1698–1758)**, a French mathematician, first formulated the relationship in 1729.



▲ Cells used in UV/Vis spectroscopy.

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

$$A = c\ell\epsilon$$

where

$$A = \text{absorbance of the sample} = \log \frac{I_0}{I}$$

I_0 = intensity of the radiation entering the sample

I = intensity of the radiation emerging from the sample

c = concentration of the sample, in moles/liter

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

ϵ = molar absorptivity (liter mol⁻¹ cm⁻¹)

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 274 nm. 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 λ_{max} 195 nm (ϵ_{max} = 9000, hexane); λ_{max} 274 nm (ϵ_{max} = 13.6, hexane). 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.

The two absorption bands of acetone in Figure 8.6 are very different in size because of the difference in molar absorptivity at the two wavelengths. Small molar absorptivities are characteristic of $n \rightarrow \pi^*$ transitions, so these transitions can be difficult to detect. Consequently, $\pi \rightarrow \pi^*$ transitions are usually more useful in UV/Vis spectroscopy.

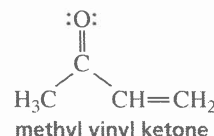
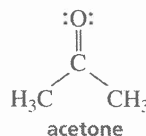
In order to obtain a UV or visible spectrum, the solution is placed in a cell. Most cells have 1-cm path lengths. Either glass or quartz cells can be used for visible spectra, but quartz cells must be used for UV spectra because glass absorbs UV light.

PROBLEM 21♦

A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0.52 at 236 nm in a cell with a 1-cm light path. Its molar absorptivity in ethanol at that wavelength is 12,600. What is the concentration of the compound?

8.11 Effect of Conjugation on λ_{max}

The $n \rightarrow \pi^*$ transition for methyl vinyl ketone is at 324 nm, and the $\pi \rightarrow \pi^*$ transition is at 219 nm. Both λ_{max} values are at longer wavelengths than the corresponding λ_{max} values of acetone because methyl vinyl ketone has two conjugated double bonds.



$n \rightarrow \pi^* \quad \lambda_{\text{max}} = 274 \text{ nm } (\epsilon_{\text{max}} = 13.6)$
 $\pi \rightarrow \pi^* \quad \lambda_{\text{max}} = 195 \text{ nm } (\epsilon_{\text{max}} = 9000)$

$\lambda_{\text{max}} = 331 \text{ nm } (\epsilon_{\text{max}} = 25)$
 $\lambda_{\text{max}} = 203 \text{ nm } (\epsilon_{\text{max}} = 9600)$



3-D Molecule:
Methyl vinyl ketone

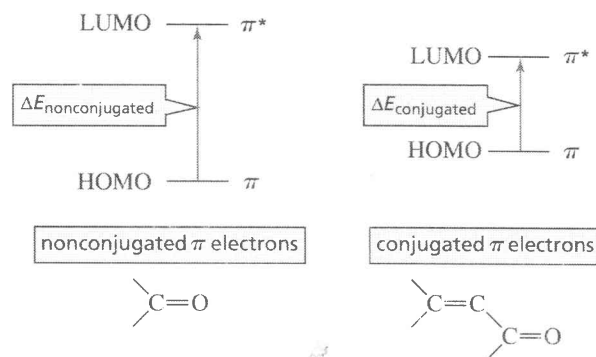




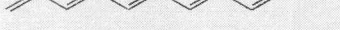


Figure 8.7
Conjugation raises the energy of the HOMO and lowers the energy of the LUMO.

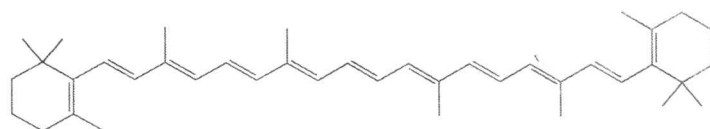
Conjugation raises the energy of the HOMO and lowers the energy of the LUMO, so less energy is required for an electronic transition in a conjugated system than in a nonconjugated system (Figure 8.7). The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs.

The λ_{\max} values of the $\pi \rightarrow \pi^*$ transition for several conjugated dienes are shown in Table 8.3. Notice that both the λ_{\max} and the molar absorptivity increase as the number of conjugated double bonds increases. Thus, the λ_{\max} of a compound can be used to predict the number of conjugated double bonds in the compound.

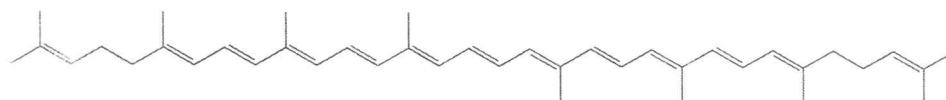
The λ_{\max} increases as the number of conjugated double bonds increases.

Compound	λ_{\max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
$\text{H}_2\text{C}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

If a compound has enough conjugated double bonds, it will absorb visible light ($\lambda_{\max} > 400 \text{ nm}$) and the compound will be colored. β -Carotene, a precursor of vitamin A, is an orange substance found in carrots, apricots, and sweet potatoes. Lycopene is red and is found in tomatoes, watermelon, and pink grapefruit.



β -carotene
 $\lambda_{\max} = 455 \text{ nm}$



lycopene
 $\lambda_{\max} = 474 \text{ nm}$



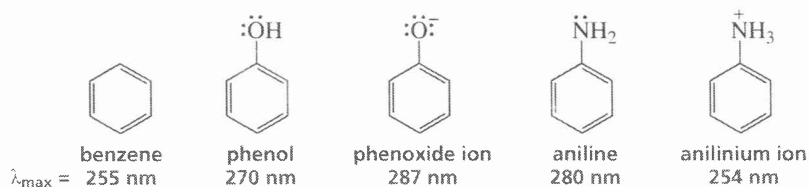
3-D Molecule:
1,3,5,7-Octatetraene

An **auxochrome** is a substituent that when attached to a chromophore, alters the λ_{\max} and the intensity of the absorption, usually increasing both; OH and NH_2 groups are auxochromes. The lone-pair electrons on oxygen and nitrogen are available for interaction with the π electron cloud of the benzene ring, and such an interaction

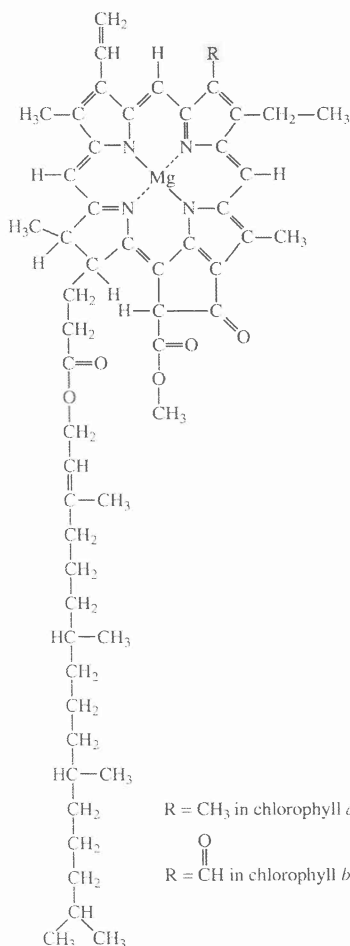
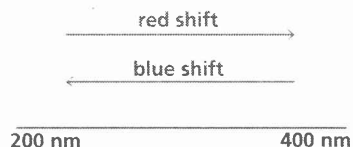


3-D Molecules:
para-Aminobenzoic acid;
 Phenol; Phenoxide ion

increases λ_{\max} . Because the anilinium ion does not have an auxochrome, its λ_{\max} is similar to that of benzene.



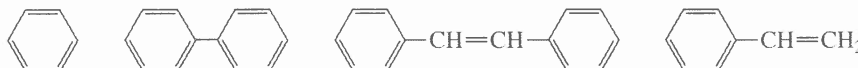
Removing a proton from phenol and thereby forming phenoxide ion (also called phenolate ion) increases the λ_{\max} because the resulting ion has an additional lone pair. Protonating aniline (and thereby forming the anilinium ion) decreases the λ_{\max} , because the lone pair is no longer available to interact with the π cloud of the benzene ring. Because wavelengths of red light are longer than those of blue light (Figure 13.11 on page 497), a shift to a longer wavelength is called a **red shift**, and a shift to a shorter wavelength is called a **blue shift**. Deprotonation of phenol results in a red shift, whereas protonation of aniline produces a blue shift.



Chlorophyll *a* and *b* are the pigments that make plants look green. These highly conjugated compounds absorb nongreen light. Therefore, plants reflect green light.

PROBLEM 22♦

Rank the compounds in order of decreasing λ_{\max} :



8.12 The Visible Spectrum and Color

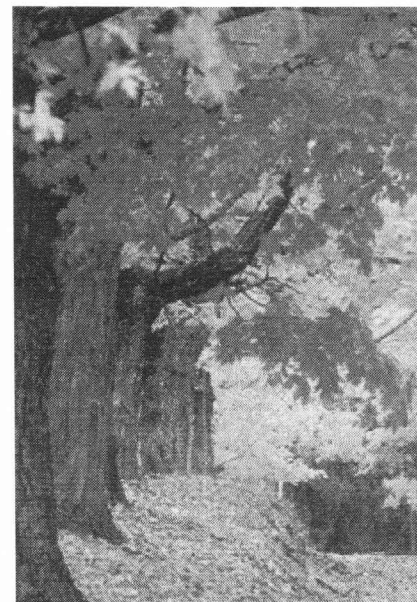
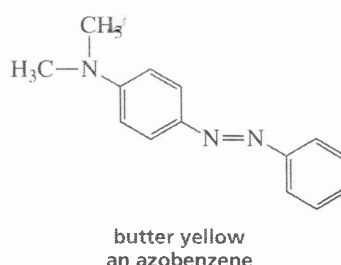
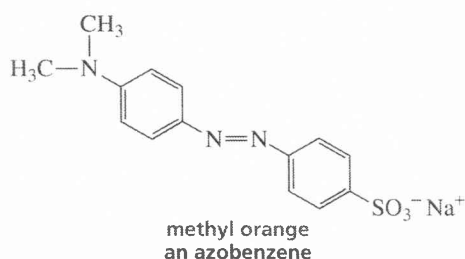
White light is a mixture of all wavelengths of visible light. If any color is removed from white light, the remaining light appears colored. So if a compound absorbs visible light, the compound will appear colored. Its color depends on the color of the light transmitted to the eye. In other words, it depends on the color produced from the wavelengths of light that are *not* absorbed.

The relationship between the wavelengths of the light absorbed and the color observed is shown in Table 8.4. Notice that two absorption bands are necessary to produce green. Most colored compounds have fairly broad absorption bands; vivid colors have narrow absorption bands. The human eye is able to distinguish more than a million different shades of color!

Table 8.4 Dependence of the Color Observed on the Wavelength of Light Absorbed

Wavelengths absorbed (nm)	Observed color
380–460	yellow
380–500	orange
440–560	red
480–610	purple
540–650	blue
380–420 and 610–700	green

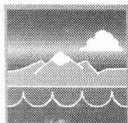
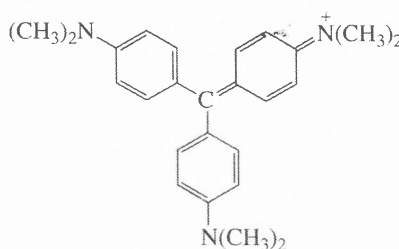
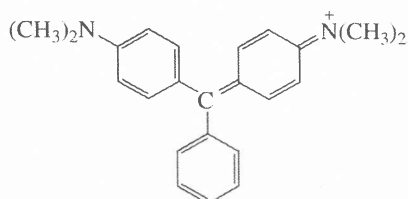
Azobenzenes (benzene rings connected by an $\text{N}=\text{N}$ bond) have an extended conjugated system that causes them to absorb light from the visible region of the spectrum. Some substituted azobenzenes are used commercially as dyes. Varying the extent of conjugation and the substituents attached to the conjugated system provides a large number of different colors. Notice that the only difference between butter yellow and methyl orange is an $\text{SO}_3^- \text{Na}^+$ group. Methyl orange is a commonly used acid-base indicator. When margarine was first produced, it was colored with butter yellow to make it look more like butter. (White margarine would not have been very appetizing.) This dye was abandoned after it was found to be carcinogenic. β -Carotene is currently used to color margarine (page 325).



▲ Lycopene, β -carotene, and anthocyanins are found in the leaves of trees, but their characteristic colors are usually obscured by the green color of chlorophyll. In the fall when chlorophyll degrades, the colors become apparent.

PROBLEM 23

- At $\text{pH} = 7$, one of the following ions is purple and the other is blue. Which is which?
- What would be the difference in the colors of the compounds at $\text{pH} = 3$?



ANTHOCYANINS: A COLORFUL CLASS OF COMPOUNDS

A class of highly conjugated compounds called anthocyanins is responsible for the red, purple, and blue colors of many flowers (poppies, peonies, cornflowers), fruits (cranberries, rhubarb, strawberries, blueberries), and vegetables (beets, radishes, red cabbage).

In a neutral or basic solution, the monocyclic fragment of the anthocyanin is not conjugated with the rest of the molecule. The anthocyanin is a colorless compound because it does not

absorb visible light. In an acidic environment, the OH group becomes protonated and water is eliminated. (Recall that water, being a weak base, is a good leaving group.) Loss of water results in the third ring's becoming conjugated with the rest of the molecule. As a result of the extended conjugation, the anthocyanin absorbs visible light with wavelengths between 480 and 550 nm. The exact wavelength of light absorbed depends on the substituents (R) on the anthocyanin. Thus, the flower, fruit, or vegetable appears red, purple, or blue, depending on what the R groups are. You can see this if you change the pH of cranberry juice so that it is no longer acidic.

