

CHAPTER



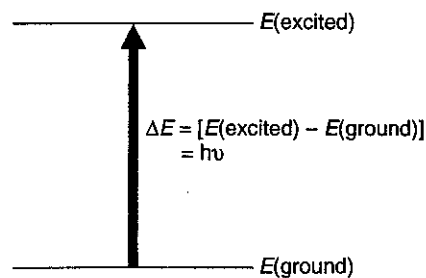
ULTRAVIOLET SPECTROSCOPY

Most organic molecules and functional groups are transparent in the portions of the electromagnetic spectrum which we call the **ultraviolet (UV)** and **visible (VIS)** regions—that is, the regions where wavelengths range from 190 nm to 800 nm. Consequently, absorption spectroscopy is of limited utility in this range of wavelengths. However, in some cases we can derive useful information from these regions of the spectrum. That information, when combined with the detail provided by infrared and nuclear magnetic resonance spectra, can lead to valuable structural proposals.

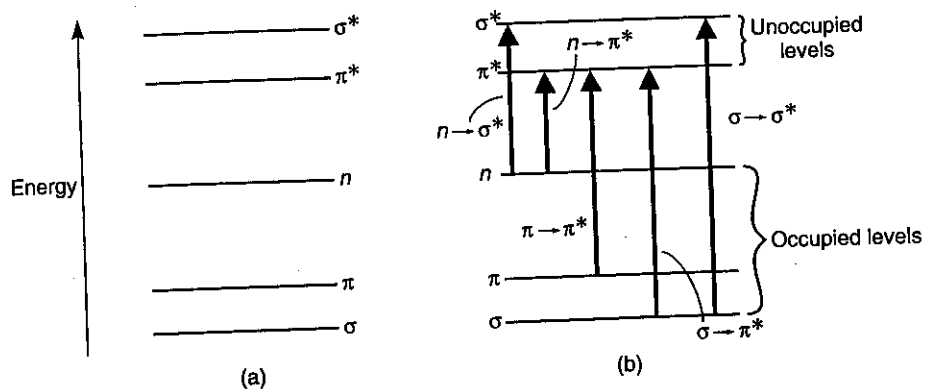
6.1 THE NATURE OF ELECTRONIC EXCITATIONS

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**). Figure 6.1 depicts this excitation process, which is quantized. The electromagnetic radiation which is absorbed has energy exactly equal to the energy *difference* between the excited and ground states.

In the case of ultraviolet and visible spectroscopy, the transitions which result in the absorption of electromagnetic radiation in this region of the spectrum are transitions between **electronic** energy levels. As a molecule absorbs energy, an electron is promoted from an occupied orbital to an unoccupied orbital of greater potential energy. Generally, the most probable transition is from



► **FIGURE 6.1** The excitation process.



► **FIGURE 6.2** Electronic energy levels and transitions.

the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**. The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole (kilojoules per mole).

For most molecules, the lowest-energy occupied molecular orbitals are the σ orbitals; which correspond to σ bonds. The π orbitals lie at somewhat higher energy levels, and orbitals which hold unshared pairs, the **nonbonding (n) orbitals**, lie at even higher energies. The unoccupied, or **antibonding orbitals (π^* and σ^*)**, are the orbitals of highest energy. Figure 6.2a shows a typical progression of electronic energy levels.

In all compounds other than alkanes, the electrons may undergo several possible transitions of different energies. Some of the most important transitions are:

↑	$\sigma \longrightarrow \sigma^*$	In alkanes
↑	$\sigma \longrightarrow \pi^*$	In carbonyl compounds
↑	$\pi \longrightarrow \pi^*$	In alkenes, carbonyl compounds, alkynes, azo compounds, and so on
↑	$n \longrightarrow \sigma^*$	In oxygen, nitrogen, sulfur, and halogen compounds
↑	$n \longrightarrow \pi^*$	In carbonyl compounds

Figure 6.2b illustrates these transitions. Electronic energy levels in aromatic molecules are more complicated than the ones depicted here. Section 6.14 will describe the electronic transitions of aromatic compounds.

Clearly, the energy required to bring about transitions from the highest occupied energy level (HOMO) in the ground state to the lowest unoccupied energy level (LUMO) is less than the energy required to bring about a transition from a lower occupied energy level. Thus, in Figure 6.2 an $n \rightarrow \pi^*$ transition would have a lower energy than a $\pi \rightarrow \pi^*$ transition. For many purposes, the transition of lowest energy is the most important.

Not all of the transitions which at first sight appear possible are observed. Certain restrictions, called **selection rules**, must be considered. One important selection rule states that transitions which 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 the numbers of electrons which may be excited at one time, with symmetry properties of the molecule and of the electronic states, and with other factors which need not be discussed here. Transitions that are formally forbidden by the selection rules are often not observed. However, theoretical

treatments are rather approximate, and in certain cases forbidden transitions *are* observed, although the intensity of the absorption tends to be much lower than for transitions which are **allowed** by the selection rules. The $n \rightarrow \pi^*$ transition is the most common type of forbidden transition.

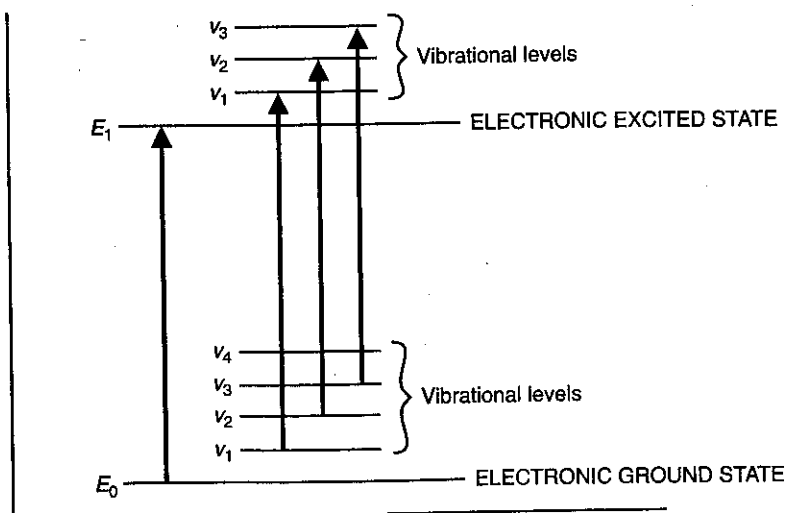
6.2 THE ORIGIN OF UV BAND STRUCTURE

For an atom which absorbs in the ultraviolet, the absorption spectrum often 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 6.3.

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.

6.3 PRINCIPLES OF ABSORPTION SPECTROSCOPY

The greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. Furthermore, the more effectively a molecule absorbs light of a given



► **FIGURE 6.3** Electronic transitions with vibrational transitions superimposed. (Rotational levels, which are very closely spaced within the vibrational levels, are omitted for clarity.)

TABLE 6.2

Solvent Shifts on the $n \rightarrow \pi^*$ Transition of Acetone

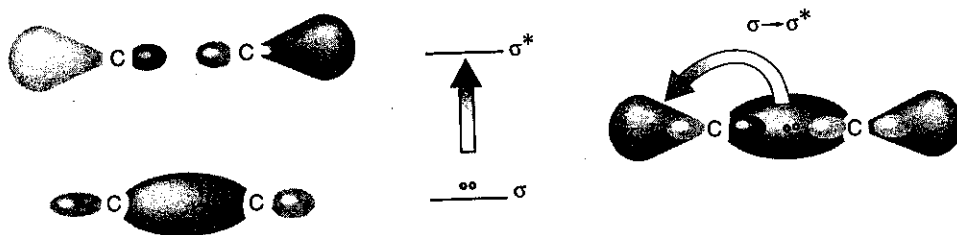
Solvent	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	CHCl ₃	C ₆ H ₁₄
λ_{max} (nm)	264.5	270	272	277	279

A third criterion for a good solvent is its ability to influence the wavelength of ultraviolet light which will be absorbed via stabilization of either the ground or the excited state. Polar solvents do not form hydrogen bonds as readily with the excited states of polar molecules as with their ground states, and these polar solvents increase the energies of electronic transitions in the molecules. Polar solvents shift transitions of the $n \rightarrow \pi^*$ type to shorter wavelengths. On the other hand, in some cases the excited states may form stronger hydrogen bonds than the corresponding ground states. In such a case, a polar solvent shifts an absorption to longer wavelength, since the energy of the electronic transition is decreased. Polar solvents shift transitions of the $\pi \rightarrow \pi^*$ type to longer wavelengths. Table 6.2 illustrates typical effects of a series of solvents on an electronic transition.

6.7 WHAT IS A CHROMOPHORE?

Although the absorption of ultraviolet radiation results from the excitation of electrons from ground to excited states, the nuclei which 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 are properties of a group of atoms rather than of electrons themselves. The group of atoms producing such an absorption is called a **chromophore**. 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, which contain nothing but single bonds and lack atoms with unshared electron pairs, the only electronic transitions possible are of the $\sigma \rightarrow \sigma^*$ 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. Figure 6.6 illustrates this type of transition. The excitation of the σ -bonding electron to the σ^* -antibonding orbital is depicted at the right.



► FIGURE 6.6 $\sigma \rightarrow \sigma^*$ transition.

SOLVENTS

The choice of the solvent to be used in ultraviolet spectroscopy is quite important. 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 which do not contain conjugated systems are most suitable for this purpose, although they vary as to the shortest wavelength at which they remain transparent to ultraviolet radiation. Table 6.1 lists some common ultraviolet spectroscopy solvents and their cutoff points, or minimum regions of transparency.

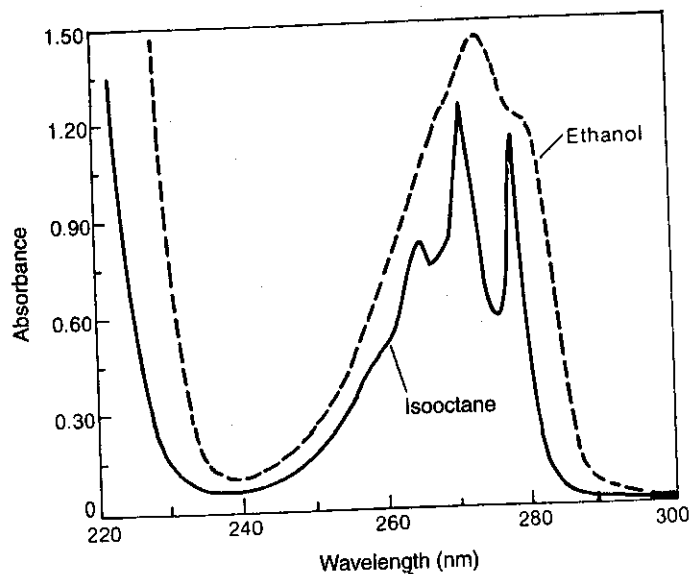
Of the solvents listed in Table 6.1, water, 95% ethanol, and hexane are most commonly used. Each is transparent in the regions of the ultraviolet spectrum where interesting absorption peaks from sample molecules are likely to occur.

A second criterion for a good solvent is its effect on the fine structure of an absorption band. Figure 6.5 illustrates the effects of polar and nonpolar solvents on an absorption band. A nonpolar 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, where fine structure is often observed. In a polar solvent, the hydrogen bonding forms a solute-solvent complex, and the fine structure may disappear.

TABLE 6.1

Solvent Cutoffs

Acetonitrile	190 nm	<i>n</i> -Hexane	201 nm
Chloroform	240	Methanol	205
Cyclohexane	195	Isooctane	195
1,4-Dioxane	215	Water	190
95% Ethanol	205	Trimethyl phosphate	210



► **FIGURE 6.5** Ultraviolet spectra of phenol in ethanol and in isooctane. (From Coggeshall, N. D., and E. M. Lang, *J. Am. Chem. Soc.*, 70 [1948]: 3288. Reprinted by permission.)