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Ultraviolet Spectroscopy

2.1 MECHANICS OF MEASUREMENT

In order to obtain useful information from the ultraviolet or visible spectrum of a compound, the wavelength of maximum absorption (λ_{\max}) and the intensity of absorption must be measured accurately. The compound should be dissolved in some suitable solvent that does not itself absorb light in the region under investigation. The most commonly used solvent for ultraviolet spectral determinations is 95% ethyl alcohol. Water and hexane are also commonly used. The positions of the absorption peaks of a compound may be shifted somewhat if different solvents are used. The λ_{\max} for nonpolar compounds is generally the same in alcohol and hexane; the λ_{\max} for polar compounds is usually shifted.

The solution must be placed in some suitable container that is transparent to light in the region being studied. Although ordinary glass is satisfactory for work in the visible region, glass absorbs ultraviolet light strongly; hence, quartz cells must be used. The most commonly used cells have 1.0 cm path length. Modern spectrophotometers provide a plot of the intensity of transmitted or absorbed light versus wavelength. The most suitable source of light in the ultraviolet region (180–400 $m\mu$) is the hydrogen-discharge lamp. A tungsten-filament lamp is usually used for the visible region (400–800 $m\mu$) of the spectrum. Most spectrophotometers are double-beam instruments. The primary source of light is split into two beams, one of which passes through a cell containing the sample solution and the other of which passes through a cell containing the reference solvent. The spectrophotometer electronically subtracts the absorption of the solvent in the reference beam from the absorption of the solution in the sample beam. Thus, effects owing to absorption of light by the solvent are minimized.

The ordinary visible-ultraviolet spectrophotometer provides acceptable spectra over the range 220–800 $m\mu$. Better instruments have mechanical improvements that extend the short-wavelength range to about 185 $m\mu$. The major limitation in this short-wavelength range is the presence of air in the instrument. Oxygen absorbs strongly at about 200 $m\mu$ and below; frequently the range of the instrument can be extended by flushing the

instrument with nitrogen, which absorbs strongly at about 150 m μ and below. The technique of using an evacuated spectrophotometer enables the range below 200 m μ to be studied. This region is frequently called the *vacuum ultraviolet region*.

Most recording spectrophotometers record wavelength versus absorbance. The absorbance A or "optical density" is given by

$$A = \log \frac{I_0}{I}$$

where I_0 is the intensity of incident light and I is the intensity of transmitted light. The range of absorbance commonly recorded is 0–2.0. The calculation of the intensity of an absorption band involves the use of Lambert's and Beer's laws. Lambert's law states that the intensity of transmitted light passing through a homogeneous medium decreases geometrically as the thickness of the layer increases arithmetically. Beer's law states that each molecule of solute absorbs the same fraction of light incident upon it, regardless of concentration, in a nonabsorbing medium. Beer's law does not hold over the entire concentration range, but in very dilute solutions, as is usually the case in ultraviolet spectroscopy, the deviations are small. These laws can be formulated by the relationship

$$\epsilon = \frac{A}{cl}$$

where ϵ is the molar extinction coefficient, c is the molar concentration, and l is the path length in centimeters. Experimental results are usually reported in terms of the molar extinction coefficient ϵ or its logarithm $\log \epsilon$. When the molecular weight of a substance is unknown, the intensity of absorption is conveniently expressed as the $E_{1\%}^{1\text{ cm}}$ (or $A_{1\%}^{1\text{ cm}}$) value, the absorbance of a 1% solution of the substance in a 1.0 cm cell. This value is easily related to the molar extinction coefficient by the expression

$$10 \epsilon = E_{1\%}^{1\text{ cm}} \times \text{mol. wt.}$$

2.2 ELECTRONIC EXCITATION

The absorption of light energy by organic compounds in the visible and ultraviolet region involves promotion of electrons in σ , π , and n -orbitals† from the ground state to higher-energy states. These higher-energy states are described by molecular orbitals that are vacant in the ground or unexcited state and are commonly called *antibonding orbitals*. The antibonding orbital associated with the σ bond is called the σ^* (sigma star) orbital and that associated with the π bond is called the π^* (pi star)

† Many molecules contain electrons that are not directly involved in bonding; these are called nonbonding or n electrons and are mainly located in atomic orbitals of oxygen, sulfur, nitrogen, and the halogens.

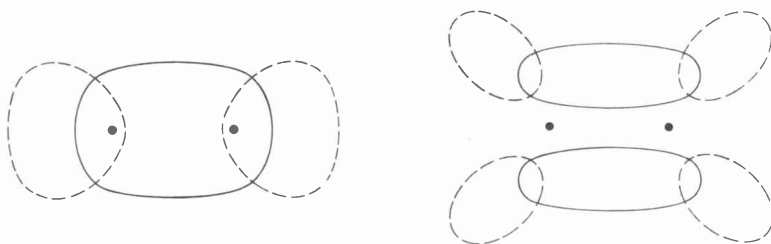


Fig. 2-1 Left, σ and σ^* orbitals; right, π and π^* orbitals.

orbital. As the n electrons do not form bonds, there are no antibonding orbitals associated with them. The generalized shapes of σ , σ^* , π , and π^* orbitals are shown in Fig. 2-1, where solid lines refer to σ and π bonding orbitals and dashed lines refer to σ^* and π^* antibonding orbitals; the dots represent atomic centers. The presence of an electron in an antibonding orbital clearly indicates that the molecule is in a high-energy state. The electron density between the atomic nuclei is *less* than that at the same distance from the nucleus in an isolated atom. In the excited state some, but not all, of the electrons in a molecule occupy antibonding orbitals; were it not for the fact that bonding orbitals in lower-energy states have sufficient bonding character to insure stability, dissociation would occur.

The electronic transitions (\rightarrow) that are involved in the ultraviolet and visible regions are of the following types: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$. The energy required for the $\sigma \rightarrow \sigma^*$ transition is very high; consequently, compounds in which all valence shell electrons are involved in single-bond formation, such as saturated hydrocarbons, do not show absorption in the ordinary ultraviolet region. An exception is cyclopropane, which shows λ_{\max} about 190 m μ . (Propane shows λ_{\max} about 135 m μ .)

Compounds that contain nonbonding electrons on oxygen, nitrogen, sulfur, or halogen atoms are capable of showing absorptions, owing to $n \rightarrow \sigma^*$ transitions. These transitions are of lower energy than $\sigma \rightarrow \sigma^*$ transitions; consequently, molecules containing nonbonding electrons usually exhibit absorption in the ordinary ultraviolet region. Examples of $n \rightarrow \sigma^*$ transitions are shown by methyl alcohol, $\lambda_{\max}^{\text{vapor}}$ 183 m μ , ϵ 150, trimethylamine, $\lambda_{\max}^{\text{vapor}}$ 227 m μ , ϵ 900, methyl chloride, $\lambda_{\max}^{\text{vapor}}$ 173 m μ , $\epsilon \sim 100$, and methyl iodide, $\lambda_{\max}^{\text{hexane}}$ 258 m μ , ϵ 378. The spectrum of trimethylamine determined in aqueous acid shows no absorption due to a $n \rightarrow \sigma^*$ transition, because the protonated amine contains no nonbonding electrons. Whether an organic compound contains a particular spectral pattern above 210 m μ or not, it will quite generally show some absorption that increases in intensity toward shorter wavelength in this region. This absorption is due in part to $n \rightarrow \sigma^*$ transitions near 200 m μ if the molecule contains oxygen, nitrogen, sulfur, or halogen atoms. This absorption is generally called *end absorption*.

Transitions to antibonding π^* orbitals are associated only with unsaturated centers in the molecule; these are of still lower energy requirement and occur at longer wavelengths, usually well within the region of the ordinary ultraviolet spectrophotometer. For example, saturated aldehydes and ketones exhibit an absorption of low intensity around $285\text{ m}\mu$, which is attributed to an $n \rightarrow \pi^*$ transition, and an absorption of high intensity around $180\text{ m}\mu$, which is attributed to a $\pi \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transitions are of intermediate energy; absorptions owing to these transitions are usually between those owing to $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Figure 2-2 shows the general relative electronic excitation energies for these transitions. The high-energy transitions ($\sigma \rightarrow \sigma^*$) occur at shorter wavelength and the low-energy transitions ($n \rightarrow \pi^*$) occur at longer wavelength.

Identical functional groups in different molecules will not necessarily absorb at exactly the same wavelength. The energy change for a particular transition dictates the position of absorption of a given group. Transitions in identical functional groups in different molecules will not necessarily have *exactly* the same energy requirement because of different structural environments.

The magnitude of the molar extinction coefficient for a particular absorption is directly proportional to the *probability* of the particular electronic transition; the more probable a given transition, the larger the extinction coefficient.

The exact electronic structures of the high-energy states of molecules that have absorbed ultraviolet or visible light are not well understood. Some appear to have greater or less polar character than the ground-state structure; some appear to be biradicals; other activated structures are possible. In any event, electronic transitions result in a redistribution of electrons within the molecule. The structures of the excited states of carbonyl compounds such as aldehydes and ketones have perhaps been

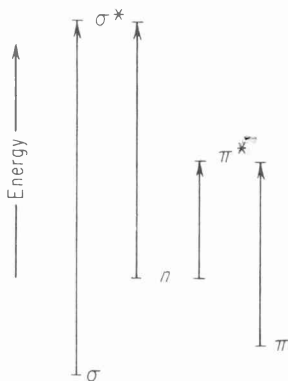


Fig. 2-2 Schematic electronic excitation energies (no quantitative aspects are intended).

studied most extensively. In the ground state the structure of the carbonyl group (>C=O) contains an important contribution from the polar form $\text{>C}^+-\text{O}^-$ ($\text{>}\overset{\delta+}{\text{C}}\cdots\overset{\delta-}{\text{O}}$). The position of an absorption that involves nonbonding electrons ($n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$) is particularly sensitive to the polarity of the solvent used in the determination. If the group is more polar in the ground state than in the excited state, the nonbonding electrons in the ground state are stabilized (*relative* to the excited state) by hydrogen bonding or electrostatic interaction with a polar solvent; the absorption is shifted to shorter wavelength (higher energy) with increasing solvent polarity. Conversely, if the group is more polar in the excited state, the nonbonding electrons of the excited state are stabilized (*relative* to the ground state) by interaction with a polar solvent; the absorption is shifted to longer wavelength (lower energy) with increasing solvent polarity. Polar solvents generally shift the $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelength and the $\pi \rightarrow \pi^*$ band to longer wavelength. The magnitude of the shift in the latter case is not usually as large as that in the former.

The α,β -unsaturated ketone mesityl oxide (4-methyl-3-penten-2-one) shows λ_{max} 230 $\text{m}\mu$, ϵ 12,600 and λ_{max} 329 $\text{m}\mu$, ϵ 41 in hexane and λ_{max} 243 $\text{m}\mu$, ϵ 10,000 and λ_{max} 305 $\text{m}\mu$, ϵ 60 in water. These data indicate that the long wavelength $n \rightarrow \pi^*$ absorption is shifted 24 $\text{m}\mu$ to shorter wavelength (higher energy) in the more polar solvent; thus the excited state would appear to be less polar than the ground state. The excited state of the $n \rightarrow \pi^*$ transition of ketones seems to have major contributions from structures such as

>C=O and $\text{>}\overset{\delta-}{\text{C}}-\overset{\delta+}{\text{O}}$ ($\text{>}\overset{\delta-}{\text{C}}\cdots\overset{\delta+}{\text{O}}$) rather than $\text{>C}^+-\text{O}^-$ as in the ground state.

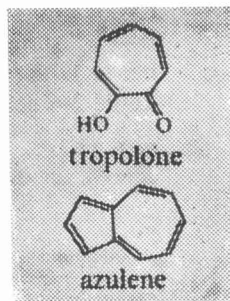
The shift to longer wavelength (lower energy) observed in the $\pi \rightarrow \pi^*$ transitions of α,β -unsaturated ketones (13 $\text{m}\mu$ for mesityl oxide) with increasing solvent polarity indicates that the excited state in this transition is more polar than the ground state. For this transition the data have been interpreted as the promotion of an ethylenic π electron to a carbonyl π^* orbital. Because intramolecular effects such as these involve the transfer of charge from one atom to another, they are frequently called *charge-transfer* spectra.

2.3 SIMPLE CHROMOPHORIC GROUPS

Saturated hydrocarbons and compounds containing only saturated alkyl groups, alcohol groups, and ether groups are transparent (that is, they show no absorption) in the region 200–1000 $\text{m}\mu$. Such compounds

have complicated spectra consisting of a number of relatively intense bands throughout most of the ultraviolet region (up to $360\text{ m}\mu$) and a number of relatively weak bands throughout most of the visible region ($500\text{--}700\text{ m}\mu$). As a consequence of the latter, azulene and most of its derivatives are blue.

The spectra of simple heterocyclic aromatic compounds grossly resemble spectra of benzenoid compounds in that they consist of an absorption peak of relatively large extinction coefficient (ϵ 5,000–15,000) at short wavelength (λ_{max} 190–240 $\text{m}\mu$) and a series of fine-structure bands of lower intensity (ϵ 1–400) at longer wavelengths (λ_{max} 240–300 $\text{m}\mu$).

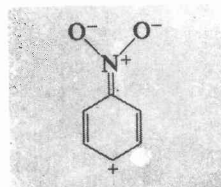


2.7 STEREOCHEMISTRY

The absorptions by compounds containing extended conjugation are caused by $\pi \rightarrow \pi^*$ transitions that arise from the delocalized π electron systems present. The intensities and positions of these peaks depend on the lengths of the conjugated systems; the longer such a system, the longer the wavelength of the absorption and the larger the extinction coefficient. When the π electron system is prevented from achieving coplanarity, the degree of overlap of the π electron system will be diminished; a marked effect on the ultraviolet spectrum results.

Hindered rotation in biphenyls is readily studied by ultraviolet spectroscopy. Then $\pi \rightarrow \pi^*$ transition of biphenyl, which readily achieves coplanarity, results in λ_{max} 246 $\text{m}\mu$, ϵ 16,300. If large groups are present in *ortho* positions, coplanarity is restricted and the length of the π electron system is effectively diminished. For example, dimesityl (2,4,6,2',4',6'-hexamethylbiphenyl) shows λ_{max} 267 $\text{m}\mu$, ϵ 545, an extinction coefficient essentially only twice that of mesitylene itself, λ_{max} 266 $\text{m}\mu$, ϵ 260. Another example of steric hindrance to coplanarity may be found in nitrobenzene derivatives (data for heptane solutions): nitrobenzene, λ_{max} 252 $\text{m}\mu$, ϵ 8,620; *o*-nitrotoluene, λ_{max} 250 $\text{m}\mu$, ϵ 5,950; *o*-nitrocumene, λ_{max} 247 $\text{m}\mu$, ϵ 3,760; for *o*-nitro-*t*-butylbenzene, there is no λ_{max} in this region, but at 250 $\text{m}\mu$, ϵ is 1,450. Because the λ_{max} of nitrobenzene is dependent on the polarity of the solvent used, the activated structure has been shown to have charge-transfer character, as shown by **5**. The presence of increasingly bulky *ortho* substituents effectively hinders the coplanarity that the nitro group achieves with the benzene ring.

Of a pair of geometrical isomers, the *cis* form would be expected to be more sterically hindered, and the *trans* form would be expected to achieve coplanarity of the π electron system more readily. Data obtained



for *cis* and *trans* isomers quite generally show that absorption due to the $\pi \rightarrow \pi^*$ transition of the *trans* isomer occurs at longer wavelength and has a larger extinction coefficient than that of the *cis* isomer. Data in Table 2-6 demonstrate this effect.

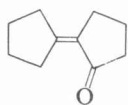
Table 2-6

ULTRAVIOLET ABSORPTION OF SOME *cis* AND *trans* ISOMERS

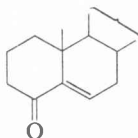
Compound	<i>cis</i> -Isomer		<i>trans</i> -Isomer	
	λ_{\max} , m μ	ϵ_{\max}	λ_{\max} , m μ	ϵ_{\max}
Cinnamic acid	268	10,700	272	15,900
Stilbene	278	9,350	294	24,000

2.8 PROBLEMS

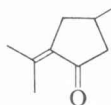
1. The following α,β -unsaturated ketones have λ_{\max} at 241 m μ (ϵ 4,700), 254 m μ (ϵ 9,550), and 259 m μ (ϵ 10,790) in ethanol. Which is which?



(1a)

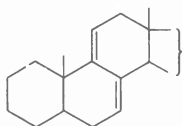


(1b)

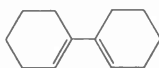


(1c)

2. The following dienes have λ_{\max} at 231 m μ (ϵ 21,000), 236 m μ (ϵ 12,000), 245 m μ (ϵ 18,000), 265 m μ (ϵ 6,400), and 282 m μ (ϵ 11,900) in ethanol. Which is which?



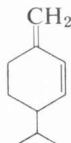
(2a)



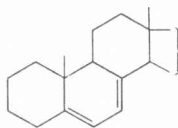
(2b)



(2c)

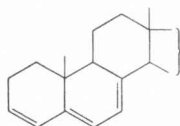


(2d)

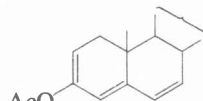


(2e)

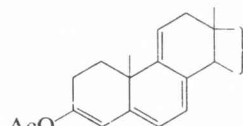
3. The following polyenes have λ_{\max} at 306 m μ (ϵ 14,500), 315 m μ (ϵ 19,800), and 355 m μ (ϵ 19,700) in ethanol. Which is which?



(3a)



(3b)



(3c)