ULTRAVIOLET SPECTROSCOPY

SEM-4, CC-8
PART-1, PPT-2

Contents

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Introduction

The UV portion of the electromagnetic spectrum is indicated in **Figure 1**. Ultraviolet light is a region of the light spectrum that is between visible light and X-rays. Wavelengths in the UV region are usually expressed in nanometers (1 nm = 10^{-9} m) or angstroms, Å (1Å = 10^{-10} m). Generally, near-UV region extends from 200 to 400 nm of the electromagnetic spectrum. The atmosphere is transparent in this region. Oxygen absorbs strongly at about 200 nm and below.

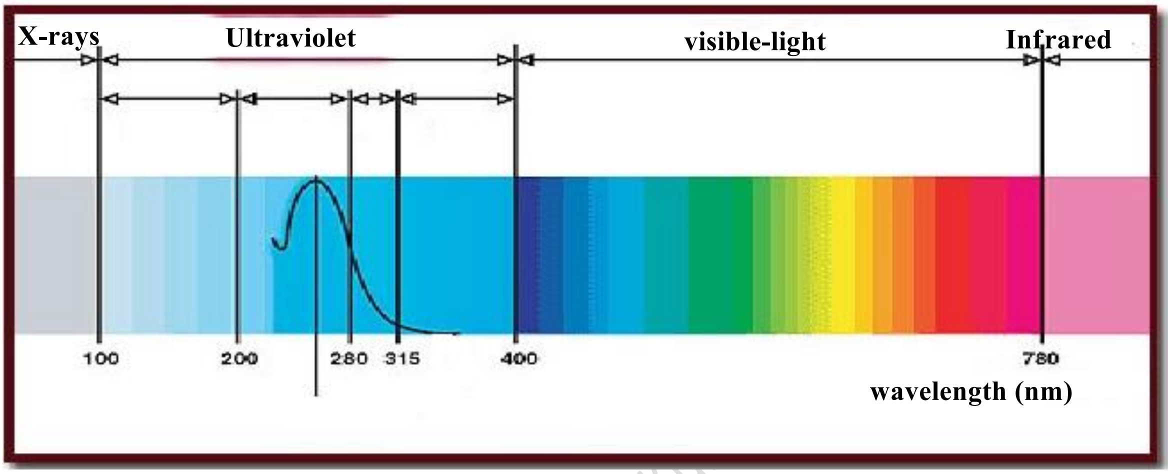

Figure 1: UV portion (200-400 nm) of electromagnetic spectrum

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. Energy of absorption corresponding to this wavelength range (200-400 nm) is 143-71.5 kcal mol^{-1}. It is obtained from the following expression:

$$\boxed{E = \frac{28600}{\lambda\ (\mathrm{nm})}\ \mathrm{kcal\ mol^{-1}}}$$

The energy absorbed is dependent on the energy difference between the ***ground state*** and the ***excited state.*** The smaller is the energy difference, the longer is the wavelength of absorption. **Figure 2** illustrates the transition.

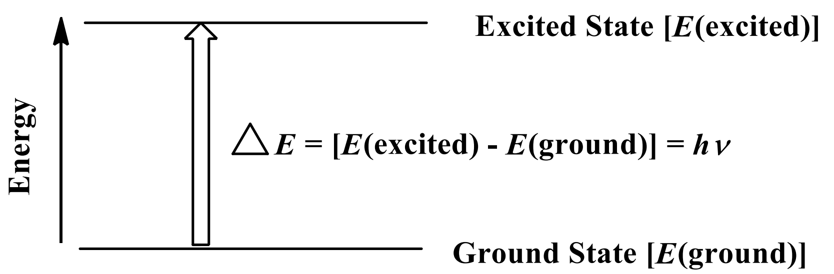

Figure 2: The excitation process

The energies noted in **Figure 2** are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called **“*electronic spectroscopy*”**.

The excess energy in the ***excited state*** may result in dissociation or ionization of the molecule, or it may be re-emitted as heat or light. The release of energy as light results in ***fluorescence*** or ***phosphorescence***.

The Nature of UV Spectrum

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength.

A UV spectrum obtained directly from an instrument is simply a plot of wavelength (or frequency) of absorption versus the absorption intensity (absorbance or transmittance) as in the isoprene spectrum shown in **Figure 3**.

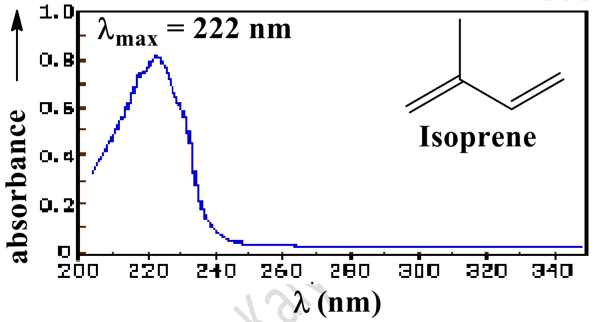

Figure 3: UV spectrum of isoprene

The data are frequently converted to a graphical plot of wavelength ***versus*** the molar absorptivity (ε_{max} or log ε_{max}). The use of molar absorptivity as the unit of absorption intensity has the advantage that all intensity values refer to the same number of absorbing species. There is an advantage to the selectivity of UV absorption. Characteristic groups may be recognized in molecules of widely varying complexities.

A large portion of a relatively complex molecule may be transparent in the UV so that a spectrum similar to that of a much simpler molecule may be obtained. For many electronic structures, the absorption does not occur in the readily accessible portion of the UV region. In practice, UV spectrometry is normally limited to conjugated systems.

The Origin of 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 normally have many excited modes of vibration and rotation at room temperature. Consequently, a collection of molecules generally has its members in many states of vibrational and rotational excitation.

The energy levels for these vibrational and rotational 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 undergo electronic and vibrational-rotational excitation simultaneously, as shown in **Figure 4**.

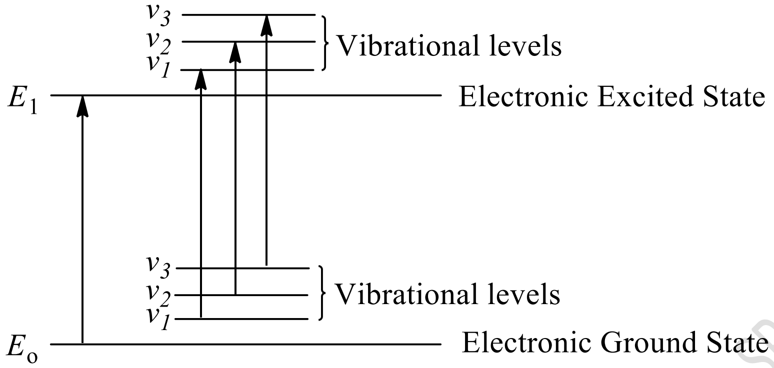

Figure 4: Electronic transitions with vibrational transitions superimposed. (Rotational levels, which are very closely spaced within the vibrational levels, are omitted here.)

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. At ordinary temperatures, the molecules in the electronic ***ground state*** will be largely in the zero vibrational level. Consequently, there are many electronic transitions that can take place from that level.

In molecules containing more atoms, the multiplicity of vibrational sublevels and the closeness of their spacing cause the discrete bands to coalesce, and broad absorption bands or “band envelopes” are obtained. The consequence of 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.

Since UV energy is quantized, the absorption spectrum arising from a single electronic transition should consist of a single, discrete line. A discrete line is not obtained since an electronic level is associated with a large number of vibrational and rotational levels, a transition from one electronic level to another may be accompanied by vibrational and rotational transitions. This results in the absorption of a range of photons, and consequently the spectrum consists of a family of lines which are usually so closely spaced that they merge into a broad band. The spectra of simple molecules in the gaseous state consist of narrow absorption bands.

The Nature of Electronic Excitations

Molecular absorption in the ultraviolet (UV) and visible region of the spectrum is dependent on the electronic structure of the molecule. Absorption of energy is quantized, resulting in the elevation of electrons from orbitals in the ***ground state to*** higher energy orbitals in an ***excited state***.

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 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.

The absorption of light energy by organic compounds in the visible and ultraviolet region involves the promotion of electrons in σ-, π- and n-orbitals from the *ground state* to the higher energy states. These higher energy states are described by molecular orbitals that are vacant in the ground or unexcited states and are called *antibonding orbitals*.

Many molecules containing electrons that are not directly involved in bonding are called nonbonding or n-electrons and are mainly located in atomic orbitals of oxygen, sulphur and the halogens. The *antibonding orbital* associated with the σ-bond is called σ^*-orbital and that associated with the π-bond is called the π^*-orbital. As the n-electrons do not form bonds, there are no *antibonding orbitals* associated with them.

The presence of an electron in an *antibonding orbital* clearly indicates that the molecule is in a high energy state. 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 electronic transitions (→) that are involved in the ultraviolet and visible regions are of the following types: $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$. Figure 5a shows a typical progression of electronic energy levels and Figure 5b illustrates these transitions.

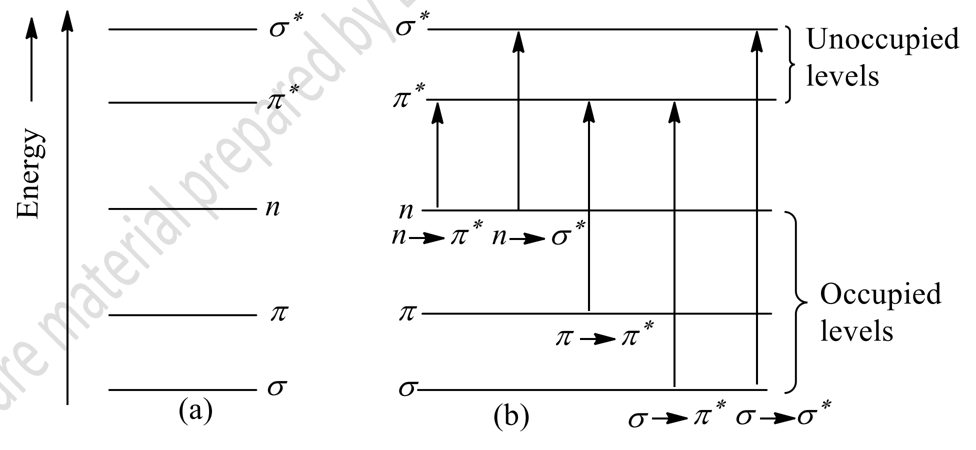

Figure 5: Electronic Energy levels and Transitions

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 5b** an $\boldsymbol{n \rightarrow \pi^*}$ transition would have a lower energy than a $\boldsymbol{\pi \rightarrow \pi^*}$ transition. In all compounds other than alkanes, the electrons may undergo several possible transitions of different energies. Some of the most important transitions are shown in **Table 1**.

Table 1: Possible Transitions in different Organic Compounds

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

The principal characteristics of an absorption band are its position and intensity. The position of absorption corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition.

Transition Probability

Not all of the electronic transitions that at first sight appear possible in the visible and ultraviolet region are observed. Certain restrictions, called **selection rules,** must be considered. On these bases, some of these transitions are allowed, i.e., have high probability, or are forbidden, i.e., have low probability. The essential condition for an electronic transition to take place is that the transition dipole (which is related to the dipole moment of the molecule) is not zero.

One transition that would lead to a zero-transition dipole is that in which there is electron spin inversion on excitation. This is the basis of selection rule of multiplicity: *no change in spin multiplicity occurs during a transition.* Thus, according to this selection rule ***singlet-singlet*** and triplet-***triplet*** transitions are allowed, but ***singlet-triplet*** and ***triplet-singlet*** transitions are forbidden. This rule is based on the assumption that a molecule has a fixed shape which remains unchanged on excitation.

In practice, there are always some vibrations in a polyatomic molecule which periodically change the shape of that molecule, e.g., bending vibrations. This enables a forbidden transition to become allowed to some extent. Other selection rules deal with the numbers of electrons that may be excited at one time, with symmetry properties of the molecule and of the electronic states involved in transition.

The principal characteristics of an absorption band are its position and intensity. The intensity of absorption is largely dependent on two factors: the probability of interaction between the radiating energy and the electronic system and the difference between the ***ground*** and the ***excited state***. The intensity of an absorption band in the UV spectrum is usually expressed as the molar absorptivity at maximum absorption, ε_{max} or log ε_{max}. The intensity of a particular transition is determined from molar extinction coefficient (ε_{max}).

The magnitude of molar extinction coefficient (ε_{max}) for a particular absorption is directly proportional to the probability of the particular transition: the more probable a given transition, the larger is the extinction coefficient (ε_{max}). The probability of transition is proportional to the square of the transition moment. The transition moment, or dipole moment of transition is proportional to the change in the electronic charge distribution occurring during excitation.

Intense absorption occurs when a transition is accompanied by a large change in the transition moment. Absorption with $\boldsymbol{\varepsilon}_{\mathbf{max}} > 10^4$ is a high intensity transition which is due to an ***allowed transition***. Low intensity transitions correspond to $\boldsymbol{\varepsilon}_{\mathbf{max}} < 10^2$. Transitions of low probability are ***forbidden transition***.

Transitions that are formally forbidden by the selection rules are often not observed. However, in certain cases forbidden transitions are observed, although the intensity of the absorption tends to be much lower than for transitions that are **allowed** by the selection rules. The $\boldsymbol{n \rightarrow \pi^*}$ transition is the most common type of ***forbidden transition.***

Highly symmetric molecules (that is molecules with the high degree of symmetry), such as benzene, have more restrictions on their electronic transitions than the less symmetric molecules. Benzene is a highly symmetric molecule. It possesses a large number of symmetry elements and belongs to the point group $\mathbf{D_{6h}}$. Therefore, many restrictions apply to the electronic transitions of benzene, and consequently, the UV absorption spectrum of benzene is relatively simple.

For an unsymmetrical molecule, the only symmetry operations that can be performed is the identity operation. For such a molecule, no symmetry restrictions apply to the electronic transitions, and consequently, many transitions may be possible from the occupied to the unoccupied molecular orbitals resulting in a very complex electronic absorption spectrum.

To decide whether a transition between two given molecular orbitals is **allowed** or **forbidden**, the following factors need to be considered:

1. The geometry of the *ground state* molecular orbital (here, *HOMO*).
2. The geometry of the *excited state* molecular orbital (here, *LUMO*).
3. The orientation of the electric dipole of the incident light that induces the electronic transition.

The $\boldsymbol{\varepsilon}_{\mathbf{max}}$ is actually a complex function which, for any particular peak in a spectrum, is dependent on the cross-sectional area (target area of the absorbing system, i.e., a chromophore) of the molecule (**A** in cm²) and its probability of transition (**P**):

$$\boldsymbol{\varepsilon = 8.7 \times 10^{19} \times P \times A.}$$

With transition probabilities ranging from: **0** < **P** <**1**, extinction coefficients generally range from 10^2 to 10^5. The transition probabilities < 0.01 are called "***forbidden***" transitions, in other words, not likely to occur relative to other more favorable routes of electronic excitation.

In summary,

- $\boldsymbol{\varepsilon}_{\mathbf{max}} \sim 10^4$ to 10^5 yields strong absorption (intensity)
- $\boldsymbol{\varepsilon}_{\mathbf{max}} \sim 10^3$ yields medium absorption (intensity)
- $\boldsymbol{\varepsilon}_{\mathbf{max}} < 10^3$ yields low absorption (intensity)