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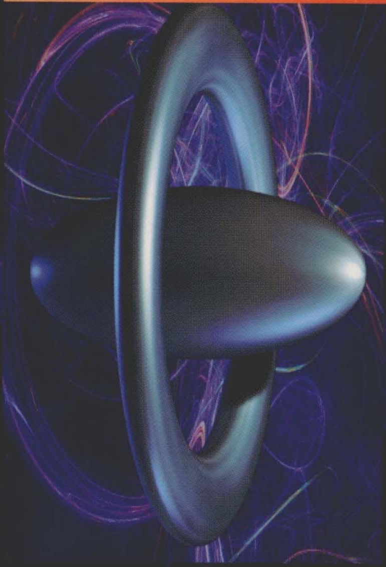

Organic Spectroscopic Analysis

by ROSALEEN J. ANDERSON, DAVID J. BENDELL
and PAUL W. GROUNDWATER

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ROSALEEN J. ANDERSON,
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PAUL W. GROUNDWATER
University of Sunderland

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Preface

The aim of this textbook is not to provide you, the reader, with large numbers of correlation tables for every form of spectroscopy used by organic chemists; nor is it designed to give you an in-depth understanding of the physical processes that occur when molecules interact with electromagnetic radiation. What we hope to do in this textbook is to provide you with a basic understanding of how each type of spectroscopy gives rise to spectra, and how these spectra can be used to determine the structure of organic molecules. This text is aimed at undergraduate students in Years 1 and 2, and is meant to provide an introduction to organic spectroscopic analysis, leading to an appreciation of the information available from each form of spectroscopy and an ability to use spectroscopic information in the identification of organic compounds.

We will concentrate upon the most commonly used techniques in organic structure determination: nuclear magnetic resonance (NMR), infrared (IR) and ultraviolet-visible (UV-Vis) spectroscopy, and mass spectrometry (MS). The amount of space devoted to each technique in this text is meant to be representative of their current usage for structure determination.

Finally, we will try to bring all of these techniques together in an attempt to show you how to go about the structure determination of an unknown compound in a (reasonably) logical manner. Our aim has been to provide spectra to illustrate every point made, but do analyse fully each of the spectra in order to obtain the maximum information available. We hope you enjoy this text and find it useful in your studies.

R. J. Anderson, D. J. Bendell and P. W. Groundwater
Sunderland

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1

General Principles

Aims

This chapter introduces the interaction of electromagnetic radiation with organic molecules. By the end of the chapter you should be able to:

- Predict the region of the electromagnetic spectrum in which the different molecular transitions occur
- Understand the relationship between the energy of a transition and its frequency, wavelength and wavenumber
- Calculate the number of double bond equivalents in a molecule from its formula

1.1 The Interaction of Electromagnetic Radiation with Molecules

You will already know from your studies that the energy levels of atoms and molecules are **quantized**, *i.e.* there are discrete energy levels in atoms and molecules (Figure 1.1).

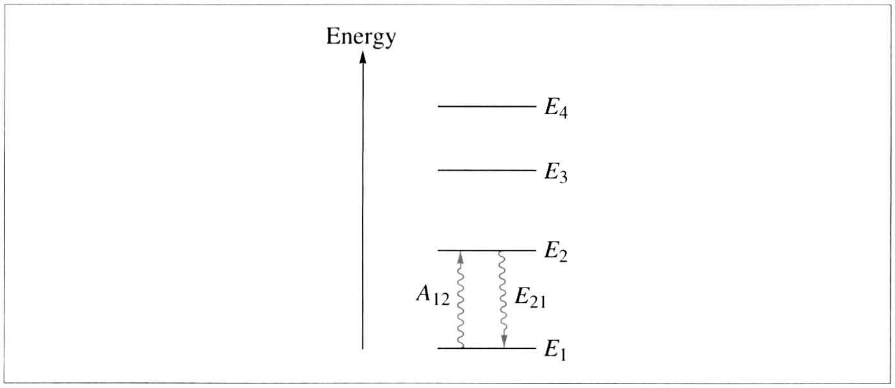


Figure 1.1 Discrete energy levels of an atom or molecule

In Figure 1.1, E_1 corresponds to the ground state of the atom/molecule, and E_2, E_3 and E_4 represent excited states. Given that these are all discrete energy levels, the difference in energy between them (and so the energy required for a particular transition) will also be a discrete value, which is called a **quantum**. We can see from Figure 1.1 that in order to excite the atom/molecule from E_1 to E_2 it must absorb an amount of energy equivalent to A_{12}. Excited states are generally short lived and relax back to the ground state by emission of energy, in this case E_{21}.

The energy difference between the excited state (E_2) and the ground state (E_1) will correspond to a certain **frequency** (ν) or **wavelength** (λ) of electromagnetic radiation, and this will depend upon the type of transition (and hence the separation between energy levels). The relationship between the energy of a transition and the frequency is given by equation (1.1):

h is Planck's constant (6.626×10^{-34} J s).

$$\Delta E = h\nu \tag{1.1}$$

and so:

$c = \lambda\nu$.

$$\Delta E = hc/\lambda \quad \text{or} \quad \Delta E = hc\bar{\nu} \tag{1.2}$$

The energy of a particular transition is, therefore, proportional to the frequency or wavenumber ($\bar{\nu} = 1/\lambda$) and inversely proportional to the wavelength (equation 1.2).

The **electromagnetic spectrum** is divided into a number of regions. The names of these regions and the associated atomic/molecular transitions, together with the corresponding energies, frequencies, wavelengths and wavenumbers, are shown in Figure 1.2.

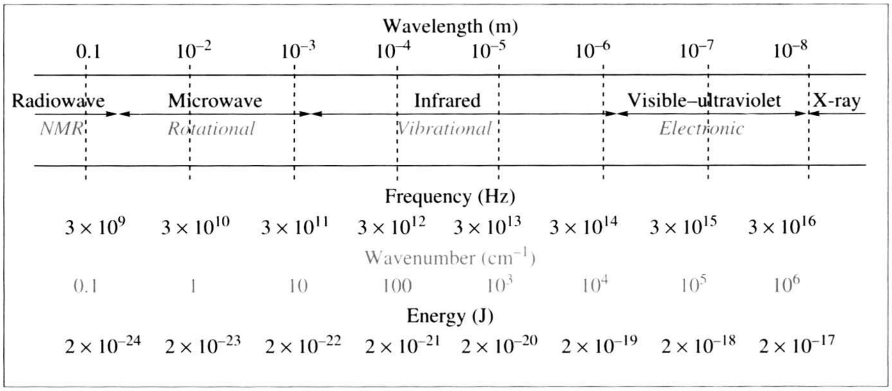

Wavelength (m)
0.1
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
Radiowave
Microwave
Infrared
Visible–ultraviolet
X-ray
NMR
Rotational
Vibrational
Electronic
Frequency (Hz)
3 × 10^9
3 × 10^10
3 × 10^11
3 × 10^12
3 × 10^13
3 × 10^14
3 × 10^15
3 × 10^16
Wavenumber (cm^-1)
0.1
1
10
100
10^3
10^4
10^5
10^6
Energy (J)
2 × 10^-24
2 × 10^-23
2 × 10^-22
2 × 10^-21
2 × 10^-20
2 × 10^-19
2 × 10^-18
2 × 10^-17

Figure 1.2 The electromagnetic spectrum

From Figure 1.2 we can see that **nuclear magnetic resonance** transitions (NMR), which correspond to wavelengths in the radiowave region of the spectrum, are those with the smallest gap between the energy levels, and electronic transitions in the **ultraviolet-visible** (UV-Vis) region have the largest energy gap between transition levels. The UV-Vis region is important, since absorptions in this region give rise to the colour associated with molecules; Figure 1.3 shows this region in more detail.

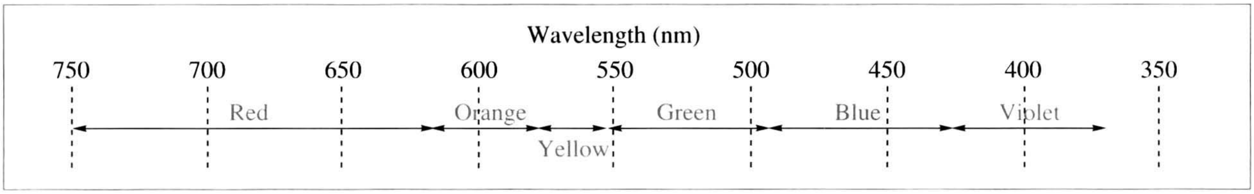


Figure 1.3 The visible region of the electromagnetic spectrum

X-rays have such high energy that they are capable of ionizing atoms and molecules, but they are also important in terms of structure determination using single-crystal X-ray diffraction. This technique is the ultimate in structure determination since it provides a "map" of the molecule in the crystal, *e.g.* Figure 1.4, but it is highly specialized, is limited to crystals and is not routinely available for all organic chemists, so it will not be discussed any further here.

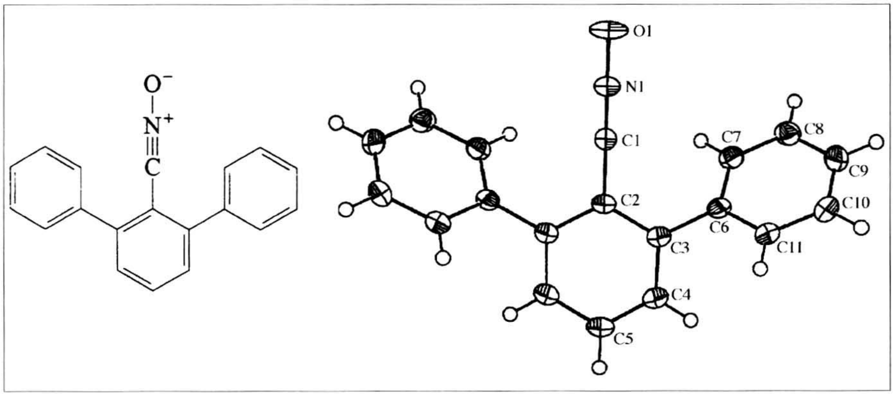


Figure 1.4 Single-crystal X-ray structure of 2,6-diphenylbenzonitrile oxide

Microwave (rotational) spectra are very complex, even for diatomic molecules, and give little useful information on organic molecules, which are relatively large. Rotational transitions are often responsible for the broadness of **infrared** (IR) bands, since each vibrational transition has a number of rotational transitions associated with it. The use of microwave spectroscopy is extremely rare in organic chemistry, and it too will be discussed no further here.

Transitions in all of the other forms of spectroscopy (UV-Vis, IR and NMR) are governed by **selection rules** that state which transitions are "**allowed**" and which are "**forbidden**" (although these latter transitions may still take place). We will mention the selection rules for each of these forms of spectroscopy when we study them in detail in Chapters 2–4.

Finally, one technique that does not rely upon electromagnetic radiation, **mass spectrometry**, will be discussed in detail in Chapter 5.

1.2 Double Bond Equivalents

Before we begin our study of these spectroscopic techniques, a reminder of a non-spectroscopic piece of information which is very useful in the determination of organic structures: the number of **double bond equivalents**, DBE (Ω), which tells us how many double bonds or rings are present in a molecule. Each double bond or ring reduces the number of hydrogens (or halogens) in a molecule by 2, so when we calculate the number of DBEs we simply compare the number of hydrogens which would be present in the fully saturated, acyclic compound with the number actually present, and divide by 2 to give the number of DBEs.

Box 1.1 Calculation of the Number of Double Bond Equivalents

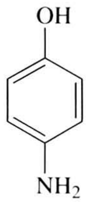
For a neutral species, we can calculate the number of double bond equivalents, DBE (Ω), by comparing the molecular formula with that of the fully saturated, acyclic parent molecule with the same number of carbons and heteroatoms, $C_nH^*_{2n+2+y}N_yO_w$, where H* is the total number of hydrogens and halogens.

To do this we can simply compare the number of hydrogens (and halogens) in the two formulae and, remembering that each double bond (or ring) results in a "loss" of 2 hydrogens from the molecular formula, calculate the number of DBEs. Alternatively, we can use the simple formula shown in equation (1.3):

$$\Omega = (C + 1) - [(H^* - N)/2] \tag{1.3}$$

where C = number of C atoms, H* = number of hydrogens or halogens, and N = number of nitrogens.

For example, the molecular formula for 4-aminophenol (**1.1**) is C_6H_7NO. The formula of the fully saturated, acyclic parent structure [$C_nH^*_{2n+2+y}N_yO_w$, where H* is the total number of hydrogens and halogens] would therefore be $C_6H_{(12+2+1)}NO$, *i.e.* $C_6H_{15}NO$. The difference in the number of hydrogens is therefore $15-7=8$, so there are 4 DBEs.



1.1

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Alternatively, using equation (1.3):

$$\Omega = (6 + 1) - [(7 - 1)/2] = 7 - 3 = 4$$

Looking at the structure of 4-aminophenol, we can see that formally it has 3 double bonds, and the ring itself makes up the total of 4 DBEs.

Worked Problem 1.1

Q Calculate (a) the wavelength, (b) the frequency and (c) the energy associated with a transition with a wavenumber of 2260 cm^{-1}.

A (a) $\bar{\nu} = 1/\lambda$, so $\lambda = 1/\bar{\nu} = 1/2600 = 4.42 \times 10^{-4}$ cm

$= 4.42 \times 10^{-6}$ m (4.42 μm).

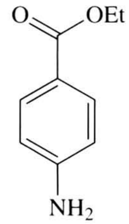
(b) $c = \nu\lambda$, so $\nu = c/\lambda = 3 \times 10^{8}\ \text{ms}^{-1}/4.42 \times 10^{-6}$ m

$= 6.79 \times 10^{13}\ \text{s}^{-1} (6.79 \times 10^{13}$ Hz).

(c) $E = h\nu = 6.626 \times 10^{-34}\ \text{J s} \times 6.79 \times 10^{13}\ \text{s}^{-1} = 4.5 \times 10^{-20}$ J.

Worked Problem 1.2

Q The local anaesthetic benzocaine has a molecular formula of $C_9H_{11}NO_2$. (a) Calculate the number of double bond equivalents; (b) identify all of the double bond equivalents in benzocaine (**1.2**).



1.2

A (a) The formula of the fully saturated, acyclic parent structure $[C_nH^*_{2n+2+y}N_yO_w$, where H* is the total number of hydrogens and halogens] would therefore be $C_9H_{(18+2+1)}NO_2$, *i.e.* $C_9H_{21}NO_2$. The difference in the number of hydrogens is therefore $21 - 11 = 10$, corresponding to 5 DBEs. Alternatively, $\Omega = (9+1) - [(11-1)/2] = 10 - 5 = 5$.

(b) Benzene ring $\equiv$ 4 DBEs ($3 \times$ C=C and 1 ring) and C=O.

Summary of Key Points

1. The energy levels of atoms and molecules (and so the difference in energy between these levels) have discrete values (quanta).

2. The wavenumber of a transition is inversely proportional to the wavelength ($\bar{\nu} = 1/\lambda$).

3. The relationship between the energy of a transition and the frequency is given by $\Delta E = h\nu$ or $\Delta E = hc/\lambda$ or $\Delta E = hc\bar{\nu}$, where h is Planck's constant. The energy of a particular transition is, therefore, proportional to the frequency or wavenumber, and inversely proportional to the wavelength.

4. NMR transitions correspond to wavelengths in the radiowave region of the spectrum, vibrational transitions correspond to wavelengths in the IR region, and electronic transitions to the UV-Vis region.

5. The number of double bond equivalents corresponds to the difference between the molecular formula and that for the saturated acyclic parent compound. Each DBE (double bond or ring) results in the subtraction of 2 hydrogens or halogens from the molecular formula of this parent structure.

Problems

1.1. Calculate the energy associated with transitions with the following frequencies, wavelength or wavenumber. What type of molecular transition is associated with each transition? (a) $\nu = 3 \times 10^8$ Hz; (b) $\lambda = 254$ nm (254×10^{-9} m); (c) $\lambda = 1.0$ cm; (d) $\bar{\nu} = 2600$ cm^{-1}; (e) $\nu = 4.1 \times 10^{14}$ Hz; (f) $\bar{\nu} = 2 \times 10^8$ m^{-1}.

1.2. How many double bond equivalents are there in each of the following molecules: (a) $C_6H_{12}O_6$; (b) $C_8H_9NO_2$; (c) $C_{27}H_{46}O$; (d) $C_5H_5N_5$; (e) $C_6H_3Cl_3O$; (f) $C_{46}H_{58}N_4O_9$.

2

Ultraviolet–Visible (UV-Vis) Spectroscopy

Aims

This chapter describes how ultraviolet–visible (UV-Vis) spectroscopy is used in organic chemistry. After you have studied this chapter, you should be able to:

- Describe briefly how the absorbance of a UV-absorbing compound is obtained
- Explain the relationship between the absorption wavelength and the energy difference between the energy levels involved
- Calculate the molar absorptivity of a molecule from its absorbance, concentration and the path length
- Recognize chromophores, and explain how conjugation and aromatic substituents can contribute to chromophores
- Explain how pH can affect the chromophore and the UV-Vis spectra of acidic and basic compounds
- Predict the absorbance maximum for unsaturated compounds using the Woodward–Fieser rules
- Summarize some practical applications of UV-Vis spectroscopy

2.1 Instrumentation

There are several different types of UV-Vis spectrometers, with the usual instrument met in an undergraduate laboratory being a double (or dual) beam spectrophotometer, which consists of a UV-visible light source, two cells through which the light passes, and a detector (usually a photomultiplier) to measure the amount of light passing through the cells. There are basic spectrometers that measure the absorbance at a specific wavelength, set by the user, and others that can scan the entire

UV-Vis range. Newer spectrometers are usually computer controlled and allow the user greater flexibility, *e.g.* in overlaying spectra of a reaction mixture over time, or constructing a calibration graph to determine the concentration of an unknown.

Single-beam UV-Vis spectrometers work on the same general principles, but measure the absorption of the reference first, followed by the sample. They can scan across the entire UV-Vis range or can be used at a single wavelength. Detector technology has improved recently: the diode array detector enables simultaneous detection over the entire range to be achieved, allowing rapid quantification of absorbing species.

The term UV-Vis normally applies to radiation with a wavelength in the range 200–800 nm. There are many groups that absorb below 200 nm, but this part of the spectrum is difficult to examine (as oxygen absorbs UV radiation below 200 nm) unless the spectra are recorded in a vacuum (vacuum UV-Vis).

In the **double-beam UV-Vis spectrophotometer** the light is split into two parallel beams, each of which passes through a cell; one cell contains the sample dissolved in solvent and the other cell contains the solvent alone. The detector measures the intensity of the light transmitted through the solvent alone (I_0) and compares it to the intensity of light transmitted through the sample cell (I). The absorbance, A, is then calculated from the relationship shown in equation (2.1):

$$A = \log_{10} \frac{I_0}{I} \qquad (2.1)$$

Ethanol is transparent to UV above 200 nm and is, therefore, commonly used as the solvent in UV-Vis spectroscopy.

2.2 Selection Rules and the Beer–Lambert Law

As you will have seen in Chapter 1, light at the short wavelength end of the electromagnetic spectrum has enough energy to promote electronic transitions in organic molecules, such that absorption of UV light (200–400 nm; 595–299 kJ mol^{-1}) or Vis light (400–800 nm; 299–149 kJ mol^{-1}) can result in the promotion of outer electrons from one electronic energy level to a higher one.

We can calculate the energy of a particular wavelength using equation (2.2):

$$E(\text{kJ mol}^{-1}) = \frac{1.19 \times 10^5}{\lambda(\text{nm})} \qquad (2.2)$$

As the relationship between E and λ is a reciprocal one, we can see that short wavelength radiation corresponds to high energy and long wavelengths correspond to low energy.

The difference between electronic energy levels is greater than the difference between any other molecular energy levels, so these transitions require the higher energy of short wavelength radiation. Promotion between other energy levels, *i.e.* vibrational or rotational, requires only the lower energy infrared (vibrational) or microwave (rotational) radiation (Figure 2.1).

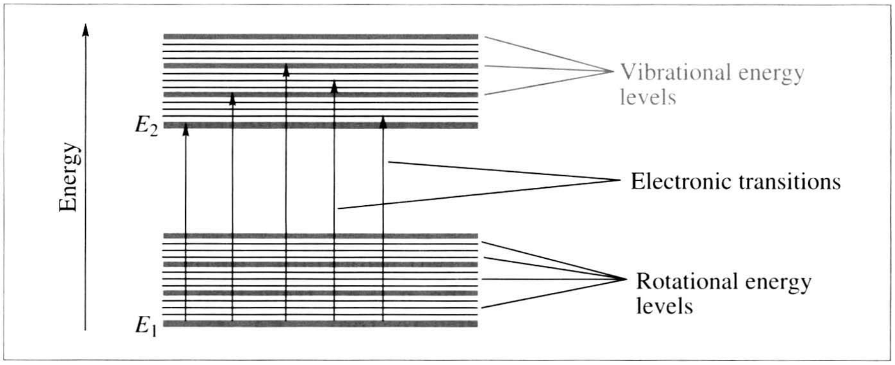


Figure 2.1 Schematic diagram showing possible molecular electronic transitions, and vibrational and rotational energy levels

At room temperature, the majority of molecules are in the lowest vibrational state of the lowest electronic energy level, the "**ground state**" (E_1). Absorption of UV or visible light leads to promotion of an electron from E_1 to the excited electronic level, E_2. The electronic transition is accompanied by vibrational and rotational transitions, so that the promotion of an electron can occur from the ground state electronic energy level of E_1 to any of the vibrational or rotational energy levels of E_2. This explains why UV-Vis absorption bands are characteristically broad, although energy transitions between rotational and vibrational energy levels within one electronic energy level can show fine structure (*e.g.* see Chapter 3 for many examples of sharp absorbances). Fine structure in UV spectra can sometimes be achieved by using a solvent that has little interaction with the sample molecules.

The fact that there are many electronic transitions possible, however, does not mean that they can or will occur. There are complex selection rules based on the symmetry of the ground and excited states of the molecule under examination. Basically, electronic transitions are allowed if the orientation of the electron spin does not change during the transition and if the symmetry of the initial and final functions is different; these are called the **spin** and **symmetry selection rules**, respectively. However, the so-called "forbidden" transitions can still occur, but give rise to weak absorptions.

According to the **Beer–Lambert law**, the **absorbance**, A, of a solution is directly proportional to the **path length** (l, length of the cell containing the solution, in cm) and the **concentration** of the absorbing molecule (c, in moles per litre), according to equation (2.3):

$$A = \varepsilon c l \tag{2.3}$$

where ε = the **molar absorptivity** of the absorbing molecule, sometimes called the molar extinction coefficient, and is characteristic of the molecule. The molar absorptivity is usually expressed in units of 100 $cm^2\ mol^{-1}$, although it is becoming more common to use units of $dm^3\ mol^{-1}\ cm^{-1}$ (these units give values of ε that differ by a factor of

10 from those values in units of 100 cm^2 mol^{-1}). The molar absorptivity, ε, is a measure of the intensity of the absorption and usually ranges from 0 to 10^6 (units of 100 cm^2 mol^{-1}). The greater the probability of a particular absorption and its associated electronic transition, the greater the ε value for that transition. For most molecules, absorptions associated with $\pi \rightarrow \pi^*$ transitions have higher ε values than the $n \rightarrow \pi^*$ transitions.

n denotes non-bonding and * an anti-bonding orbital (excited state).

In general, forbidden transitions give rise to low-intensity (low ε) absorption bands ($\varepsilon < 10{,}000$), but two important "forbidden" absorptions are seen quite commonly: the $n \rightarrow \pi^*$ transition of ketones at approximately 300 nm (ε usually 10–100), and the weak $\pi \rightarrow \pi^*$ absorption of benzene rings at about 260 nm (ε about 100–1000).

2.3 Chromophores

The part of the molecule containing the electrons involved in the electronic transition which gives rise to an absorption is called the **chromophore**. The wavelength of the maximum of the broad absorption is labelled λ_{max}. Most of the simple, non-conjugated chromophores give rise to high-energy (low-wavelength) absorptions with low-intensity (ε) values, but the majority of these absorptions are lost in atmospheric oxygen absorptions (Table 2.1).

Table 2.1 Absorption wavelengths of simple, non-conjugated chromophores

λ_{max}/nm	*Chromophore*	*Transition causing absorption*
~150	C—C or C—H σ-bonded electrons	$\sigma \rightarrow \sigma^*$
~185–195	—X: (X = O, N, S) Lone pair electrons	$n \rightarrow \sigma^*$
~300	C═O:	$n \rightarrow \pi^*$
~190	Lone pair electrons	$n \rightarrow \sigma^*$
~190	C═C (isolated) π-bonded electrons	$\pi \rightarrow \pi^*$

With the exception of the high-energy $\sigma \rightarrow \sigma^*$ transition of saturated alkyl systems, these transitions require either a lone pair or a π-bond from which the electron can be promoted. In fact, UV spectra are generally only of interest if the system is unsaturated; chromophores with the greatest degree of unsaturation give rise to the most intense absorptions at longest wavelength.

We can show electronic transitions using molecular orbital diagrams, *e.g.* the $\pi \rightarrow \pi^*$ transition of ethene, $CH_2{=}CH_2$, is shown in Figure 2.2. Here we can see that UV radiation at 190 nm provides the required energy (626.3 kJ mol^{-1}) to promote a bonding electron from the π-bonding

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