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INTRODUCTION

1.1 GENERAL PRINCIPLES OF ABSORPTION SPECTROSCOPY

Spectroscopy involves resolving electromagnetic radiation into its component wavelengths (or frequencies) and absorption spectroscopy is the absorption of electromagnetic radiation by matter as a function of wavelength.

In Organic Chemistry, we typically deal with molecular spectroscopy, *i.e.* the spectroscopy of atoms that are bound together in molecules rather than absorption by individual atoms or ions.

An absorption spectrum is a plot or graph of the absorption of energy (radiation) as a function of its wavelength (λ) or frequency (ν). A schematic absorption spectrum is given in Figure 1.1.

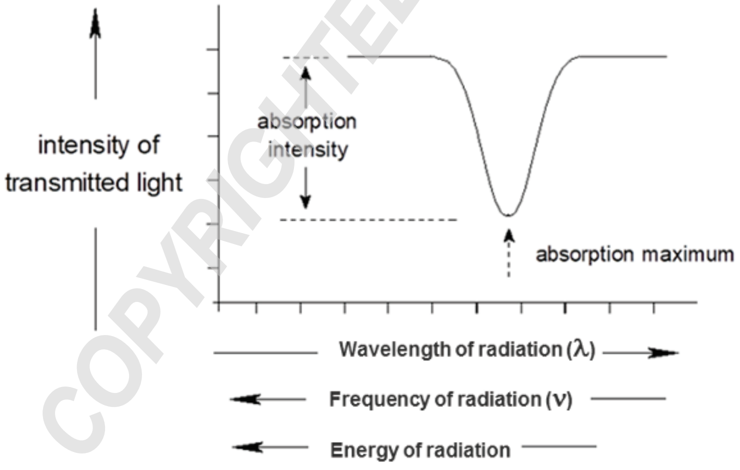


Figure 1.1 **Schematic Absorption Spectrum**

It follows that the x-axis in Figure 1.1 is an **energy** scale, since the frequency, wavelength and energy (E) of electromagnetic radiation are interrelated by the Planck–Einstein relation:

$$E = h.\nu$$
$$\text{and} \quad \nu.\lambda = c$$

where ν is the frequency of the electromagnetic radiation, λ is the wavelength of the electromagnetic radiation, and c is the velocity of light.

Organic Structures from Spectra, Sixth Edition, L. D. Field, H. L. Li and A. M. Magill

An absorption band can be characterised primarily by two parameters:

(a) the wavelength (or frequency) at which maximum absorption occurs

(b) the intensity of absorption at this wavelength compared to base-line (or background) absorption

A spectroscopic transition takes a molecule from one energy state to a state of higher energy. For any spectroscopic transition between energy states (*e.g.* E_1 and E_2 in Figure 1.2), the change in energy (ΔE) is given by:

$$\Delta E = h\nu$$

where h is Planck's constant and ν is the frequency of the electromagnetic energy absorbed.

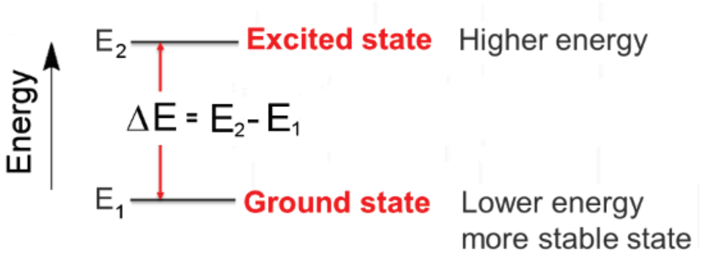


Figure 1.2 **Definition of a Spectroscopic Transition**

It follows that $\Delta E \propto \nu$ and that $\Delta E \propto 1/\lambda$; *i.e.* the larger ΔE, the *higher* the frequency of radiation required for absorption to take place or the *shorter* the wavelength of radiation required for absorption to take place.

The *y*-axis in Figure 1.1 measures the intensity of the absorption band and this depends on the number of molecules observed (the Beer–Lambert Law) and the probability of the transition between the energy levels.

A spectrum consists of distinct bands or transitions because the absorption (or emission) of energy is quantised. The energy gap for a transition (and hence the absorption frequency) is a ***molecular property*** and it is ***characteristic of molecular structure***. The absorption intensity is also a molecular property and both the frequency and the intensity of a transition can provide structural information.

1.2 CHROMOPHORES

In general, any spectral feature, *i.e.* a band or group of bands, is due not to the whole molecule, but to an identifiable part of the molecule, which we loosely call a *chromophore.*

A chromophore may correspond to a functional group (*e.g.* a hydroxyl group or the double bond in a carbonyl group). However, it may equally well correspond to a single atom within a molecule or to a group of atoms (*e.g.* a methyl group) that is not normally associated with chemical functionality.

The detection of a chromophore permits us to deduce the presence of a *structural fragment* or a *structural element* in the molecule. The fact that it is the chromophores and not the molecule as a whole that give rise to spectral features is fortunate because it permits complete molecular structures to be built up piece-by-piece from the molecular fragments.

1.3 DEGREE OF UNSATURATION

Traditionally, the molecular formula of a compound was derived from elemental analysis and its molecular weight, and these were determined independently. The concept of the **degree of unsaturation** of an organic compound derives simply from the tetravalency of carbon. For a non-cyclic hydrocarbon (*i.e.* an alkane) the number of hydrogen atoms must be twice the number of carbon atoms plus two, any "deficiency" in the number of hydrogens must be due to the presence of unsaturation, *i.e.* double bonds, triple bonds or rings in the structure.

The degree of unsaturation can be calculated from the molecular formula for all compounds containing C, H, N, O, S or the halogens. There are three basic steps in calculating the degree of unsaturation:

Step 1 – take the molecular formula and replace all halogens by hydrogens

Step 2 – omit all of the sulfur or oxygen atoms

Step 3 – for each nitrogen, omit the nitrogen and omit one hydrogen

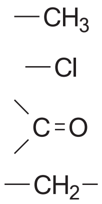
After these three steps, the molecular formula is reduced to C_nH_m and the degree of unsaturation is given by:

$$\text{Degree of Unsaturation} = n - \frac{m}{2} + 1$$

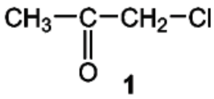
The degree of unsaturation indicates the number of π bonds or rings that the compound contains. For example, a compound whose molecular formula is $C_4H_9NO_2$ is reduced to C_4H_8, which gives a degree of unsaturation of 1. This indicates that the molecule must have one π bond or one ring. Note that a triple bond (*e.g.* the –C≡C– bond in an alkyne or the –C≡N bond in a nitrile) contributes two units of unsaturation (two π bonds). Note also that any compound that contains an aromatic ring always has a degree of unsaturation greater than or equal to 4, since the aromatic ring contains a ring plus three π bonds. Similarly, if a compound has a degree of unsaturation greater than or equal to 4, one should suspect the possibility that the structure contains an aromatic ring.

1.4 CONNECTIVITY

Even if it were possible to identify sufficient structural elements in a molecule to account for the molecular formula, it may not be possible to deduce the structural formula from a knowledge of the structural elements alone. For example, it could be demonstrated that a substance of molecular formula C_3H_5OCl contains the structural elements:

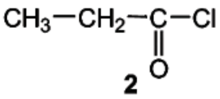


and this leaves two possible structures:



$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_2-Cl$ **1**

and



$CH_3-CH_2-\underset{\underset{O}{\parallel}}{C}-Cl$ **2**

Not only the presence of various structural elements, but also their juxtaposition, must be determined to establish the structure of a molecule. Fortunately, spectroscopy often gives valuable information concerning the *connectivity* of structural elements and in the above example it would be very easy to determine whether there is a ketonic carbonyl group (as in **1**) or an acid chloride (as in **2**). In addition, it is possible to determine independently whether the methyl ($–CH_3$) and methylene ($–CH_2–$) groups are separated (as in **1**) or adjacent (as in **2**).

1.5 SENSITIVITY

Sensitivity is generally taken to signify the limits of detectability of a chromophore. Some methods (*e.g.* ^{1}H NMR spectroscopy) detect all chromophores accessible to them with equal sensitivity while in other techniques (*e.g.* UV spectroscopy) the range of sensitivity towards different chromophores spans many orders of magnitude. Mass spectroscopy is the most sensitive of the common spectroscopic techniques and requires only very small amounts of sample ($< 10^{-10}$ g) whereas ^{13}C NMR typically requires tens of milligrams of sample. In terms of overall sensitivity:

$$\text{MS} > \text{UV} > \text{IR} > {}^1\text{H NMR} > {}^{13}\text{C NMR}$$

but the relative sensitivity of different spectroscopic techniques often depends on the specific chromophores present in a molecule.

1.6 PRACTICAL CONSIDERATIONS

The five major spectroscopic methods (MS, UV, IR, ^{1}H NMR and ^{13}C NMR) have become established as the principal tools for the determination of the structures of organic compounds because, between them, they detect a wide variety of structural elements.

The instrumentation and skills involved in the use of all five major spectroscopic methods are now widely spread, but the ease of obtaining and interpreting the data from each method under real laboratory conditions varies.

In very general terms:

(a) While the ***cost*** of each type of instrumentation differs greatly (NMR instruments cost between \$50,000 and several million dollars), as an overall guide, MS and NMR instruments are much more costly than UV and IR spectrometers. With increasing cost comes increasing difficulty in maintenance and the required operator expertise, thus compounding the total outlay.

(b) In terms of ***ease of usage*** for routine operation, most UV and IR instruments are comparatively straightforward bench-top laboratory instruments. NMR spectrometers are also common as "hands-on" instruments in most chemistry laboratories and the users require routine training and a degree of basic computer literacy. Similarly some mass spectrometers are now designed to be used by researchers as "hands-on" routine instruments. However, the more advanced NMR spectrometers and most mass spectrometers are still sophisticated instruments that are usually operated and maintained by specialists.

(c) The ***scope*** of each spectroscopic method can be defined as the amount of useful information it provides. This is a function of the total amount of information obtainable and also how difficult the data are to interpret. The scope of each method varies from problem to problem, and each method has its aficionados and specialists, but the overall utility undoubtedly decreases in the order:

$$\text{NMR} > \text{MS} > \text{IR} > \text{UV}$$

with the combination of ^{1}H and ^{13}C NMR spectroscopy providing the most useful information.

(d) The ***theoretical background*** needed for each method varies with the nature of the experiment, but the minimum overall amount of theory needed decreases in the order:

$$\text{NMR} >> \text{MS} > \text{UV} \approx \text{IR}$$