UV/Visible Spectroscopy

Learner's Outcomes

a. Explain that UV/visible light absorption in organic molecules requires electronic transitions between energy levels in chromophores which contain a double or triple bond, a delocalized system or a lone pair of electrons [detailed theory of why chromophores have absorptions of appropriate energy is not required, nor is any consideration of molecular orbitals involved].

b. Explain qualitatively how increasing conjugation in an organic molecule decreases the gap between energy levels and hence shifts the absorption towards longer wavelength and predict whether a given organic molecule will absorb in the ultraviolet/visible region.

c. Apply UV/visible spectroscopy to quantitative analysis of a given species in solution and use Beer's Law, absorbance = $\lg (I0/I) = \varepsilon cl$, to calculate the concentration of a given species in solution.

Principle		When a **photon** is absorbed by a molecule, an **electron** from the **lower energy orbital** gains the photon's energy and is promoted to a **higher energy orbital** in **$\pi \rightarrow \pi^*$** or **$n \rightarrow \pi^*$** transitions. Only molecules with **n** or **π** electrons absorb in the uv-visible light region (n: non-bonding electrons). The **absorbance** of an analyte is **proportional to its concentration** according to Beer's Law: $a = \epsilon cl$. Thus, quantitative determination can be carried out.
Factors	Conjugation	A **more conjugated system reduces** the HOMO-LUMO **energy gap**, and causes the molecule to absorb at a **higher wavelength**. With increased conjugation, there is more than one possible $\pi \rightarrow \pi^*$ transition, resulting in **multiple absorption bands**.
	Lone Pairs	The incorporation of an atom with a **lone pair** of electrons **reduces the energy gap** between orbitals, causing the molecule to absorb at a **higher wavelength**.
Formulae		$E = hf = hc/\lambda$ where h is the Planck constant and c is the speed of light. Transmittance = $I/I_0 \times 100\%$ Absorbance = $-\lg(I/I_0)$ where I is the intensity of the emergent beam and I_0 is the intensity of the incident beam. Absorbance = ϵcl where ϵ is the molar extinction coefficient, c is the concentration of the compound in mol dm^{-3} and l is the path length in cm. For mixtures of more than one compound, the total absorbance is the sum of the individual absorbance.

Infrared Spectroscopy

Learner's Outcomes

a. Explain the origin of IR absorption of simple molecules.
b. Predict the number of IR absorptions for a given simple molecule, and identify the molecular vibrations which give rise to them.
c. Identify characteristic absorptions in the IR spectrum of a compound containing up to three functional groups and suggest structures for a compound from its IR spectrum.

Principle		Different **modes of vibrations** in a molecule give rise to different **vibrational energy levels**, such as stretching and bending. For a vibrational mode to be **active** in the IR region, there must be a **net change in the dipole moment** of the molecule when the vibration takes place.
Factors	Bond Strength	**Stronger bonds** have a larger force constant and vibrate at **higher frequencies** than weaker bonds.
	Mass	Bonds between atoms of **lower masses** vibrate at **higher frequencies** than bonds between heavier atoms.
Simple Molecules		Symmetrical diatomic molecules (e.g. H_2) do not absorb in the IR region. Polar diatomic molecules (e.g. HCl) exhibit only one mode of molecular vibration, the stretching of the bond. For simple molecules, **symmetrical stretching**, **asymmetrical stretching** and **bending** can occur. In linear molecules like CO_2, symmetrical stretching does not cause a change in the dipole moment and hence does not cause IR absorption. In bent molecules like SO_2, all three vibrational modes cause IR absorption.
Key Features		**1700** cm^{-1}: C=O stretch. **3500** cm^{-1}: O-H and N-H stretch. –OH has a broad peak and –NH has a sharp peak.

Mass Spectrometry

Learner's Outcomes

a. Identify the basic features of the mass spectrometer.
b. Calculate the relative atomic mass of an element given its mass spectrum and analyze mass spectra in terms of isotopic abundances and molecular fragments.
c. Recognize that rearrangements accompanying fragmentation processes are possible [mechanism of rearrangement is not required].
d. Suggest the identity of major fragment ions in a given mass spectrum, and hence the possible structure of a molecule, using the molecular ion peak to determine relative molecular mass, the (M+1) peak caused by ^{13}C for determining the number of carbon atoms in organic molecules and the (M+2) and (M+4) peaks in the identification of halogen compounds containing up to two Cl and Br.
e. Explain the use of high resolution mass spectrometry in distinguishing between molecules of similar relative molecular mass.

<table>
<tr><td rowspan="2">Peaks</td><td>M+1</td><td>The M+1 peak is due to naturally occurring ^{13}C in a molecule.

$n = 100(A_{M+1})/1.1(A_M)$ where n is the number of C atoms, and A_{M+1} and A_M are the abundances of the M+1 and M peaks respectively.</td></tr>
<tr><td>M+2
M+4</td><td>The ratio of ^{35}Cl to ^{37}Cl is 3:1 while that of ^{79}Br to ^{81}Br is 1:1. A molecule containing Cl or Br shows a M and M+2 peak, while a molecule containing 2 Cl or Br atoms shows a M, M+2 and M+4 peak.
<table>
<tr><th>M</th><th>M+2</th><th>M+4</th><th>Halogen Present</th></tr>
<tr><td>3</td><td>1</td><td>-</td><td>1 Cl</td></tr>
<tr><td>1</td><td>1</td><td>-</td><td>1 Br</td></tr>
<tr><td>9</td><td>6</td><td>1</td><td>2 Cl</td></tr>
<tr><td>1</td><td>2</td><td>1</td><td>2 Br</td></tr>
<tr><td>3</td><td>4</td><td>1</td><td>1 Cl, 1 Br</td></tr>
</table></td></tr>
<tr><td colspan="2">Rearrangement</td><td>Rearrangements can occur to produce a ion with m/e one unit more than expected.</td></tr>
<tr><td colspan="2">High Resolution Mass Spectrometry</td><td>High resolution mass spectrometry can measure m/e ratios to a high accuracy so as to determine its molecular formula since the accurate A_r of individual atoms are not exact whole numbers.</td></tr>
</table>

Nuclear Magnetic Resonance

Learner's Outcomes

a. Outline the principles of nuclear magnetic resonance and explain the use of the δ scale with TMS as the reference.

b. Explain how the chemical environment of a proton affects the magnetic field it experiences, and hence the absorption of energy at resonance and describe the effects of adjacent protons on the magnetic field experienced by a given proton.

c. Predict the number of protons in each group present in a given molecule by integration of peak area and the number of protons adjacent to a given proton from the spin-spin splitting pattern, limited to splitting patterns up to a quadruplet only [knowledge of the theory of why coupling occurs is not required].

d. Identify protons in chemically identical environments in simple molecules.

e. Interpret ^{1}H NMR spectra of simple organic molecules containing no more than three functional groups.

f. Describe how the addition of D_2O may be used to identify labile protons.

Principle	A proton spins and generates a magnetic moment. When an external magnetic field is applied, the magnetic moment aligns with or against the applied magnetic field. To switch from the lower energy spin state that aligns with the applied field to the higher energy state that aligns against the applied field, radio-frequency radiation is absorbed. The exact frequency of absorption depends on the chemical environment of the proton.
TMS	TMS is used as a standard in 1H NMR spectroscopy. The chemical shift of its 12 chemically equivalent protons serves as a reference point (e.g. 0 ppm on the delta scale) and the chemical shift of any proton in a sample is measured relative to it. The use of TMS as a reference compound allows the chemical shifts of protons in a sample to be more conveniently and accurately measured. TMS is used because · it is chemically inert and volatile · its 12 protons give a strong signal at low concentration · its protons experience greater shielding than in most other molecules, i.e. the signal from TMS does not interfere with the signals from the protons of the sample (which tends to be more downfielded)
Labile Protons	D2O is used to detect or identify labile protons in a molecule. · Examples of such protons include the –OH proton in alcohols (ROH) and phenols, and the –COOH proton in carboxylic acids. · The NMR spectrum of a sample suspected to contain labile protons is first

	obtained. D2O is then added to the sample and another NMR spectrum is obtained for this sample with the added D2O. · Should any labile proton be present, it will give rise to a signal in the first NMR spectrum but not in the second NMR spectrum. · This is because D2O undergoes a rapid chemical exchange with the labile proton, for example, the –OH proton in ROH: ROH + D2O ⇌ ROD + HOD The replacement of the labile proton by deuterium leads to the disappearance of the signal due to the labile proton. · Note: A signal due to HOD at d = 4.7 ppm may appear in the second spectrum.