Chapter 11

UV and IR Spectra

Both UV and IR spectroscopy rely on the absorption of electromagnetic radiation to provide analytical information. To explain the differences in presentation of the spectra we need to consider the relationship between the energy supplied by photons and their wavelength. Planck described this in his well-known equation $E = h\nu$ E is the energy of a photon having a frequency ν and h is Planck's constant.

Frequency and wavelength are related by the following equation; $\nu = c/\lambda$. The frequency ν indicates the number of vibrations of an electric or magnetic field per unit time in s^{-1} or Hz (Hertz). The velocity of propagation in a vacuum is the same for all electromagnetic waves with $c = 2.997925 \times 10^8$ m s^{-1}. (The velocity of propagation of electromagnetic waves is more colloquially known as the speed of light.) The wavelength λ can be derived from the equation $c = \lambda\nu$ as follows $\lambda = c/\nu$.

Derivation of the Beer-Lambert Law

The Beer and Lambert relationships are combined and expressed by the differential equation:

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Where I is the intensity of the light, b the optical path length through the absorbing solution, c the concentration of the absorbing species and k is proportionality constant.

Integration yields:

$$\ln\left(\frac{0}{}\right)$$

Where I_0 is the intensity of the light as it enters the solution (incident intensity) and I_t is the intensity of the light leaving the solution (transmitted intensity).

Expressing this equation in logs to the base ten gives:

$$\left(\frac{0}{}\right)$$

Where a is referred to as the absorptivity constant and A is the absorbance.

This relationship is commonly referred to as the **Beer-Lambert Law**. This is a very important equation and some care needs to be taken over the units and nomenclature found in the literature.

EI and CI mass spectrometry

A typical mass spectrum has a few key features to look for:

- The molecular ion may be visible, depending upon the ionisation technique used, and it gives a firm indication of the molecular mass of the unknown compound.
- The most intense peak in the mass spectrum is called the Base Peak and the intensities of all other peaks in the spectrum are measured relative to the Base Peak.
- Some classes of molecules have characteristic fragmentation patterns or give rise to particular ions and these can be used to identify common residues. For example, aromatic compounds that have a methyl or methylene group attached to a benzene ring are likely to give rise to the tropylium ion $[C_7H_7]^+$ at m/z 91, often regardless of the presence of any other substituent on the ring; this can decompose further to give another ion $[C_5H_5]^+$ at m/z 65. In a similar manner, loss of 43 mass units from any ion may indicate the presence of an acetyl group CH_3CO- within the molecular structure. (See Figure 11.1 for tropylium ion formation.)

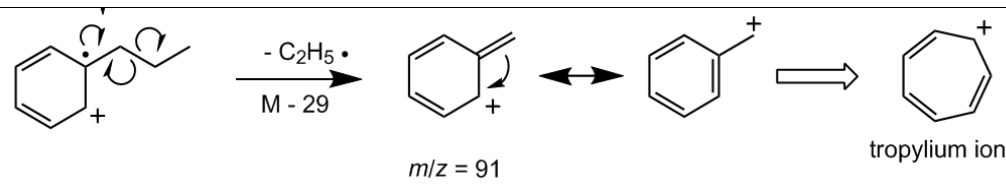

Figure 11.1: Formation of a tropylium ion from propylbenzene in an EI mass spectrometer. Electron impact mass spectrometry ionises a compound by removing an electron, leaving a radical cation. This rearranges to give fragment ions.

- Again, correlation tables are useful for the analysis of mass spectra.

Common Fragmentations		Fragment Ions	
Mass	**Fragment loss**	**m/z**	**Fragment**
M - 15	CH_3▪	15	CH_3^+
M - 17	HO▪	18	H_2O^+▪
M - 18	H_2O	26	$CH{\equiv}CH^+$▪
M - 26	$CH{\equiv}CH$, ▪$C{\equiv}N$	28	CO^+▪, $CH_2{=}CH_2^+$▪
M - 27	$CH_2{=}CH$▪, $HC{\equiv}N$	30	$CH_2{=}NH_2^+$▪
M - 28	$CH_2{=}CH_2$, CO	31	$CH_2{=}OH^+$
M - 29	CH_3CH_2▪, ▪CHO	41	$CH_2{=}CH{-}CH_2^+$
M - 30	NH_2CH_2▪, CH_2O	43	CH_3CO^+, $C_3H_7^+$
M - 31	▪OCH_3, ▪CH_2OH	44	CO_2^+▪
M - 43	C_3H_7▪, CH_3CO▪	77	$C_6H_5^+$
M - 44	CO_2	91	$C_6H_5CH_2^+$
M - 45	CH_3CH_2O▪	105	$C_6H_5CO^+$

Fig. 11.2: A correlation table containing details of common fragment ions found in mass spectra

The mass spectrum of aspirin may be analysed using knowledge of common fragmentations and some intuition:

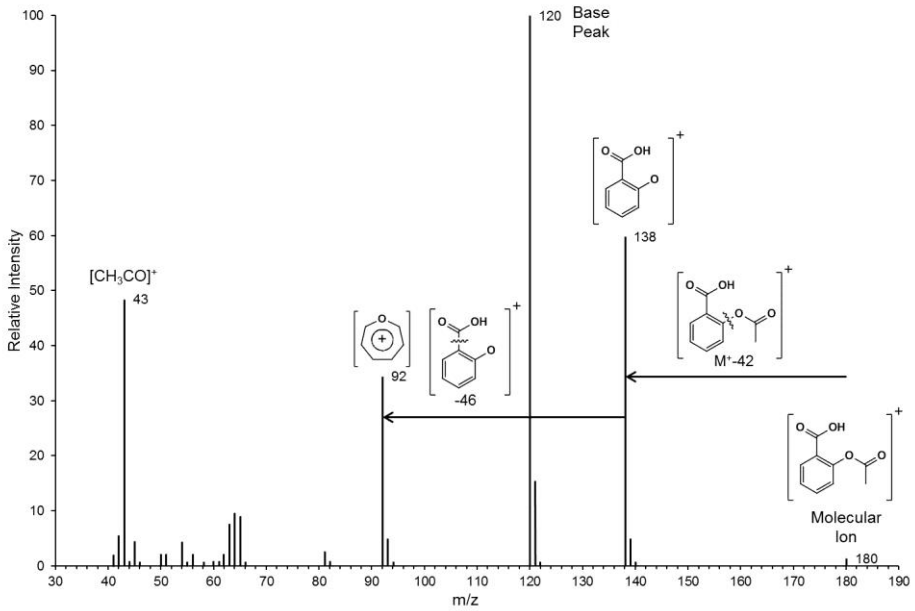

Fig. 11.3: The EI mass spectrum of aspirin

As you can see, the molecular ion is not very intense compared with the intensities of the fragment ions. It is fairly easy to determine the origin of some of the fragment ions, and the ion which is characteristic for the loss of an acetyl group is clearly visible. The best way to analyse mass spectra of small organic molecules is to examine which peaks are present and determine whether any characteristic ions or losses are visible in the spectrum, then use your knowledge of chemistry, and some common sense, to put the pieces of the jigsaw in place.

NMR Spectrometers

The magnetic field is generated by a current flowing within a coil of superconducting material; the coil is surrounded by liquid helium (boiling point 4.22 K) which, in turn, is surrounded by liquid nitrogen (boiling point 77.36 K) and is encased within a heavily insulated, non-ferrous container.

The spectrometer generates a powerful pulse of radio frequency radiation that is transmitted to a compound situated in the probe, which itself is within the superconducting magnet. Nuclei which are NMR-active absorb energy from the radiation at a particular resonant frequency, raising them to the high energy, excited state; the nuclei remain in this high energy state until the irradiation stops, after which time they give up their energy, known commonly as Relaxation, and return to the low energy ground state. Fortuitously, the nuclei

release their energy as radio frequency radiation which is detected by the spectrometer, just like a digital radio receiver.

As noted above, 300 MHz is the frequency of radiation which is required to raise a proton to the high energy, excited state in a 7.05 Tesla magnetic field. However, not all protons within a compound are in exactly the same environment. The electrons associated with covalent bonds within a molecule generate small, local magnetic fields as they flow within the bonds; these small local fields affect the resonant frequency for each proton. In a bond that is not polarised this local field effectively 'shields' the proton from the applied field and the signal obtained as that proton relaxes appears upfield, close to the normal resonant frequency. However, in a polar bond, in which the bonding electrons are drawn towards the more electronegative atom, the proton is 'deshielded'; this causes the proton to resonate downfield at a higher frequency. This effect causes each proton in a molecule to have a characteristic resonant frequency and the difference between this and the frequency of irradiation is termed the Chemical Shift (δ) and is expressed in parts per million (ppm). Tetramethylsilane (TMS) is used as a universal reference compound from which all chemical shifts are measured. Certain chemical shifts are characteristic for particular magnetic environments, thus correlation tables are particularly useful when analysing spectra.

In the NMR experiment adjacent excited nuclei may both be opposed to the applied field, or only one of them may be opposed to the field whilst the other remains in the lower energy alignment. These two situations give rise to very slightly different chemical shifts, which are often measureable if the instrument has a stable magnetic field. Thus a proton with one other proton adjacent to it will give two peaks in the ^{1}H NMR spectrum, known as a doublet, and the distance between the peaks is the 'coupling constant' *J*. If there is a second adjacent proton, the doublet is itself doubled, resulting in a double doublet if the coupling constants are different. More usually in small molecules, the coupling constants are the same, and a 1:2:1 triplet is formed as shown in Figure 11.4. This illustrates the so-called 'n+1' rule, in that the number of peaks observed for a nucleus equals the number of equivalent adjacent nuclei plus one; a proton with two adjacent protons will give rise to a triplet, *etc*. The intensities of the peaks are additively as shown in Fig. 11.4; this is known as a Pascal's triangle. The coupling constant is measured in Hertz and takes the same value for both coupling nuclei; if H_A couples to H_B with J = 7 Hz, both H_A and H_B will show a 7 Hz splitting in the NMR spectrum.

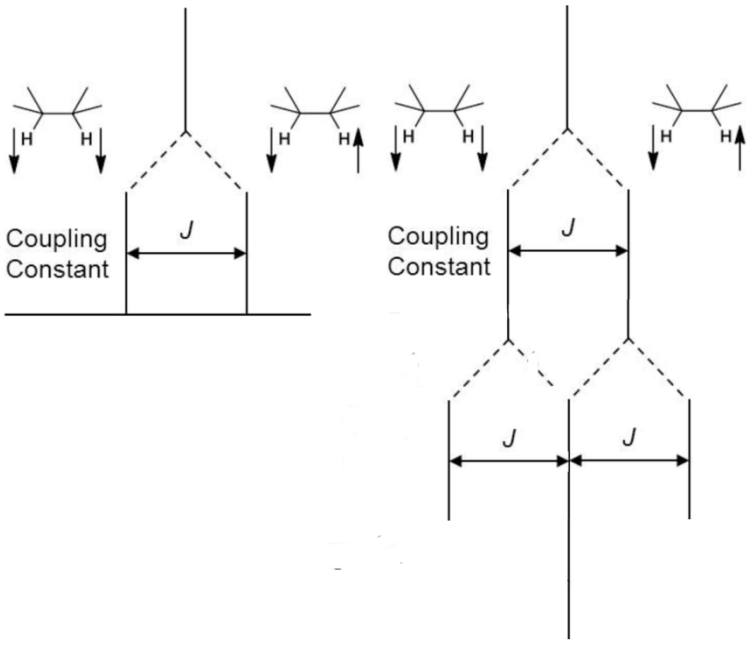

Fig. 11.4: The origin of three-bond spin-spin coupling; the protons of interest are separated by three covalent bonds.