

ORGANIC SPECTROSCOPY NOTES

Basics of Spectroscopy

UV/vis, IR and NMR are all types of Absorption Spectroscopy, where EM radiation corresponding to exactly the energy of specific excitations in molecules is absorbed.

This is then measured by a spectrometer. These always consist of:

- The radiation source.
- The monochromator (continuous recording instruments).
- The sample container.
- The frequency analyser.
- The detector.
- The recorder.

Continuous recording implies scanning through a range of appropriate frequencies and producing the difference in detected intensities (relative to a sample) in a spectrum.

An alternative procedure is to use a Fourier Transform spectrometer. The sample in this case is subjected to a broad pulse of radiation covering the whole frequency range. The absorbed frequencies which are re-emitted as the excited molecules decay back to their ground states are recorded together and the complex signal is then broken down to its component frequencies by subsequent computer assisted manipulation. This can improve sensitivity and is usually faster.

Mass Spectrometry is completely different from the above, however. It doesn't involve absorption of EM radiation, and is hence known as spectrometry as opposed to spectroscopy. It analyses sample molecules one at a time rather than the bulk sample. Its primary use is obtaining the molecular weight of quite large and complicated molecules.

Ultraviolet/Visible Spectroscopy

Rarely used as a first analytical tool now, as it doesn't show much information. Organic molecules always absorb UV radiation in the region below about 150nm, as this corresponds to the σ framework. Solvents typically absorb up to 200nm. Hence, scan at 200-400nm to avoid these.

Lone pairs (n) and π -electrons are more mobile, as they require less energy for excitation to their antibonding orbitals, and so we see conjugated systems at longer frequencies, e.g. butadiene $\pi \rightarrow \pi^*$ corresponds to 217nm.

It is conjugated systems, such as polyenes and poly-yenes (referred to as chromophores), that give rise to diagnostic absorptions in the UV-visible region of the EM spectrum. For unsaturated systems the most commonly observed transition is $\pi-\pi^*$ and $n-\pi^*$.

The spectrometer shows A vs. λ , where $A = \log(I_0/I) = \epsilon c l$ (the Beer-Lambert Law). This comes from:

Beer's Law – absorption is proportional to the number of molecules.

Lambert's Law – I_0/I is constant for our range of I_0 .

ϵ is the extinction coefficient, c is the concentration, and l is the length, usually 1.

It is possible to find λ_{\max} and ϵ_{\max} from each peak on the graph.

Examples:

Allene	Not conjugated, not seen.
trans-PhHC=CHPh	Planar, p overlap. $\lambda_{\max} = 296\text{nm}$, $\epsilon = 31600 \text{ cm}^2 \text{ mol}^{-1}$
cis-PhHC=CHPh	Twist \rightarrow p not fully overlapped. Hence, $\lambda_{\max} = 280\text{nm}$, $\epsilon = 4000 \text{ cm}^2 \text{ mol}^{-1}$

Woodward's Rules can be used to predict λ_{\max} (based on steroids). Conjugation increases the wavelength, corresponding to a smaller energy of transition between $\pi-\pi^*$. So phenol is basic in solutions shows a $\lambda_{\max} = 298\text{nm}$ compared to only 255nm in acid. This is due to the negative charge on the oxygen in the phenoxide ion being fully conjugated with the ring.

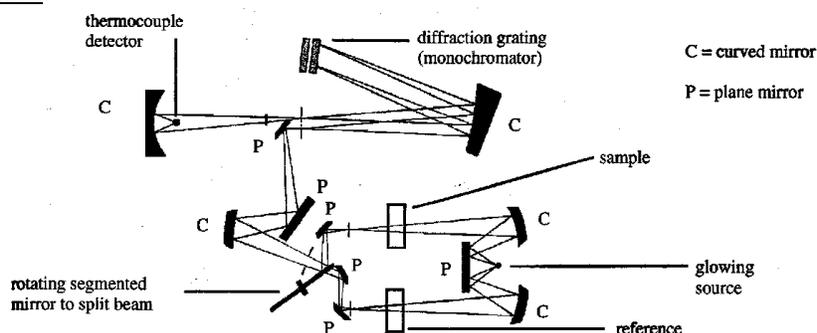
UV Spectra functional groups are hence:

Dienes	$\lambda_{\max} \sim 230\text{nm}$
α,β -unsaturated ketones	$\lambda_{\max} \sim 220\text{nm}$
Phenols	
Benzenes	

Can hence see why it is not that much use as a first analytical tool!

Infrared Spectroscopy

Spectrometer

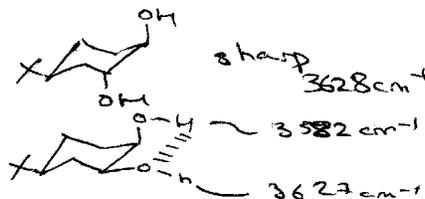


Theory

From simple harmonic motion, it is noted that frequency of oscillation increases with the stiffness of the bond, and decreases with the reduced mass. A bond will absorb at the energy corresponding to one of its resonant frequencies of oscillation, therefore the absorbed frequency is proportional to the inverse square root of k . k is the force constant, which is characteristic of the bond.

Molecular vibrations occur in the range 2500 to 15400cm^{-1} . Wavenumber of absorption is then plotted against transmission.

The peak width is related to ϵ , which is proportional to the dipole change squared. Thus, broad peaks are usually a result of H-bonding or increased concentration. This can be useful, e.g.



Peak appearance can also vary for different functional groups. For example, an alcohol OH gives a smooth broad peak, while the carboxylic OH (which is in the same frequency range) has a wavering line instead.

Carbonyls

Influences on position:

R-CO-X

Increasing electronegativity of X increases wavenumber.

α,β -unsaturated ketone

Decreases wavenumber by $15-40\text{cm}^{-1}$, except in amides.

Ring strain	Increases wavenumber (large) – distinguishes ring size.
(Intramolecular) H-bonding to the carbonyl	Decreases wavenumber by 40-60cm ⁻¹

Typical peaks

3600	Sharp	Free OH
3500-3000	Broad	H-bonded OH, amine or amide
3300	Sharp & Strong	Alkyne-H bond
3100-2700		Alkane-H bond. Stronger for sp ³ than sp ² .
3500-2500	Broad	H-bonded carboxylic OH
2200	Weak	C≡C
1850-1650		C=O
1650-1500	Weak unless conjugated	C=C. Absent for symmetrical alkenes.
Fingerprint region		C-O, C-Cl, aromatics, NO ₂ , P=O, SO ₂ .

Note that the carbonyl stretch can be sub-divided further:

1750-1850	C(O)X system
1740	Ester
1730	Aldehyde
1710	Ketone
1650-1690	α,β-unsaturated
1670	Amide

Mass Spectrometry

Individual molecules are bombarded with high energy electrons which cause the ejection of one or more electrons from the substrate on impact (electron impact ionisation). The positively charged ions are then accelerated along an electrical potential through a magnetic field which causes them to be deflected to an extent which is dependent upon the charge on the molecule and the magnetic field strength, and is inversely dependent upon the momentum (i.e. mass).

Chemical ionisation can also be used for molecules too fragile to withstand the 70eV bombardment. This transfers either H⁺ or NH₄⁺ to M, giving [M+1]⁺ or [M+18]⁺ respectively. This does not lead to fragmentation in the way mass spec does, and so it is used solely to determine M_r.

Interpretation

The molecular ion peak relates to the loss of a single electron from the target molecule due to a bombarding of electrons. The molecular ion (M⁺) has the same mass as M, and so gives the mass of the compound. This might however be an unstable ion, and so no molecular ion peak can be recorded in the detector. In this case, a milder (chemical) ionisation technique could be used.

It should be remembered that isotope effects exist (e.g. 1% of the carbon will weigh 13u instead of 12u). This can actually be useful for determining proportions of isotopes, since the peaks responsible for each isotope can be compared.

The Nitrogen Rule

Nitrogen is the only commonly encountered odd valency element possessing an even atomic weight in organic molecule. Any compound containing one or an odd number of nitrogen atoms will have an odd molecular weight; conversely, compounds lacking nitrogen or containing even numbers of nitrogens have an even molecular weight.

Fragmentation Pathways

The fragmentation that occurs can give us the structure of the molecule as well. Fragmentations often occur at labile bonds or to give particularly stable fragments. Fragmentation may involve cleavage of a single bond or cleavage of two bonds.

One-bond Cleavage –

Radical cations may fragment by either heterolytic cleavage to give a cation and a radical, or homolytic cleavage to generate a new radical cation. However, cations only degrade by a heterolytic process, as homolytic cleavage is energetically unfavourable. This leads to the even electron rule, a guideline which states that even-electron species do not fragment to odd-electron species. In other words, a cation will not fragment to form a radical and a radical cation. One-bond cleavage gives fragments that are valence unsatisfied.

Two-bond Cleavage –

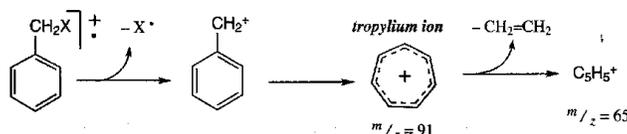
These result from chemical reactions of the radical cation. Even molecular weight compounds give even molecular weight two-bond cleavage fragments, and vice versa. This makes their cleavages easy to identify.



The fragment that retains the charge and is detected can be predicted by the Stephenson-Audier Rule, which states that the positive charge will reside on the fragment with the lowest ionisation potential (i.e. that which is most able to stabilise it, either inductively or by resonance).

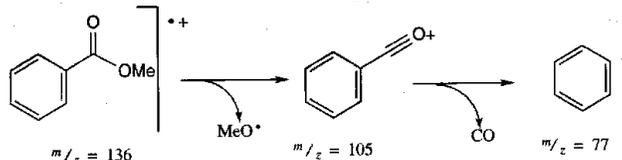
Common Fragmentation Pathways

Tropylium Ion

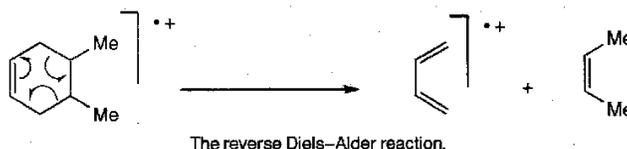


Acylium Ion

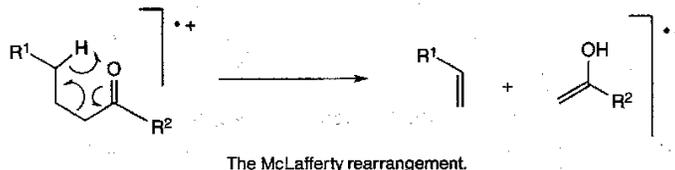
e.g. acetates and methyl ketones give a strong peak at $m/z = 43$, and phenyl ketones a strong peak at $m/z = 105$. These are peaks corresponding to the subsequent extrusion of CO.



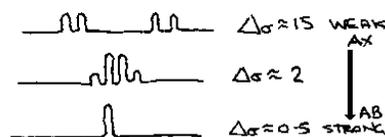
Reverse Diels-Alder



McLafferty Rearrangement



field. In strong coupling the centres of resonance multiplet may not reflect the true chemical shifts, line splittings may not represent true coupling constants and due to roofing effects the intensities become distorted.

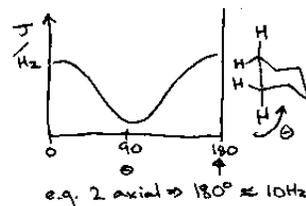


When $\Delta\sigma$ is small, the H_A and H_B absorptions are so close together that they do not couple because they have become equivalent. A similar example is the AMX system. In this system, strong coupling between AM distorts the spectra, in addition to the roofing of AM, X splits into four lines. This virtual coupling cannot be explained using the first order approximation.

Coupling pathways do not extend throughout the whole molecule, and coupling efficiency falls off with the number of intervening bonds. Geminal couplings, between protons on the same carbon (2J) generally are between -10Hz and -15Hz for saturated CH_2 (much smaller for unsaturated). Electronegative groups make J more positive, so coupling falls. They are of limited use in structure elucidation.

A three bond coupling (vicinal) is more useful, and the magnitude of J is related to substituent effects, bond lengths, bond angles and dihedral angles. For a saturated system, $^3J \leq 14\text{Hz}$ and for unsaturated $^3J \leq 18\text{Hz}$. J becomes smaller with electronegative group on the CH-CH pathway. The coupling between the 1,2 protons in benzene and cyclohex-1-ene is larger for the cyclohexene, as the pathway has full double bond character, and so is shorter than in benzene with the longer aromatic bond (10Hz vs.8Hz). J also depends on the bond angles, as demonstrated by considering the series cyclohexene \rightarrow cyclopentene \rightarrow cyclobutene, where J decreases from 10 to 3 Hz.

The Karplus Curve gives the variation of 3J with ϕ where $^3J = A - B \cos \phi + C \cos 2\phi$ where A, B, C depend on the substituents. This factor is dictated by the orbital overlap. This enables us to see that in alkenes $^3J_{\text{trans}} > ^3J_{\text{cis}}$, and that in cyclohexanes, $^3J_{\text{ax-ax}} > ^3J_{\text{ax-eq}} = ^3J_{\text{eq-eq}}$.



The longer range couplings are typically much smaller (3Hz) and operate only over particular pathways.

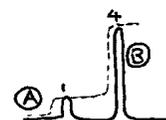
Typical Coupling Constants:

CH_2	10-15	H-C-C-H	7	HC-CH=C	5-7	C=CH-CH=C	10-15
C=CH ₂	1-2	HC=CH (cis)	8-10	HC=CH (trans)	14-16	H-C=C-CH	0-1
H-Ph (ortho)	7-8	H-Ph (meta)	1-2	H-Ph (para)	0-1	HC-C=C	2-3

Protons which are magnetically inequivalent show couplings with each other and so display multiplet structures. Protons which are magnetically equivalent are necessarily chemical equivalent, but not vice versa. So where as in CH_3CHCl_2 the methyl protons are magnetically equivalent and couple to H_2 in exactly the same way, the protons in $H_2C=CF_2$ are not magnetically equivalent.

Intensities

An NMR plot reveals not only the chemical environments of 1H nuclei, but the number of nuclei in that environment. The area under a peak relates to proportionally the number of nuclei in that environment.



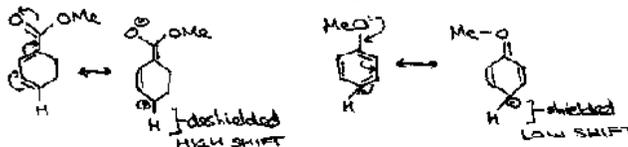
The simple spectrum above indicates that there are four times as many nuclei in the environment corresponding to B as there are in A. This means there must be four equivalent protons in the B environment.

Chemical Shifts

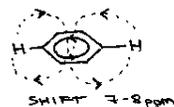
The energy of transition (chemical shift) is measured in units of ppm and as mentioned previously relates to the functional group environment that the proton is found in. Chemical

shifts are independent of the magnetic field strength, but the dispersion increases with the field as absolute frequencies increase. The anisotropic effect is a result of the asymmetry of electron density in bonds, and is most pronounced in unsaturated systems with circulating π -electrons, such as alkenes and allenes.

Protons found within the plane in alkenes are said to be deshielded and are shifted to the high frequency end of the spectra. In comparison, the protons within the core of an alkyne are highly shielded, and so give rise to a resonance at lower frequencies. This is caused by the fact that lower electron density about the nucleus influences the degree of nuclear shielding. Electronegative groups such as NO_2 remove electrons from the ^1H nucleus and deshield it, whereas $-\text{Et}$ shield the nucleus and force the absorption to lower frequencies. In conjugated systems where several resonance forms can be drawn, a positive charge on one atom means the adjacent proton is deshielded and there is a higher shift observed as in methyl benzoate.



Aromatics often show very large shifts due to ring currents. The applied magnetic field induces a current in the ring which produces its own magnetic field.



Outside the ring, these fields add, and so a larger than expected shift is observed. In larger aromatics, with hydrogens inside the ring, shifts of -3ppm are observed.

Carbon-13 NMR

^{13}C has spin $\frac{1}{2}$ and so is also NMR active, making in an alternative to ^1H NMR. ^{13}C has low natural abundance, and so ^{13}C - ^{13}C homonuclear coupling is insignificant and ^{13}C -H couplings are removed by broadband proton decoupling for a clearer spectrum. The spectra have a simple appearance with a single line for each carbon site. The chemical shifts for ^{13}C are roughly 20 times that of the attached proton. CO is typically at about 160ppm and alkanes at about 20ppm. Symmetry in the molecule gives rise to equivalent peaks.

