NMR Spectroscopy

NMR (**N**uclear **M**agnetic **R**esonance) enables the precise structure of the molecule to be determined. It involves the interaction of materials with the low-energy radio wave region of the electromagnetic spectrum.

Nuclear magnetic resonance (NMR) gives information about the position of ^{13}C or ^{1}H atoms in a molecule.

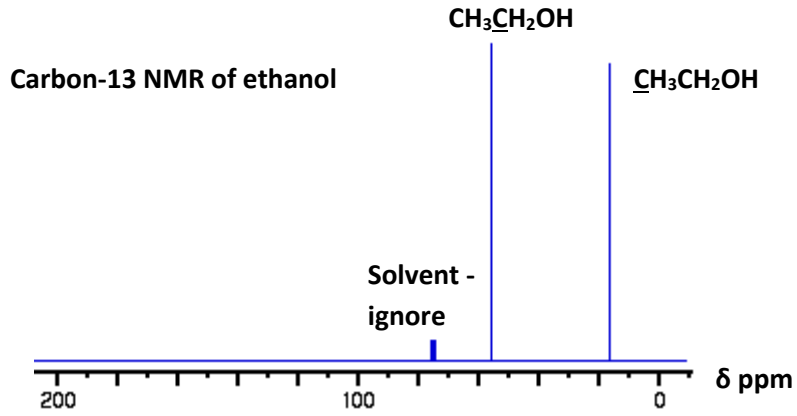
^{13}C NMR gives simpler spectra than ^{1}H NMR.

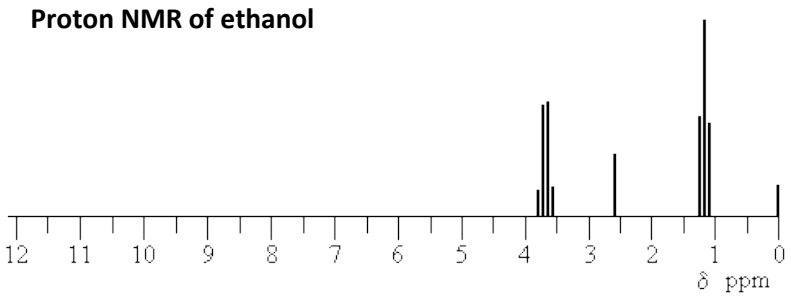
We use of the δ scale for recording chemical shift. The chemical shift depends on the molecular environment.

A carbon-13 NMR spectrum shows the different environments of carbon atoms in the molecule. From the spectrum you can make predictions about:

- The different types of carbon present, from chemical shift values.
- Possible structures of the molecule.

The spectrum plots absorption of energy against Chemical Shift (δ ppm)





This method depends on the magnetic properties of ^{1}H nuclei (usually referred to as **Protons**)

Equivalent protons are those which are in an identical chemical environment to each other. Protons joined to the same carbon atom are always equivalent to each other - symmetrical molecules will have equivalent protons joined to more than one carbon atom.

Neighbouring protons are not equivalent to each other but are joined to carbons which are adjacent in a carbon chain or ring.

Four distinct types of evidence can be gained from a spectrum

1. Each peak represents a different type of proton within the molecule this is very useful for distinguishing between isomers. **If two molecules are isomers the one with the fewer peaks is the more symmetrical**

2. The intensity of the peak (recorded as a number above the peak or as an integration trace) tells us a ratio of protons of that type contained in the molecule. Linked with 1 this will distinguish all simple isomers.

3. Chemical Shift tells us about the chemical environment of that type of proton. It is useful for confirming the identity of compounds or the presence of eg aldehydes or aromatic rings

4. The Splitting Patterns for a peak tells us the number of the number of non-equivalent protons adjacent to a given proton.

The peaks are not always single absorptions (known as **singlets**). There may be two adjacent absorptions (a **doublet**), or three (a **triplet**), or four (a **quartet**) or more (a **multiplet**). This is because the environment of each hydrogen atom is affected by its immediate neighbours. Look at the carbon to which the hydrogen atom(s) of one environment is/are attached. Count up the number of hydrogen atoms attached to the adjacent carbon atom(s). Add one. This will be the number of peaks you see on the spectrum (known as n+1 rule).

This information is used to confirm the structure of simple molecules - you should not need to use coupling as a primary means of identification.

Labile protons are acidic - they exchange easily with the solvent. Protons bonded to oxygen and nitrogen are always labile this means that:-

- **Coupling does not occur through oxygen or nitrogen atoms** eg ethanol
- **Deuterium**, the **^{2}H** isotope, does not have a magnetic moment so does not appear in an NMR spectrum.

  If D_2O is added to a sample the peaks of labile protons will disappear from the spectrum as the protons are replaced by deuterium.

Looking at the NMR of ethanol:

There is a triplet at δ1.2, a singlet at δ 2.6 and a quartet at δ 3.7. Three peaks in total.

The H attached to the oxygen behaves as if it has no neighbours, so gives the singlet at δ 2.6. Checking the data sheet confirms that an OH hydrogen would appear in this region of the spectrum.

The three methyl (CH_3) hydrogen atoms have two hydrogen neighbours on the adjacent carbon, so appear as a triplet (2 + 1). The data sheet confirms δ 1.2 as the correct region of the spectrum for a methyl, alkane-like group.

Finally, the two CH_2 hydrogen atoms appear as a quartet (3 + 1) as they have three hydrogen atom neighbours on the adjacent carbon atom. Being attached to the oxygen has shifted the peak up the spectrum and it appears at δ 3.7. This agrees with the data sheet.

Tetramethylsilane (TMS) is used as a standard for chemical shift measurements. The protons in TMS and carbons in TMS are assigned a chemical shift value of 0. It is chosen because it has 4 carbon atoms all of which are in exactly the same environment and 12 hydrogen atoms all of which are in exactly the same environment. That produces a single peak in both carbon-13 and proton NMR, but it's also a strong peak (because there are lots of carbon and hydrogen atoms all doing the same thing).

Solvents NMR spectra are usually measured using solutions of the substance being investigated. A commonly used solvent is $CDCl_3$. This is a trichloromethane (chloroform) molecule in which the hydrogen has been replaced by its isotope, deuterium. CCl_4 is also used as a solvent.

$CDCl_3$ is also commonly used as the solvent in proton-NMR because it doesn't have any ordinary hydrogen nuclei (protons) which would give a line in a proton-NMR spectrum. It *does* give a line in the carbon-13 NMR, but the line has an easily recognisable chemical shift and so can be removed from the final spectrum.

Other uses NMR spectroscopy is the same technology as that used in 'magnetic resonance imaging' (MRI) to obtain diagnostic information about internal structures in body scanners.

Combined techniques

For organic compounds containing any of the following atoms: C, H, N and O you need to be able to:

- analyse infrared absorptions in an infrared spectrum to identify the presence of functional groups in a molecule
- analyse molecular ion peaks and fragmentation peaks in a mass spectrum to identify parts of structures
- combine evidence from a number of spectra: NMR, IR and mass spectra, to deduce structures.

Remember IR and Mass Spectra are covered in **2.2.3 Modern Analytical Techniques**