FACTFILE:
GCE CHEMISTRY

5.2 NUCLEAR MAGNETIC RESONANCE

Rewarding Learning

Nuclear Magnetic Resonance (NMR)

Learning Outcomes

5.2.1 demonstrate understanding of the difference between low resolution and high resolution nmr spectra;

5.2.2 demonstrate understanding the reasons for the use of TMS (tetramethylsilane) as a standard;

5.2.3 demonstrate recognition of chemically equivalent hydrogen atoms;

5.2.4 demonstrate recognition that chemical shifts depend on the chemical environment of hydrogen atoms;

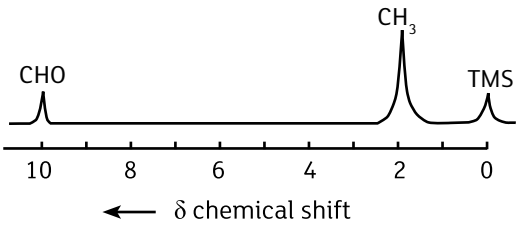
5.2.5 use integration curves to determine the relative number of protons in different chemical environments;

5.2.6 apply the n+1 rule to analyse spin-spin splitting, limited to doublets, triplets and quartets where n is the number of hydrogen atoms on an adjacent carbon atom; and

5.2.7 deduce a molecular structure from an nmr spectrum, limited to simple splitting patterns.

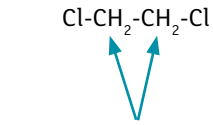
Nuclear magnetic resonance spectroscopy can be used to analysed the hydrogen atoms in a compound. Any nucleus which has an odd mass number or odd atomic number possesses spin – for example hydrogen has spin but carbon does not The spin of a nucleus gives it a magnetic field, similar to that of a bar magnet. The nuclei can be aligned with the magnetic field (low energy position) or, if they are given energy by radio waves, they are flipped into the high energy position where they are opposed to the magnetic field (this is called resonance). This is what happens in an nmr spectrometer, the energy of the radio waves is changed, and each hydrogen nuclei absorbs a different amount of energy, to flip to the high energy position where it is opposed to the field. A trace is printed out.

A simple low resolution NMR spectrum for ethanal looks like this:

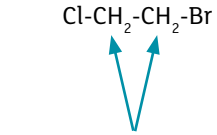


Often the spectrum is drawn more simply as a series of lines.

Chemical equivalent hydrogen atoms (protons) – these are hydrogen nuclei (protons) which are in a chemically identical environment and have the same chemical shift. They give one peak in the nmr and are not distinguishable.



These hydrogens are in exactly the same environment and so are said to be **equivalent.**



These hydrogens are not in exactly the same environment and so are not **equivalent.**

If there are 2 sets of chemically equivalent hydrogens in a molecule, as in CH_2ClCH_2Br there will be two peaks (apart from the TMS peak).

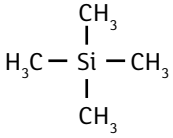
NMR interpretation.

Chemical shift
The horizontal scale in an nmr spectrum is shown as (ppm). is called the **chemical shift** and is measured in parts per million - ppm.

Chemical shift is a measurement of the magnetic environment of the hydrogen nuclei. It is measured relative to TMS which is given a value of zero.

A peak at a chemical shift of 2.0 is said to be downfield of TMS. The further to the left a peak is, the more downfield it is.

TMS = tetramethylsilane $Si(CH_3)_4$



Why is TMS chosen?

1. Its 12 hydrogens are chemically equivalent and produce a single peak which is strong due to the large number of hydrogen atoms
2. TMS does not interact with the molecule being tested
3. The electrons in the C-H bonds are closer to the hydrogens in this compound than in almost any other one. That means that these hydrogen nuclei are the most shielded from the external magnetic field, and so the magnetic field would need to be increased by the greatest amount to bring the hydrogens back into resonance. The net effect of this is that TMS produces a peak on the spectrum at the extreme right-hand side. Almost everything else produces peaks to the left of it.

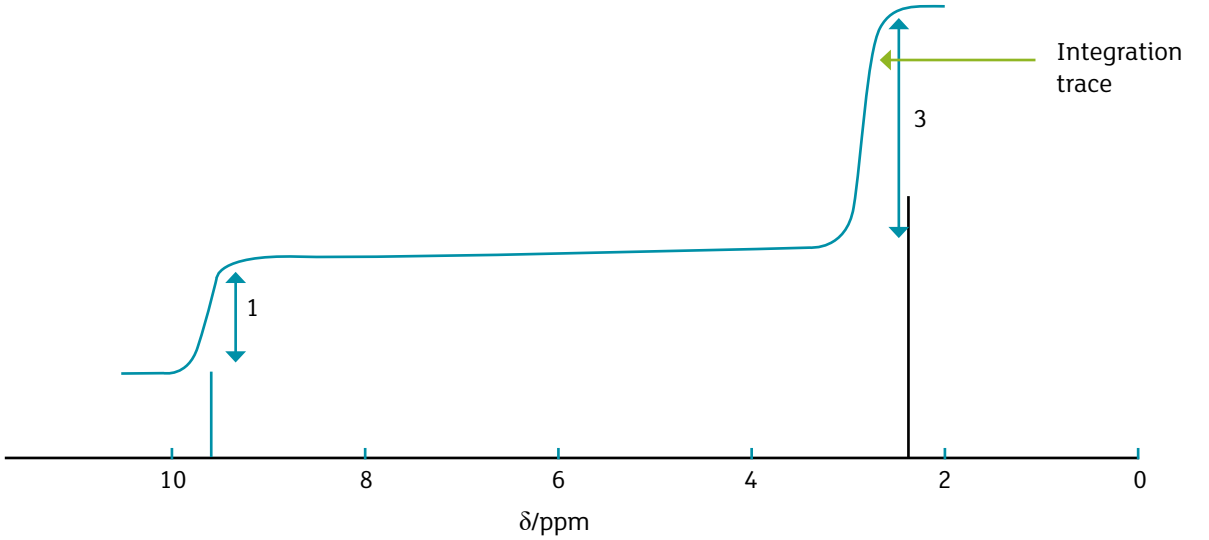
Chemical shift values give information about the environment in which the ^1H nuclei are found in the molecule. Those nuclei in the same environment appear at the same chemical shift on an n.m.r. spectrum. A higher chemical shift usually indicates that the ^1H nuclei are closer to an electronegative group or atom or an electron withdrawing group such as a benzene ring.

Highly electronegative neighbouring atoms reduce the electron density around the hydrogen atoms and so the hydrogen atoms are more deshielded and occurs at a higher chemical shift on a nmr spectrum.

Due to the way the nmr is printed out on the machine, zero is on the right and chemical shift increases to the left

What species have the highest chemical shift?
A hydrogen attached to an electronegative species. An electronegative atom draws electrons to itself and away from the hydrogen atom so the hydrogen atom is deshielded and appears at a higher chemical shift.

Peak integration -The area under the peaks is proportional to the relative number of hydrogens of each different type. An integrator trace measures the relative areas under the various peaks in the spectrum, it is a computer generated line which is superimposed on an NMR spectrum. The height of the trace is proportional to the area under the peak.



The peak integration trace is shown in the low resolution spectrum above. The ratio of the difference in heights (measured using a ruler) give the integration ratio 3:1.

The difference between high and low resolution spectra

From a low resolution spectra you can tell –

- The number of chemically equivalent hydrogens from the number of peaks
- The ratio of hydrogen atoms of each type from the peak integration
- The environment of the hydrogen from the chemical shift

Low resolution nmr produces a spectrum which does not show the splitting pattern.

High resolution nmr produces a spectrum which does show the spin-spin splitting pattern.

Neighbouring ^{1}H nuclei have an effect on each other. ^{1}H nuclei will be split into a number of peaks depending on the number of ^{1}H nuclei bonded to the adjacent carbon atoms. Splitting of peaks is called spin spin splitting and can be observed only in high resolution nmr spectra. The splitting pattern follows the **n+1 rule. n = the number of hydrogen neighbours** i.e the number of hydrogen atoms bonded to the carbon atom or atoms **next door** to the one you are currently interested in.

If there are 5 peaks (n+1) on the spectrum, this is caused by 4 (n) hydrogen nuclei on adjacent carbon atoms. The table shows the names and the ratios of the heights

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Number of hydrogen atoms bonded to adjacent arbon atoms [n]	Number of peaks (n+1)	Intensity of peaks	Name of pattern
0	1	(1)	Singlet
1	2	(1:1)	Doublet
2	3	(1:2:1)	Triplet
3	4	(1:3:3:1)	Quartet

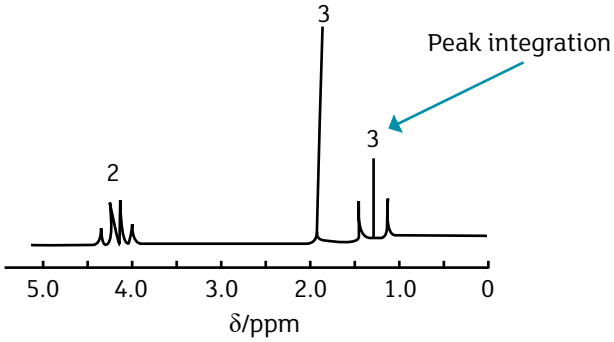
A doublet is a signal which appears as a pair of lines of equal intensity

A triplet is a signal which appears as three lines in the approximate intensity ratio (1:2:1)

A quartet is a signal which appears as four lines in the approximate intensity ratio (1:3:3:1)

The intensity of the peaks in a cluster is given by Pascal's triangle.

Below is the high resolution nmr spectrum for a compound with the molecular formula $C_4H_8O_2$.



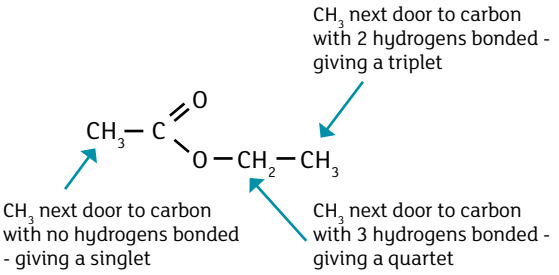
There are three clusters of peaks and so three different environments for the hydrogens. The peak

integration shows that the hydrogens in those three environments are in the ratio 2:3:3. Since there are 8 hydrogens altogether, this represents a CH_2 group and two CH_3 groups.

The CH_2 group at about 4.1 ppm is a quartet. Hence n+1 = 4 and so it has n =3 hydrogen atoms bonded to adjacent carbon atoms. This tells you that it is next door to a carbon with three hydrogen atoms attached - a CH_3 group.

The CH_3 group at about 1.3 ppm is a triplet. Hence n+1 = 3 and so it has n=2 hydrogen atoms bonded to adjacent carbon atoms. This tells you that is must be next door to a CH_2 group.

Finally, the CH_3 group at about 2.0 ppm is a singlet. This means n+1 = 1 and so it has n=0 hydrogen atoms bonded to adjacent carbon atoms. That means that the carbon next door doesn't have any hydrogen atoms attached.



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Nuclear magnetic resonance has been developed into the medical scanning technique known as magnetic resonance imaging MRI. The photograph shows a patient moving into a full body MRI scanning machine

Revision Questions

1 Nuclear magnetic resonance spectroscopy (nmr) is used to help understand the structure of molecules.

a) TMS is the standard used in nmr.
(i) What is the chemical name for TMS?

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(ii) Give two reasons why TMS is suitable for use as a standard in nmr.

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b) Sketch the nmr spectrum for methyl propanoate, $CH_3CH_2COOCH_3$ showing the integration curve together with the splitting patterns. Indicate which hydrogen atoms are responsible for each peak.

[5]

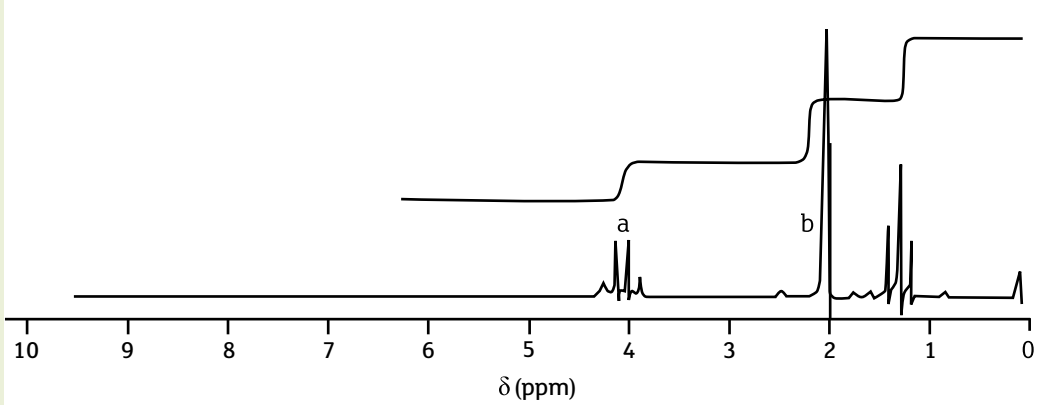
Revision Questions

2 The first person to extract ethanoic acid from vinegar was the alchemist Jabir ibn Hayyan Geber (c. 721-815 AD). However the pure compound was not produced for another ten centuries.

a) The mass spectrum of ethanoic acid shows a distinct peak at m/e=59. State the formula of the species giving rise to this peak.

.....[1]

b) Ethanoic acid reacts with ethanol to form the ester ethyl ethanoate, $CH_3COOC_2H_5$. The nmr spectrum of ethyl ethanoate consists of three sets of peaks as shown below.



(i) Explain the peak integrations.

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.....[2]

(ii) Explain the chemical shifts.

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.....[2]

(iii) Explain the splitting pattern **a**.

.....[1]

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Revision Questions

(iv) Explain why **b** is a singlet.

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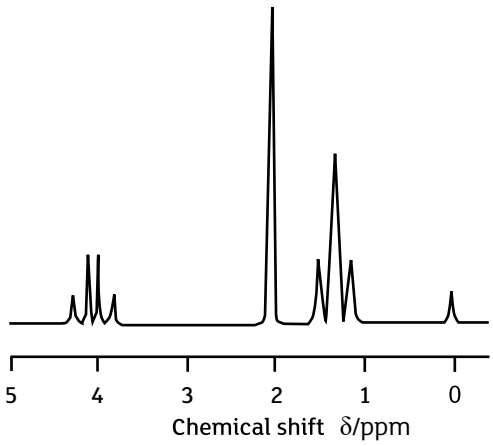
.....[1]

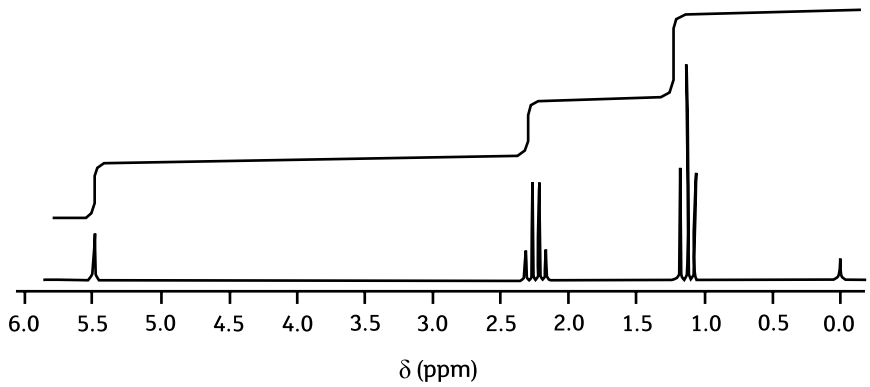
3 The nmr spectrum of a compund X is shown below.
Which one of the following is **X**?

A $CH_3CH_2CH_2COOH$
B $CH_3CH_2COOCH_2CH_3$
C $CH_3COOCH_2CH_3$
D CH_3CH_2COOH



Revision Questions

4 The nmr spectrum of propanamide is shown below.



(i) The signal at 0 ppm is due to TMS. Explain why TMS is used as a standard.

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..... [2]

(ii) Explain why the signal at 1.15 ppm is a triplet.

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..... [1]

(iii) Explain why the signal at 2.25 ppm is a quartet.

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(iv) Explain why the signal at 5.5 ppm is at the highest chemical shift in the spectrum.

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..... [1]

(iv) Explain three ways in which this spectrum would differ from the spectrum of the N-methylated compound, $CH_3CH_2CONHCH_3$.

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..... [3]