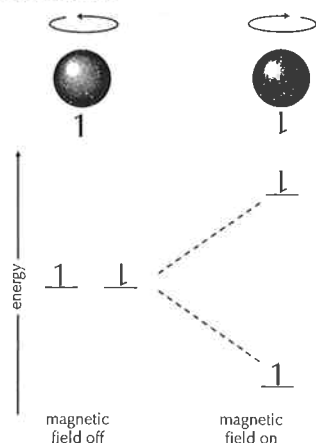




Nuclear magnetic resonance (NMR) spectroscopy (1)

NUCLEAR SPIN



Unlike most other branches of spectroscopy NMR involves the interaction of **nuclei**, not electrons, with electromagnetic radiation. NMR concerns nuclei with uneven mass numbers, e.g. ^1H , ^{13}C , ^{19}F , and ^{31}P . All nuclei that possess spin behave as small magnets. In the absence of a magnetic field the two orientations of spin have the same energy. In the presence of a magnetic field the two orientations have a small difference in energy as they line up with or against the magnetic field. Nuclei can absorb energy as they move from the lower to the higher state. This small difference in energy corresponds to radio frequencies in the region of 10^7 to 10^8 s^{-1} (Hz).

To obtain an NMR spectrum the sample, either a pure liquid or in solution, together with a reference is placed in a cylindrical tube. The tube is then placed between the poles of a powerful electromagnet. A probe coil connected to a radio-frequency generator and receiver surrounds the sample. The spectrum is obtained either by varying the radio frequency or more commonly by varying the strength of the magnetic field.

THE MAIN FEATURES OF ^1H NMR SPECTRA

1. The number of different absorptions (peaks)

Each proton in a particular chemical environment absorbs at a particular frequency. The number of peaks thus gives information as to the number of different chemical environments occupied by the protons.

2. The area under each peak

The area under each absorption is proportional to the number of hydrogen atoms in that particular chemical environment. Normally each area is integrated and the heights of the integrated traces can be used to obtain the ratio of the number of hydrogen atoms in each environment.

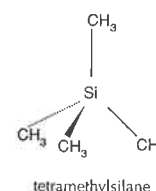
3. The chemical shift

Because spinning electrons create their own magnetic field the surrounding electrons of neighbouring atoms can exert a shielding effect. The greater the shielding the lower the frequency for the resonance to occur. The 'chemical shift' (δ) of each absorption is measured in parts per million (ppm) relative to a standard. The normal standard is tetramethylsilane (TMS) which is assigned a value of 0 ppm. This has been mentioned previously in 11. Topic 20 – Organic Chemistry and a table of chemical shifts is to be found in the IB Data Booklet.

4. Splitting pattern

In ^1H NMR spectroscopy the chemical shift of protons within a molecule is slightly altered by protons bonded to adjacent carbon atoms. This spin-spin coupling shows up in high resolution ^1H NMR as splitting patterns. If the number of adjacent equivalent protons is equal to n then the peak will be split into $(n + 1)$ peaks.

Tetramethylsilane as a reference sample

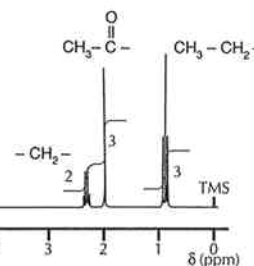
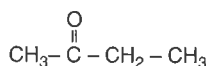


The advantages of using tetramethylsilane $\text{Si}(\text{CH}_3)_4$ as the standard reference are:

- All the protons are in the same environment so it gives a strong single peak.
- It is not toxic and is very unreactive (so does not interfere with the sample).
- It absorbs upfield well away from most other protons.
- It is volatile (has a low boiling point) so can easily be removed from the sample.

INTERPRETING AN ^1H NMR SPECTRUM

^1H NMR spectrum of butanone



1. The three different peaks show that the hydrogen atoms within the molecule are in three different chemical environments.

2. The integrated trace shows that the hydrogen atoms are in the ratio 2:3:3.

3. The chemical shifts of the three peaks identify them as:



4. The $-\text{CH}_2-$ group has three adjacent protons so is split into a quartet, $(n+1=4)$.

The $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ protons contain no adjacent protons so no splitting occurs.
The CH_3- group next to the $-\text{CH}_2-$ group is split into a triplet $(n+1=3)$.

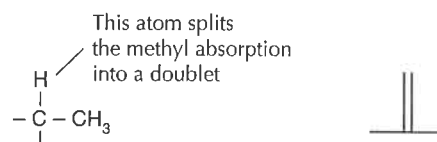




Nuclear magnetic resonance (NMR) spectroscopy (2)

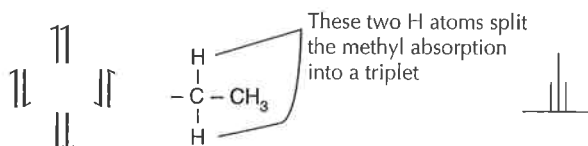
SPIN-SPIN COUPLING

Splitting patterns are due to spin-spin coupling. For example, if there is one proton ($n = 1$) adjacent to a methyl group then it will either line up with the magnetic field or against it. The effect will be that the methyl protons will thus experience one slightly stronger and one slightly weaker external magnetic field resulting in an equal splitting of the peak. This is known as a doublet ($n + 1 = 2$).



If there is a $-\text{CH}_2-$ group ($n = 2$) adjacent to a methyl group then there are three possible energy states available.

1. Both proton spins are aligned with the field
2. One is aligned with the field and one against it (2 possible combinations)
3. Both are aligned against the field.

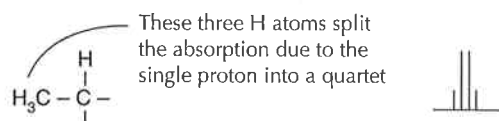


This results in a triplet with peaks in the ratio of 1:2:1.

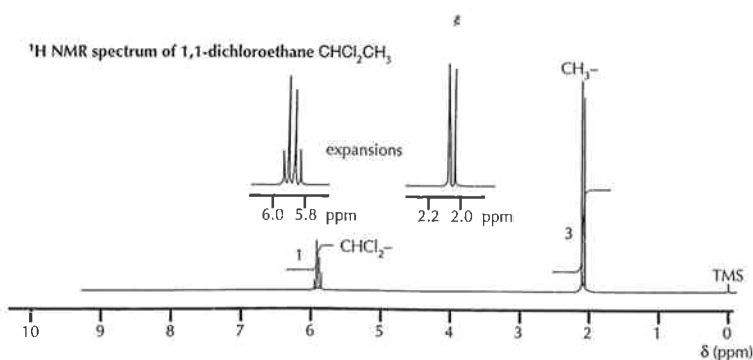
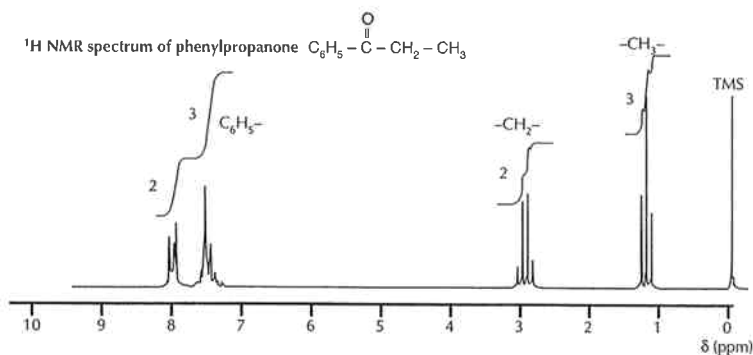
The pattern of splitting can always be predicted using Pascal's triangle to cover all the possible combinations.

Number of adjacent protons (n)	Splitting pattern			Type of splitting
0	1			singlet
1	1	1		doublet
2	1	2	1	triplet
3	1	3	3	quartet
4	1	4	6	quintet

Thus a methyl group ($n = 3$) next to a proton will result in the absorption for that proton being split into a quartet with peaks in the ratio 1:3:3:1.



FURTHER EXAMPLES OF ^1H NMR SPECTRA INVOLVING SPLITTING PATTERNS



USES OF NMR SPECTROSCOPY

1. Structural determination

^1H NMR is a particularly powerful tool in structural determination as it enables information to be gained on the precise chemical environment of all the protons in the molecule. Similarly ^{13}C and other forms of NMR can also provide very detailed structural information including, for example, distinguishing between *cis*- and *trans*-isomers in organometallic compounds.

2. Medicinal uses

NMR is particularly useful in medicine as the energy of the radio waves involved is completely harmless and there are no known side effects. ^{31}P is particularly useful in determining the extent of damage following a heart attack and in monitoring the control of diabetes. ^1H NMR is used in body scanning. The whole body of the patient can be placed inside the magnet of a large NMR machine. Protons in water, lipids, carbohydrates, etc. give different signals so that an image of the body can be obtained. This is known as MRI (magnetic resonance imaging). The image can be used to diagnose and monitor conditions, such as cancer, multiple sclerosis, and hydrocephalus.