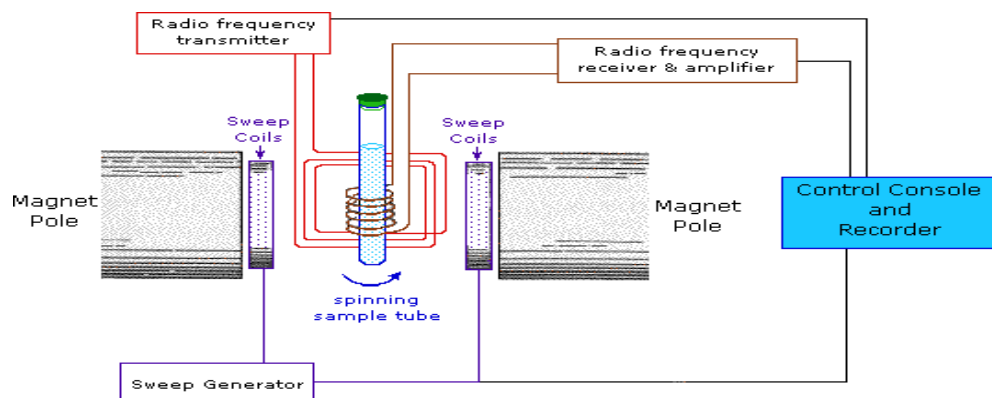


Nuclear Magnetic Resonance [NMR]

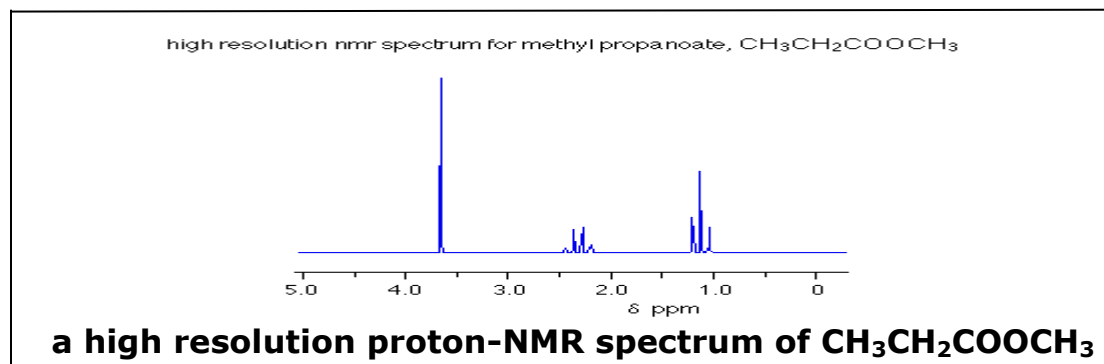
Nuclear magnetic resonance spectroscopy [NMR] is a powerful qualitative tool for determining the structure of complex organic molecules.

- NMR is concerned with the magnetic properties of certain nuclei, such as $^1\text{H}_1$ and $^{13}\text{C}_6$, which have an odd number of nucleons in their nucleus
- The nuclei of these isotopes [$^1\text{H}_1$ and $^{13}\text{C}_6$] act as tiny magnets and when placed in a powerful magnetic field, will align themselves, just like compass needles.
- But if enough energy is applied to these aligned ^1H and ^{13}C nuclei, they will eventually "flip" their alignment to the opposite direction ... this flipping is called **resonance**.
- Proton-NMR and carbon-13 NMR deal with the absorption of **radio-frequency [RF]** electromagnetic energy to flip the polarity of the $^1\text{H}_1$ or $^{13}\text{C}_6$ nuclear magnets when they are in an external magnetic field.
- The NMR spectrum is displayed as a peak on a graph, indicating when exactly the right magnetic field strength is being applied to allow the nuclei magnets to undergo resonance when exposed to a set RF energy

The NMR Spectrometer

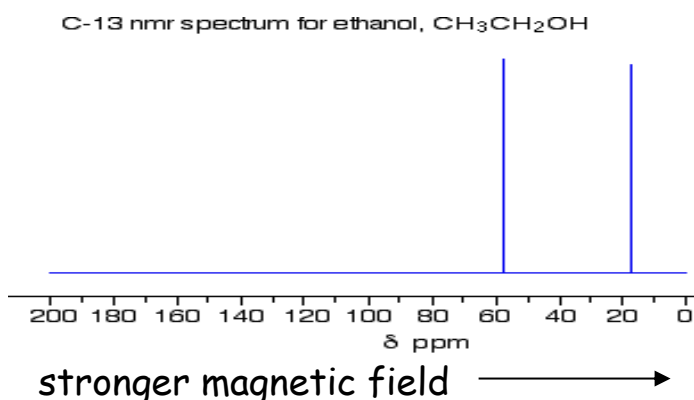


- the sample is spun at high speed inside a powerful magnetic field
- an RF transmitter exposes the sample to a varying RF energy and an RF receiver detects the point at which the target nuclei undergo resonance



C-13 Nuclear Magnetic Resonance

- C-13 NMR deals with the absorption of radio-frequency energy to flip the polarity of the C-13 nuclear magnets when they are in an external magnetic field.
- The C-13 NMR spectrum is displayed as a **peak on a graph**, indicating when exactly **the right magnetic field strength** is being applied to allow the **C-13 nuclei magnets to undergo resonance** when exposed to a **set RF energy**.



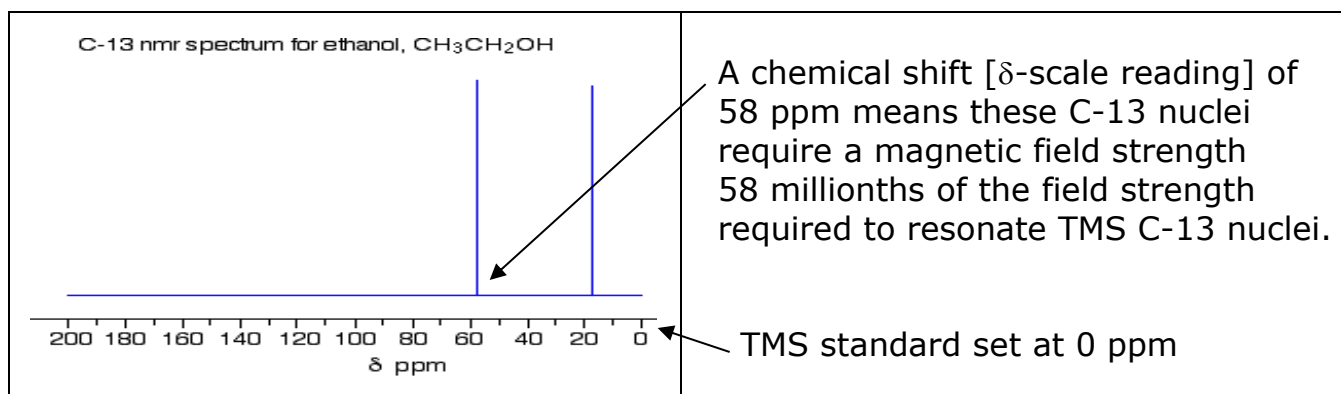
- There are two "different" carbons in ethanol, one as part of a methyl side chain, the other has an OH attached ... and so there are 2 peaks on the NMR spectrum
- These "different" carbon atoms require different magnetic field strengths to set their C-13 nuclei magnets resonating

Effect of the Carbon Environment

- For a given radio-frequency energy, each C-13 atom in a different molecular environment will need a slightly different magnetic field applied to it to keep it resonating, so the magnetic field strength needed gives us a useful guide to the atoms attached to the C atoms.

Setting the Standard

- the horizontal scale on the NMR spectrum has a zero point, at the RHS of the scale.
- Tetramethylsilane [TMS] is chosen as the zero point standard, because its 4 carbon atoms have only one C environment [\therefore 1 strong peak]
- The horizontal δ -scale, measured in **ppm** is called the **chemical shift**

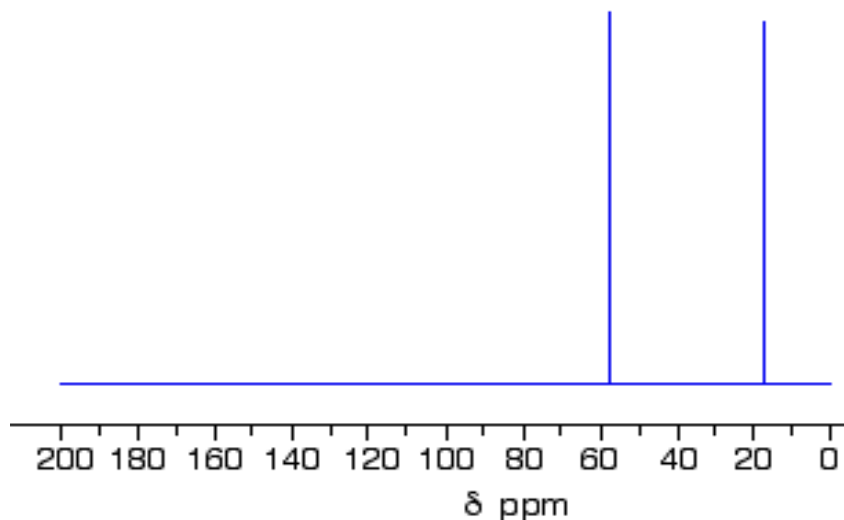


C13 NMR Chemical Shift Data

Type of carbon	Chemical shift [ppm]
-CH ₃	8-27
-CH ₂	27-50
-CH	37-60
R ₄ -C	36-45
-C-X [X = F, Cl, Br, I]	15-80
C-N	43-78
C-O	50-88
C≡C	77-98
C=C	108-150
C=O	160-220

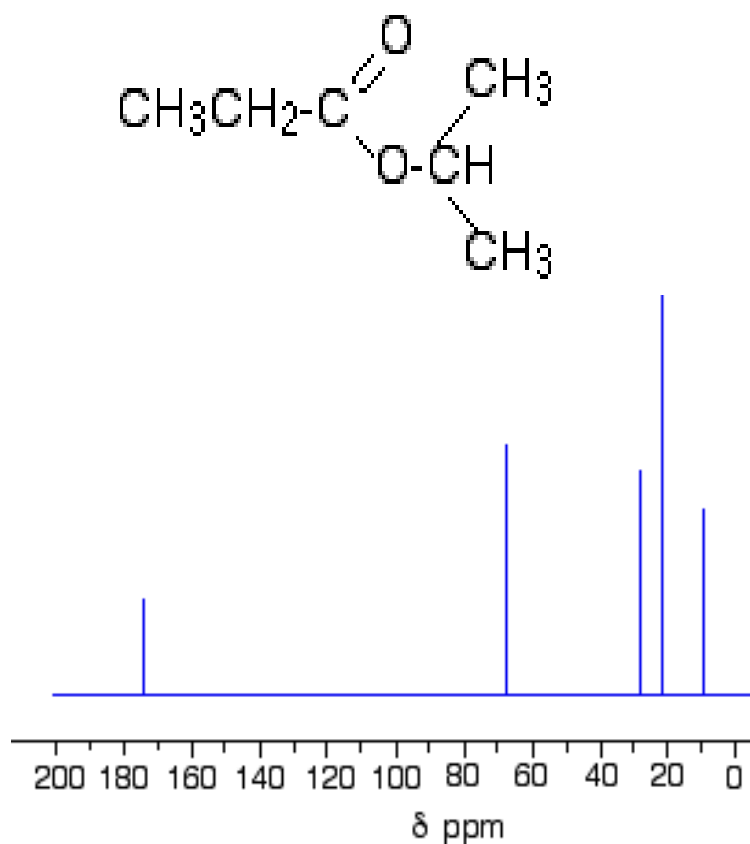
An example of a C-13 NMR Spectra

-C-13 NMR Spectrum of Ethanol CH₃CH₂OH



- There are 2 peaks because there are two different environments for the carbons ... -CH₃ and -CH₂OH
- The peaks are ≈ the same height because there is one carbon of each type.
- The peak with a chemical shift of 58 ppm corresponds to that expected for R-CH₂-OH [50-88 ppm]
- The peak with the chemical shift of 18 ppm corresponds to that expected for R-CH₃ [8-27 ppm].

Analysing the C-13 NMR of 1-methylethyl propanoate

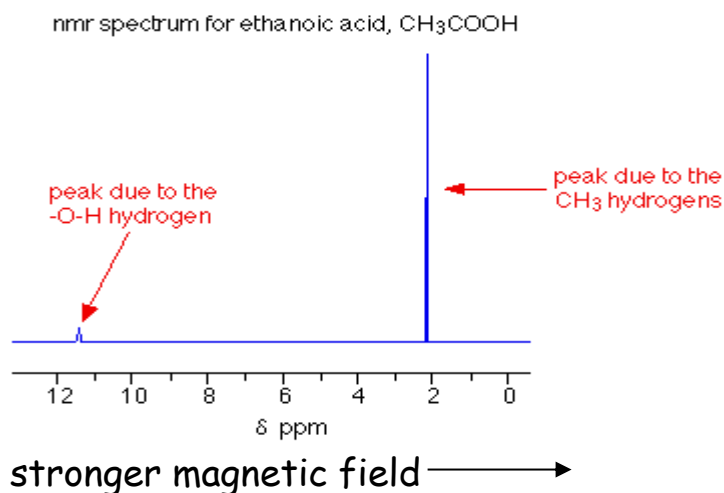


- It has 5 peaks ... therefore there must be 5 different environments for the carbon atoms.

Peak [ppm]	C environment	typical chemical shift [ppm]	Carbon identification
8	-CH₃	8 – 27	<u>C</u> H ₃ CH ₂ COOCH(CH ₃) ₂
22	-CH₃	8 – 27	CH ₃ CH ₂ COOCH(<u>C</u> H ₃) ₂ ... the extra peak height as there are 2 carbons in same environment
28	-CH₂-	27 – 50	CH ₃ <u>C</u> H ₂ COOCH(CH ₃) ₂
63	-CH-	37 – 60	CH ₃ CH ₂ COO <u>C</u> H(CH ₃) ₂
175	-C=O	160 – 220	CH ₃ CH ₂ <u>C</u> OOCH(CH ₃) ₂

Proton-NMR [^1H Nuclear Magnetic Resonance]

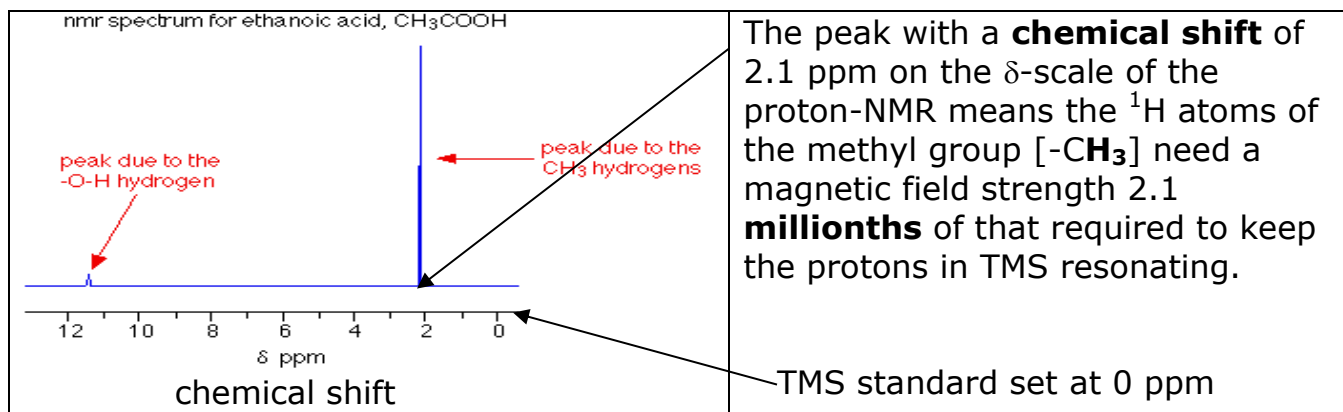
- Proton-NMR deals with the absorption of radio-frequency energy to flip the polarity of the ^1H nuclear magnets when they are in an external magnetic field.
- The proton-NMR spectrum is displayed as a **peak on a graph**, indicating when exactly **the right magnetic field strength** is being applied to allow the **^1H nuclei magnets to undergo resonance** when exposed to a **set RF energy**.



- there are two “different” types of hydrogen in CH_3COOH , one in a methyl group, the other attached to the O atom... and so there are 2 peaks on the NMR spectrum
- these “different” hydrogens atoms require different magnetic field strengths to set their ^1H nuclei magnets resonating
- the right hand peak is much taller as it represents 3 H atoms in the CH_3 compared to only 1 H in the OH group.

Effect of the H atom's Environment

- For a given RF energy, each ^1H atom with a different environment in a molecule will need a slightly different magnetic field applied to it to keep it resonating ... so the magnetic field strength needed is a useful guide to the H atoms environment in the molecule.



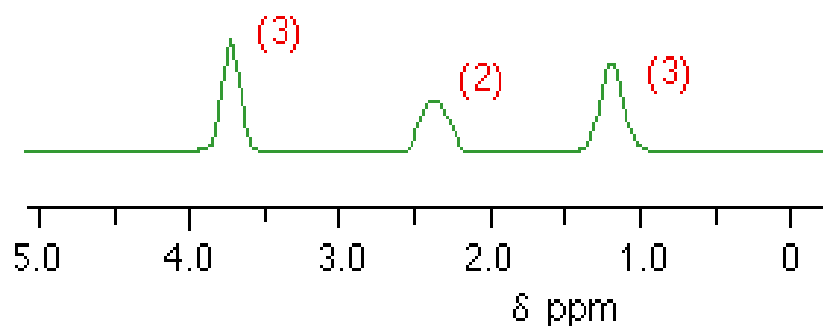
Typical ^1H NMR Chemical Shift Data

Type of carbon	Chemical shift [ppm]
R- CH ₃	0.7 – 1.6
R- CH ₂ -R	1.3
RCH=CH- CH ₃	1.7
R ₃ - CH	2.0
CH ₃ COO-R	2.0
H -C(O)-	9 – 10
CH ₃ CO-R	2.1
R- CH ₂ -X [X = Cl, Br, F]	3 – 4
R- CH ₂ OH	3.6
R- CH ₂ (CO)-	2.0 – 2.9
R- OH	1 – 6
R- NH ₂	1 – 5
R-O- CH ₃ or -O- CH ₂ -R	3.3 – 4.3
-COO H	11 – 12

Low and High Resolution Proton NMR

1. Low Resolution NMR of methyl propanoate

low resolution nmr spectrum for methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$

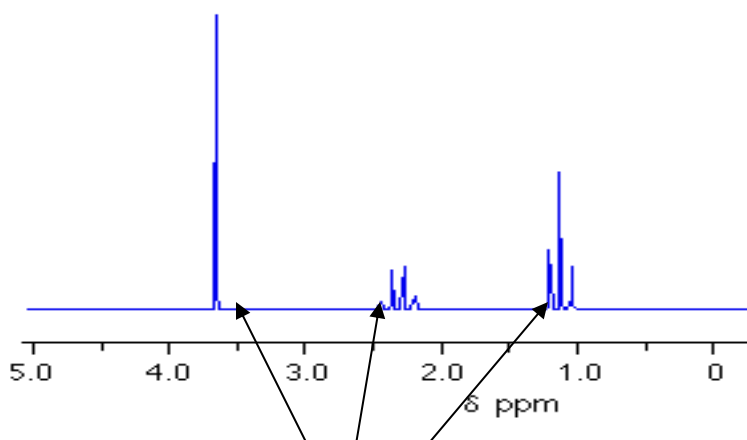


- the 3 broad peaks indicate 3 types of hydrogen present
- the ratio of peak areas gives the ratio of H's in the environments ...
the 3 broad peaks are in the ratio 3:2:3 [as would be expected from the $\text{CH}_3\text{-O-}$, $\text{-CH}_2\text{-}$ and -CH_3 groups]

Chemical shift	Relative peak area	Typical Chemical Shifts
1.2	3	R-CH ₃ [0.7 – 1.6]
2.4	2	R-CH ₂ C=O [2.0 – 2.9]
3.8	3	-O-CH ₃ [3.3 – 4.3]

2. High Resolution NMR of methyl propanoate

high resolution nmr spectrum for methyl propanoate, CH₃CH₂COOCH₃



Peak area ratio is 3: 2: 3

- the 3 clusters of peaks indicate there are 3 types of hydrogen present
- the area of peak clusters is in the 3: 2: 3 ratio
- **The splitting of peaks in a high resolution proton-NMR can be used to indicate the number of H atoms on the C atom next door ...**

The n+1 Rule

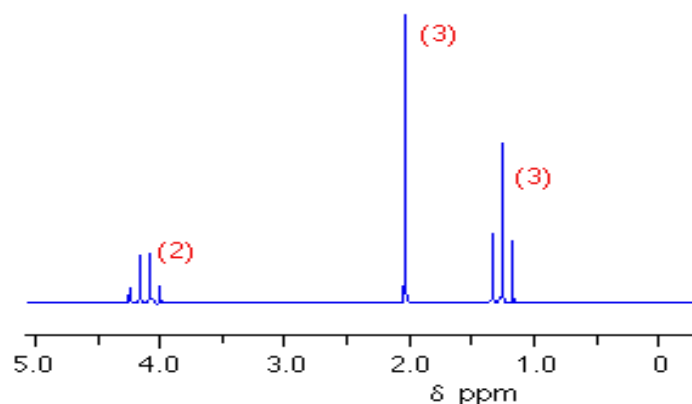
The amount of splitting indicates the number of hydrogens attached to the neighbouring atoms ... the number of peak splits in a cluster is one more than the number of hydrogens attached to the carbons next door

So, if there's only 1 carbon atom next to the one your looking at ...

- a singlet = a C atom next door with no H atoms on it
- a doublet = a C atom next door with 1 H atom attached
- a triplet = a C atom next door with 2 H atoms attached
- a quartet = a C atom next door with 3 H atoms attached

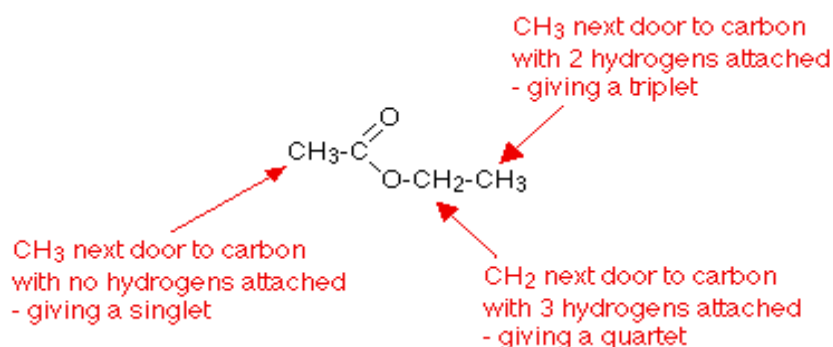
- the triplet at 1.2 ppm indicates that there are 2 H on the C next door [-CH₂]; the quartet at 2.4 ppm suggests there are 3 H on the C next door [-CH₃]

Analysing the proton-NMR of a compound, C₄H₈O₄



- there are 3 broad peaks – 3 different H environments
- the ratio of areas of different H's attached to the carbons is 2:3:3, so this represents two –CH₃ and one –CH₂– [if there are 8 H atoms]
- the cluster at 4.1 ppm is a quartet, meaning the carbon next to it has 3 carbons ie. –CH₃
- the cluster at chemical shift 1.2 ppm is a triplet, meaning the carbon next to it has 2 carbons ie. CH₂ ... the combination of a triplet and a quartet is common and suggests an ethyl group –CH₂CH₃
- the singlet at chemical shift 2.1 suggests that a neighbouring carbon has no hydrogen attached.
- the singlet at 2.1 next to a carbon with no hydrogens could be in the form of CH₃COO-R, which is expected at a chemical shift of 2.0 ppm
- the quartet at chemical shift 4.1 ppm is probably in the form of –O-CH₂CH₃ which is expected at a chemical shift of 3.3 – 4.3 ppm
- the triplet at 1.2 ppm could be in the form –CH₂CH₃ which has a chemical shift of 0.7-1.6

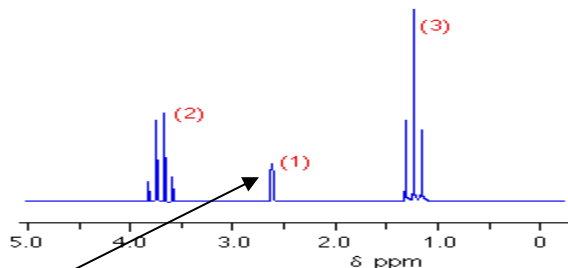
So, the molecule could be ...



Splitting in alkanols

- The position of the R-OH peak in a ^1H -NMR spectrum varies considerably [1 – 6 ppm], depending on the conditions employed

nmr spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ - source SDBS

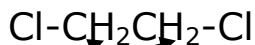


in ethanol, the proton-NMR -OH peak is a singlet at 2.7 ppm

- The ^1H on the R-OH group doesn't seem to interact with ^1H atoms on neighbouring carbons, so doesn't contribute to their NMR splitting, and the R-OH peak on a proton-NMR is a **singlet**.

Equivalent Hydrogens

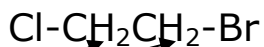
- Hydrogen atoms attached to the same atom are said to be equivalent, have no effect on each other and don't cause any splitting
- Hydrogen atoms attached to neighbouring carbons can also be equivalent if they have the exactly the same environment.



these H atoms have exactly the same environment

\therefore single peak and no splitting

- The H atoms above have exactly the same environment and would produce a single peak with no splitting.
- A slightly different environment however and the hydrogens on adjacent C atoms are no longer equivalent ...



these H atoms now have slightly different environments

\therefore two peaks, each split into triplets

- A high resolution ^1H NMR would now have two triplet clusters, splitting caused by the effect of non-equivalent H atoms on adjacent carbons.