Proton NMR Spectroscopy

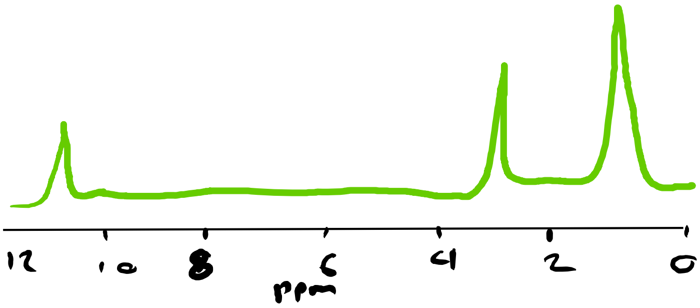
There are two different spectrums that can be produced for proton NMR.

1.

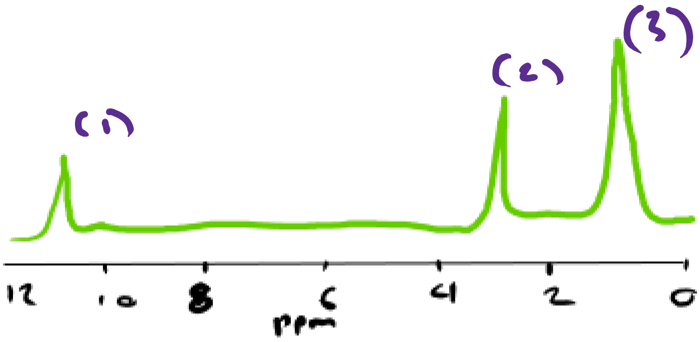
2.

This type of spectroscopy relies on the magnetic properties of the hydrogen-1 isotope. The key points to note are as follows:

- The number of tells us the number of different (proton) environments.

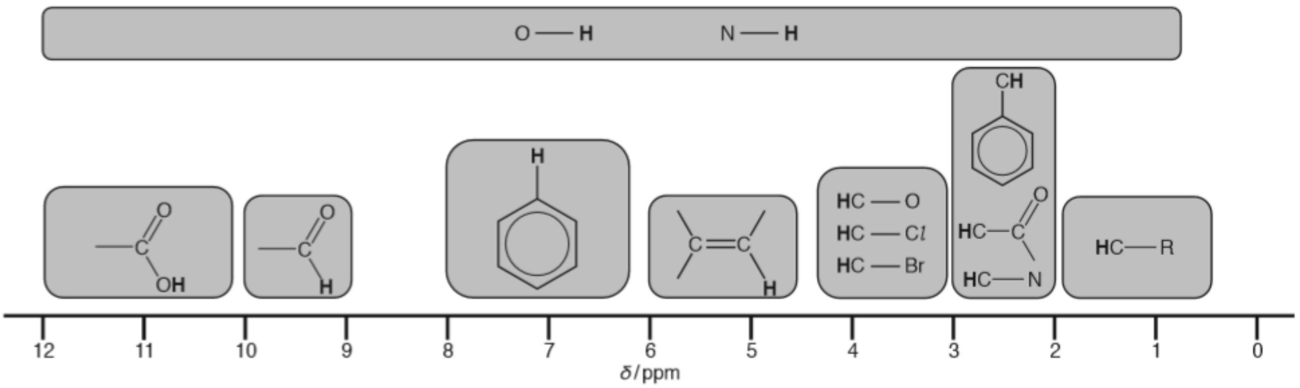


- The under the peaks tells us the between the different proton environments. This is often shown on the spectrum using an . Often it seen as in brackets next to a peak.

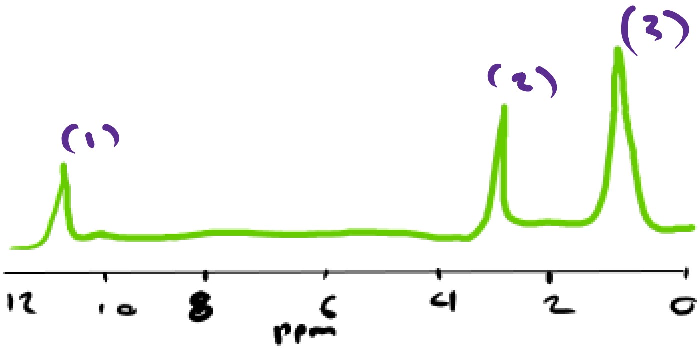


- The tells us what each hydrogen belongs to.

^{1}H NMR chemical shifts relative to TMS



Chemical shifts are variable and can vary depending on the solvent, concentration and substituents. As a result, shifts may be outside the ranges indicated above.
OH and **NH** chemical shifts are very variable and are often broad. Signals are not usually seen as split peaks.
Note that **CH** bonded to 'shifting groups' on either side, e.g. O–CH_2–C=O, may be shifted more than indicated above.



- **Only** in NMR. The of a peak gives us information of how many are attached to the carbon atom.

  Splitting patterns can be worked out using:

Equivalent hydrogen atoms

Hydrogen atoms attached to the same carbon atom are said to be

. They are said to be in the same .

Equivalent hydrogen atoms have no effect on each other - so that one hydrogen atom in a CH_2 group doesn't cause any splitting in the spectrum of the other one e.g.

But hydrogen atoms on carbon atoms can also be equivalent if they are in exactly the same .

Draw the displayed formula of 1,2-dibromoethane.

This molecule would show peak in proton NMR.

If one atom is changed in the molecule the environments may no longer be .

Draw the displayed formula of 1-bromo,2-iodoethane.

This molecule would show in proton NMR.

Low resolution NMR

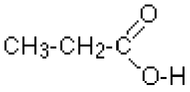
The spectrum produced by this resolution does not give us any information about hydrogens on adjacent carbon atoms.

The integration trace measures the area under the peak. This tells us the ratio of how many hydrogens are in each different chemical environment.

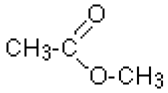
We can use the chemical shift values to identify the different chemical environments for the protons.

An organic compound was known to be one of the following. Use its low resolution NMR spectrum to decide which it is.

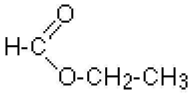
propanoic acid

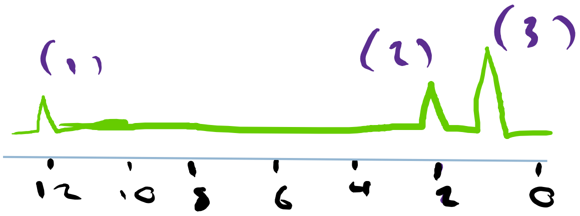


methyl ethanoate



ethyl methanoate





How many different chemical environments for hydrogen atoms are there?

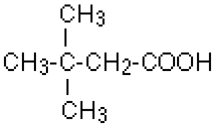
What would be the ratio of these environments?

How can we identify the compound from the chemical shift values?

Identifying a compound from number of peaks

Draw the isomers of the carbonyl containing compounds that have the molecular formula C_3H_6O. Determine how you could tell how you can identify these two molecules solely from number of peaks in a low resolution NMR spectrum.

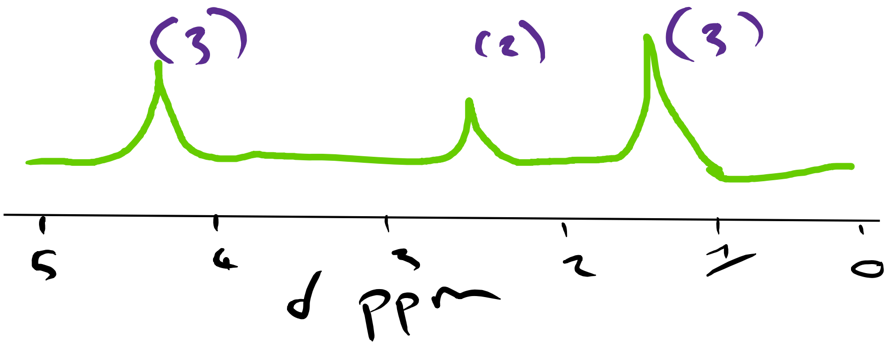
How many peaks would there be in the low resolution NMR spectrum of the following compound, and what would be the ratio of the areas under the peaks?



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-COOH$$

Answer the following question:

The low resolution proton NMR of a compound with the molecular formula $C_4H_8O_2$ is shown below. Identify a suitable structure and provide reasoning for your answer.



How many different chemical environments?

What information does the integration trace tell us?

How can we deduce the structure from the chemical shift values?

High Resolution NMR

High resolution NMR gives us additional information on the of hydrogen environments. The peak can be split dependent on the number of on the adjacent carbon atom.

This is due to .

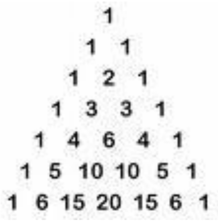
Spin-spin coupling

In a high resolution NMR spectrum the signal is split into a distinctive pattern. The splitting is called spin-spin coupling and is caused by the interactions between protons on adjacent carbon atoms.

This splitting pattern can be used to find the number of protons on an carbon. The pattern is predicted using the n+1 rule. This rule states that

"for n protons on an adjacent carbon, the number of peaks in a splitting pattern equals n+1"

The actual ratio of peak areas in the splitting pattern is related to Pascal's triangle as shown below:



1
1 1
1 2 1
1 3 3 1
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1

A single peak is called a .

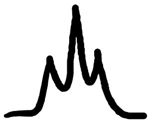
A double peak is called a .

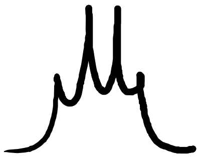
A triplet

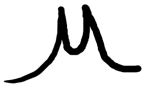
A quartet

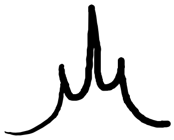
A multiplet

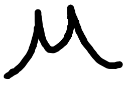
Common combinations in a spectrum:





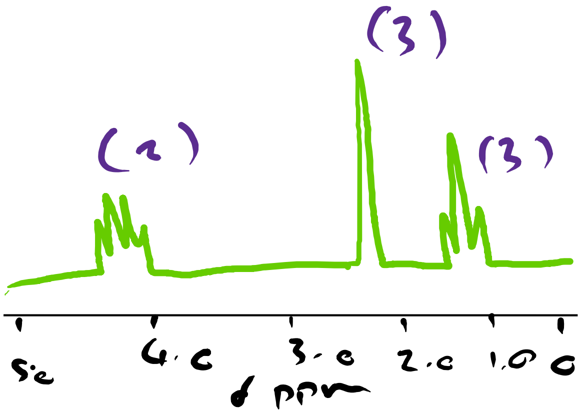






Using the n+1 rule

What information can you get from this NMR spectrum?



The spectrum above is a high resolution spectrum of a compound with the molecular formula $C_4H_8O_2$.

How many different hydrogen environments?

What is the number of hydrogens in each environment (look at the integration trace)?

What information can we gain from the splitting patterns of the peaks?

Confirm your structure by using the chemical shift values

Therefore, the structure must be

Identifying OH and NH peaks:

Look at your data sheet why might it be very difficult to pick out an OH and NH peak by using chemical shift values?

OH and NH peaks always appear as . They are never split even if they are next to a carbon with hydrogens on it. The hydrogen environment next to these two peaks never splits as well.

How can we tell the difference between an OH/NH peak and carbon with only one hydrogen on it? Wouldn't they produce a singlet for the splitting pattern of a neighbouring carbon?

The use of D_2O

Deuterium is an of hydrogen with one extra .

can remove an or peak from a .

This happens because the deuterium atom can replace a hydrogen atom in the or . Take for example ethanol. Ethanol is weakly . This means it can interact with water by:

$$CH_3CH_2OH + D_2O \longrightarrow CH_3CH_2O^- + HD_2O^+$$

The interchange can then occur again but this time with the deuterium atom:

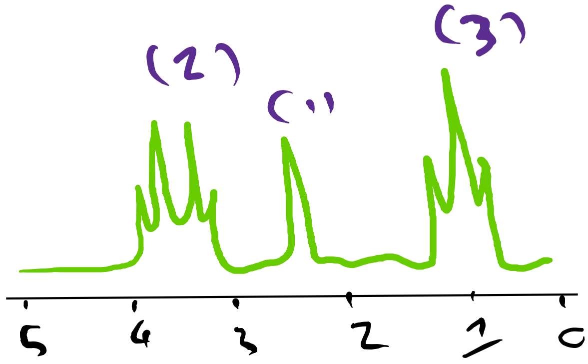
$$CH_3CH_2O^- + HD_2O \longrightarrow CH_3CH_2OD + HDO$$

Deuterium atoms do not produce peaks because they have an number of .

Using D_2O

1. Produce a spectrum of a sample normally.
2. Add to the sample and produce a spectrum.
3. The or peak would off the second spectrum!

An organic molecule has the molecular formula of C_2H_6O it can be reacted with a carboxylic acid to produce an ester using a concentrated sulphuric acid catalyst. It's high resolution spectrum is shown below:



What information can we get from the splitting pattern on the above spectrum?

What information can we gain from the chemical shift values?

What could be the structure of the molecule?

Draw the spectrum you would expect to see if D_2O is added to the sample.