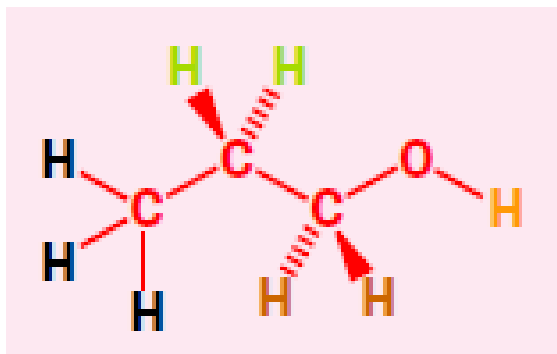


NMR Spectroscopy

Nuclear magnetic resonance (NMR)

What does it do?

Nuclear magnetic resonance (NMR) allows us to detect atomic nuclei and say what sort of environment they are in, within their molecule.



NMR can easily distinguish between different sorts of hydrogen atoms present. The technique is called ^1H -NMR or proton-NMR spectroscopy

Likewise, NMR can easily distinguish between the three different carbon atoms. The technique is called ^{13}C -NMR or carbon-NMR spectroscopy

One can determine the entire structure of a molecule.

Nuclear magnetic resonance (NMR)

The nuclei of all elements carry a charge.

Every nuclei have an intrinsic value of spin quantum number, I which may have value like 0, $\frac{1}{2}$, 1, 2, 3, $\frac{3}{2}$

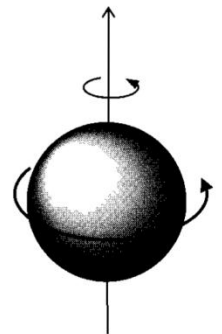
General guideline to have an idea about the nuclear spin quantum numbers

Mass Number	Number of Protons	Number of Neutrons	Spin (I)	Example
Even	Even	Even	0	$^{12}_6\text{C}(0)$, $^{16}_8\text{O}(0)$, $^{34}_{16}\text{S}(0)$
	Odd	Odd	Integer (1,2,...)	$^2_1\text{H}(1)$, $^{14}_7\text{N}(1)$, $^{10}_5\text{B}(3)$
Odd	Even	Odd	Half-Integer ($\frac{1}{2}$, $\frac{3}{2}$,...)	$^{13}_6\text{C}(\frac{1}{2})$, $^{17}_8\text{O}(\frac{1}{2})$, $^{29}_{14}\text{Si}(\frac{1}{2})$
	Odd	Even	Half-Integer ($\frac{1}{2}$, $\frac{3}{2}$,...)	$^1_1\text{H}(\frac{1}{2})$, $^3_1\text{H}(\frac{1}{2})$, $^{15}_7\text{N}(\frac{1}{2})$.

Nuclei having non zero spin quantum number spins around its axis

As nuclei has charge, spinning nuclei generates a magnetic dipole

Each nuclei acts a tiny magnet



Nuclear magnetic resonance (NMR)

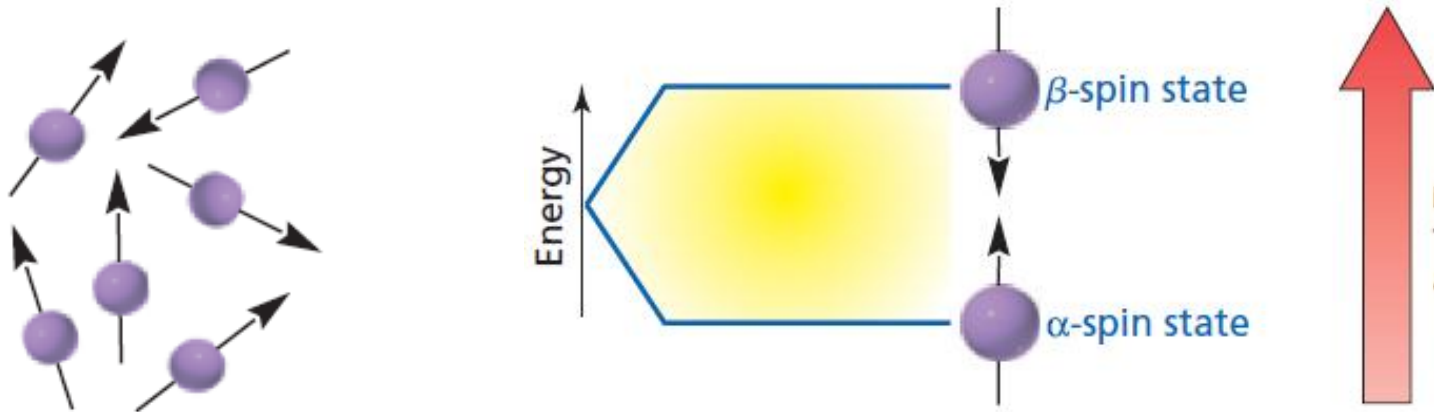
In the absence of an applied magnetic field, the nuclear spins are randomly oriented.

In an applied magnetic field, the nuclei twist and turn to align themselves *with or against the field* of the larger magnet.

More energy is needed for a proton to align against the field than with it.

Protons that align with the field are in the lower-energy α -spin-state; protons that align against the field are in the higher-energy β -spin-state

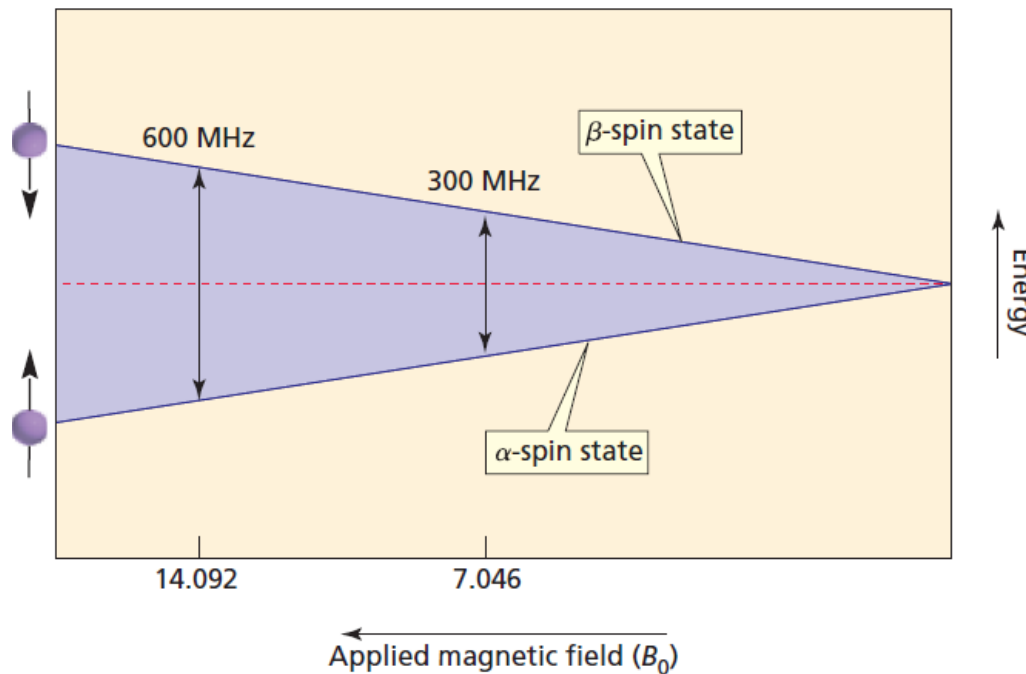
More nuclei are in the α -state than in the β -state.



Nuclear magnetic resonance (NMR)

The energy difference between the α - and β -states depends on the strength of the applied magnetic field

The greater the strength of the magnetic field to which nucleus is exposed, the greater is the difference in energy between the α - and β -states



The earth's magnetic : 2×10^{-5} tesla.

A typical NMR-magnet: between 2 and 10 tesla
 10^5 times stronger than the earth's field.

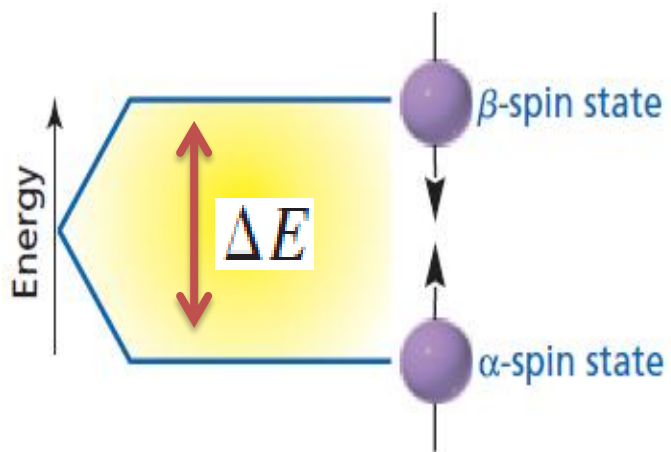
Now here is an unfortunate thing about NMR

The energy difference between the nuclear spin being aligned with the magnetic field and against it is really *very small*

so small that we need a very, very strong magnetic field to see any difference at all.

Nuclear magnetic resonance (NMR)

When a nuclei is irradiated with a radiation of energy corresponding to the difference in energy between the α - and β -states, nuclei in the α -state are promoted to the β -state.



Because the energy difference between the α - and β -states is so small only a small amount of energy is needed to flip the spin.

The radiation required is in the radiofrequency (rf) region of the electromagnetic spectrum and is called **rf radiation**.

When the nuclei undergo relaxation (i.e., return to their original state), they emit electromagnetic signals whose frequency depends on the difference in energy between the α - and β -states.

The NMR spectrometer detects these signals and displays them as a plot of signal frequency versus intensity—an NMR spectrum.

Nuclear magnetic resonance (NMR)

Energy difference (ΔE) between the spin states depends on the operating frequency (ν) of the spectrometer, which in turn depends on the strength of the magnetic field (B_0), and the *gyromagnetic ratio* (γ)

$$\Delta E = h\nu = h \frac{\gamma}{2\pi} B_0$$
$$\nu = \frac{\gamma}{2\pi} B_0$$

The **gyromagnetic ratio (also called the magnetogyric ratio)** is a constant that depends on the magnetic moment of the particular kind of nucleus.

$$\gamma (^1\text{H}) = 2.675 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$$

$$\gamma (^{13}\text{C}) = 6.688 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}$$

$$\nu = \frac{\gamma}{2\pi} B_0$$

Operating frequency of a particular spectrometer is the radio frequency required to flip the spin of a particular unshielded nucleus in that spectrometer

$$= \frac{2.675 \times 10^8}{2(3.1416)} \text{ T}^{-1} \text{ s}^{-1} \times 7.046 \text{ T}$$

$$= 300 \times 10^6 \text{ Hz} = 300 \text{ MHz}$$

A NMR spectrometer is equipped with a magnet with a magnetic field ($B_0 = 7.046 \text{ T}$) the spectrometer will require an operating frequency of 300 MHz for unshielded proton to flip the spin

Nuclear magnetic resonance (NMR)

What frequency (in MHz) is required to cause a ^{13}C to flip its spin when it is exposed to a magnetic field of $B_0 = 7.046 \text{ T}$?

$$\nu = \frac{\gamma}{2\pi} B_0$$

$$\gamma (^{13}\text{C}) = 6.688 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}$$

$$= \frac{6.688 \times 10^7}{2(3.1416)} \text{ T}^{-1} \text{ s}^{-1} \times 7.046 \text{ T}$$

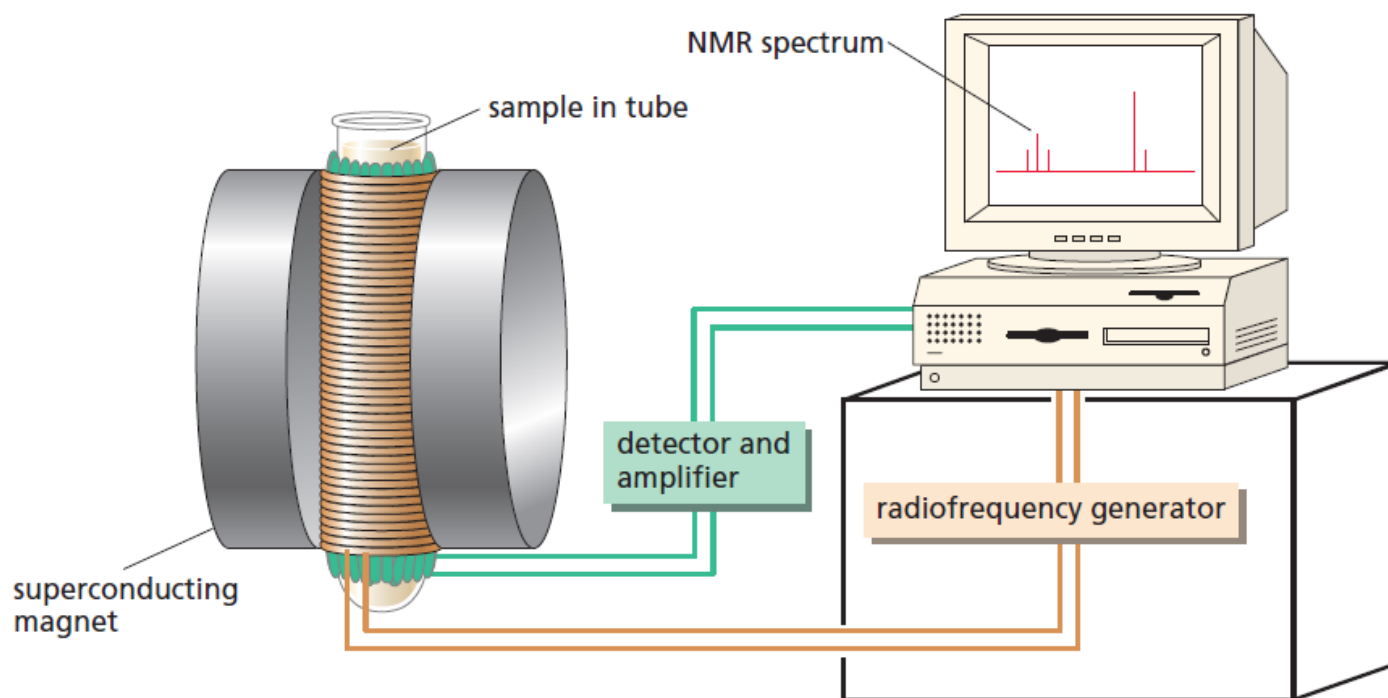
$$= 75 \times 10^6 \text{ Hz}$$

An NMR spectrometer with a magnet requiring a frequency of **300 MHz** to flip the spin of an ^1H nucleus requires a frequency of **75 MHz** to flip the spin of a ^{13}C nucleus.

What frequency (in MHz) is required to cause an unshielded proton to flip its spin when it is exposed to a magnetic field of 1 tesla?

Nuclear magnetic resonance (NMR)

- 1 The sample of the compound is dissolved in a suitable solvent and put in a very strong magnetic field.
- 2 The sample is irradiated with a short pulse of radiofrequency. This disturbs the equilibrium balance between the two energy levels: some nuclei absorb the energy and are promoted to a higher energy level
- 3 We then detect the energy given out when the nuclei fall back down to the lower energy level using a sophisticated radio receiver
- 4 After lots of computation, the results are displayed in the form of intensity (i.e. number of absorptions) against frequency.



Nuclear magnetic resonance (NMR)

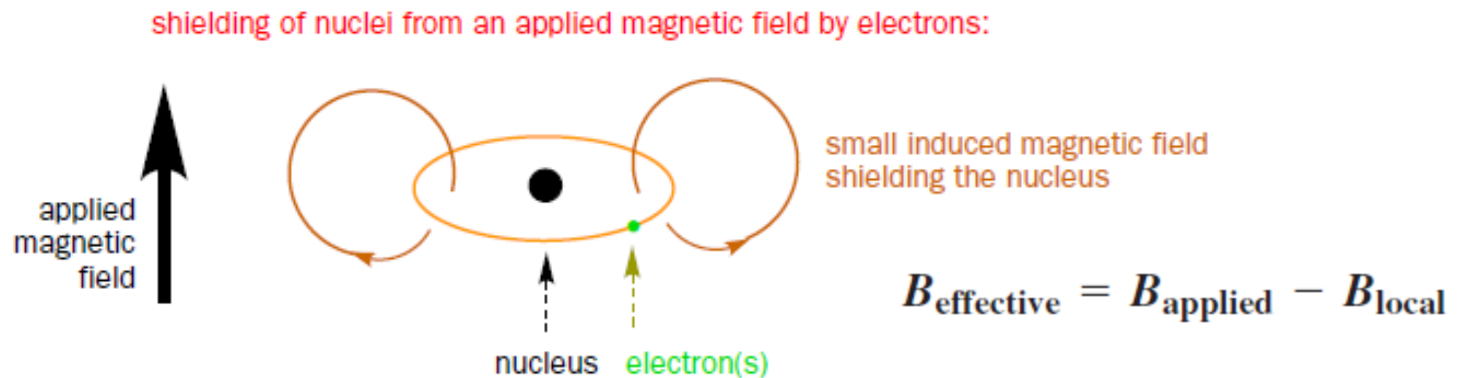
Why do chemically distinct nuclei absorb energy at different frequencies?

two factors that affect the energy difference (and therefore the frequency): the magnetic field strength and what sort of nucleus is being studied.

$$\Delta E = h\nu = h \frac{\gamma}{2\pi} B_0$$

So you might expect all carbon-13 nuclei to resonate at one particular frequency and all protons(^1H) to resonate at one (different) frequency.

But they don't.



Each nucleus is surrounded by electrons, and in a magnetic field these will set up a tiny electric current. This current will set up its own magnetic field, which will oppose the magnetic field that we apply.

The electrons are said to **shield the nucleus from the external magnetic field**.

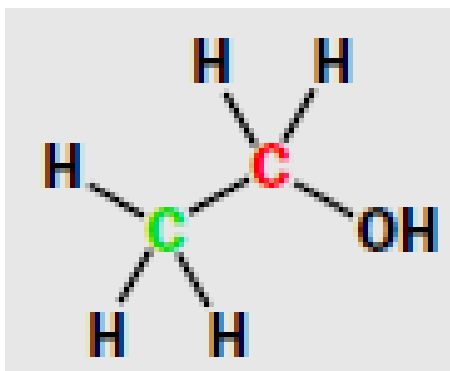
If the electron distribution varies from ^{13}C atom to ^{13}C atom

so does the local magnetic field

and so does the effective magnetic field and resonating frequency of the ^{13}C nuclei.

Nuclear magnetic resonance (NMR)

The carbon attached to the OH group will have relatively fewer electrons around it compared to the other carbon since the oxygen atom is more electronegative and draws electrons towards it, away from the carbon atom.

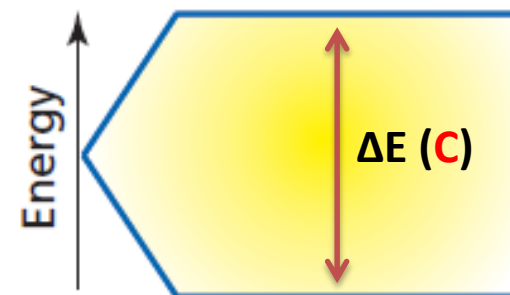


$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$$

$$B_{\text{loc}} (\text{red C}) < B_{\text{loc}} (\text{green C})$$

$$B_{\text{eff}} (\text{red C}) > B_{\text{eff}} (\text{green C})$$

$$\Delta E (\text{red C}) > \Delta E (\text{green C})$$

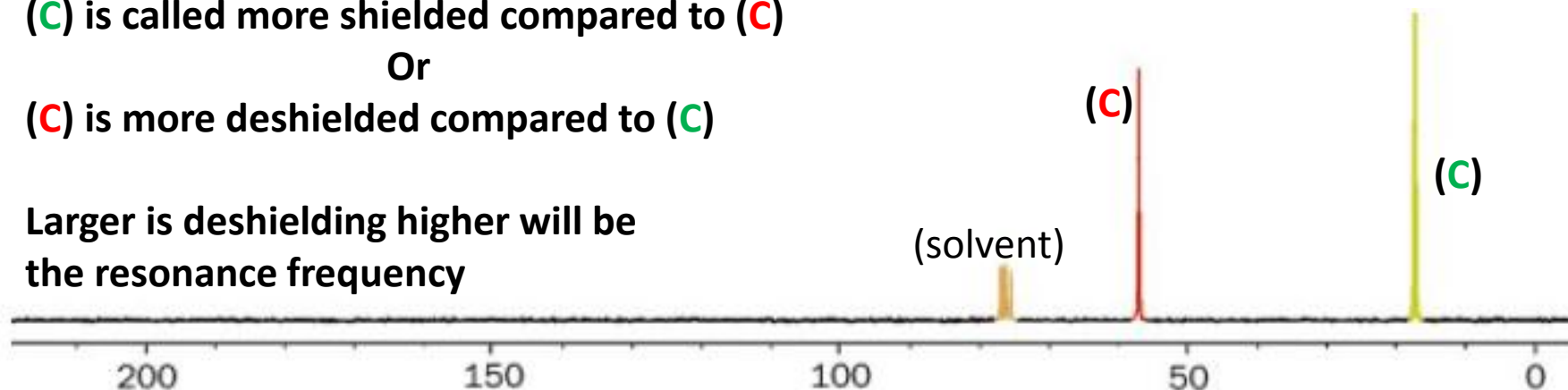


(green C) is called more shielded compared to (red C)

Or

(red C) is more deshielded compared to (green C)

Larger is deshielding higher will be the resonance frequency



^{13}C - NMR spectrum of ethanol in CDCl_3

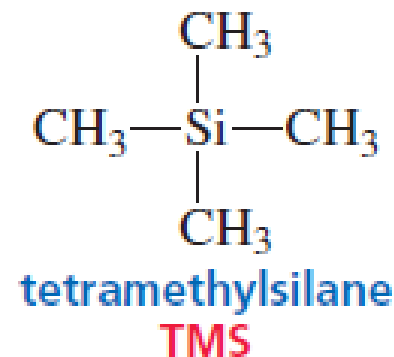
Nuclear magnetic resonance: Chemical Shift

The exact frequency at which the nucleus resonates depends on the external applied magnetic field.

This means that, if the sample is run on a machine with a different magnetic field, it will resonate at a different frequency.

The resonance frequency is measured with respect to that of a reference sample (to represent the resonance frequency with a value independent of operating frequency i.e. strength of the magnet)

The relative resonance frequency is termed as **chemical shift**, which is a measure of how far the signal is from the reference TMS signal.



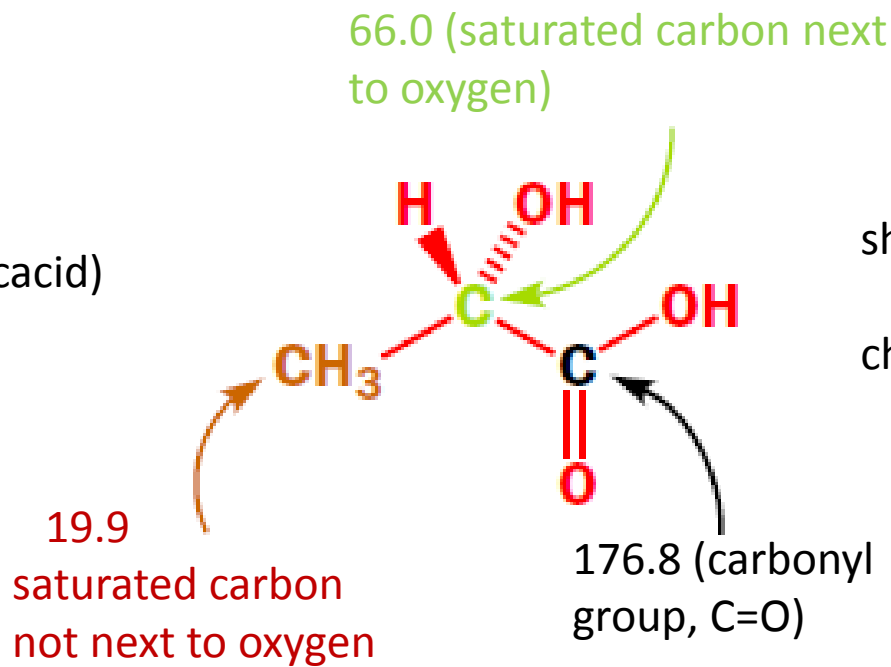
The chemical shift, δ , in parts per million (p.p.m.)

$$\delta = \frac{\text{Resonance frequency (Hz)} - \text{frequency of TMS (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

By definition TMS itself resonates at 0 p.p.m.

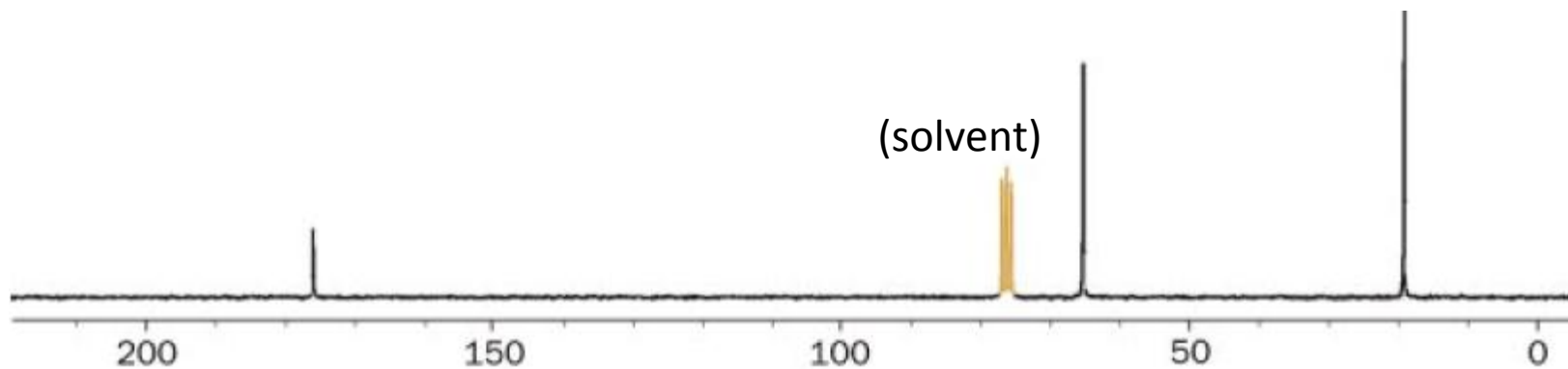
Nuclear magnetic resonance: Chemical Shift

lactic acid (2-hydroxypropanoic acid)



shielding order : (C) < (C) < (C)

chemical shift (δ): (C) > (C) > (C)

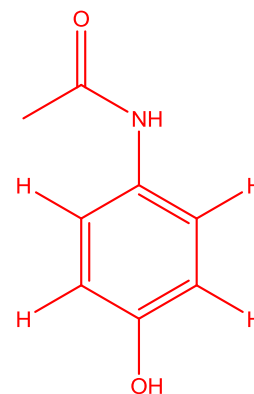
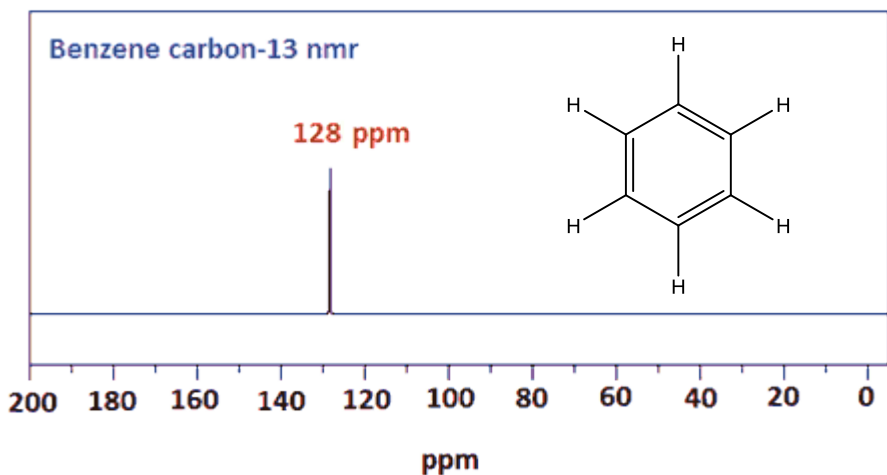


^{13}C - NMR spectrum of lactic acid in CDCl_3

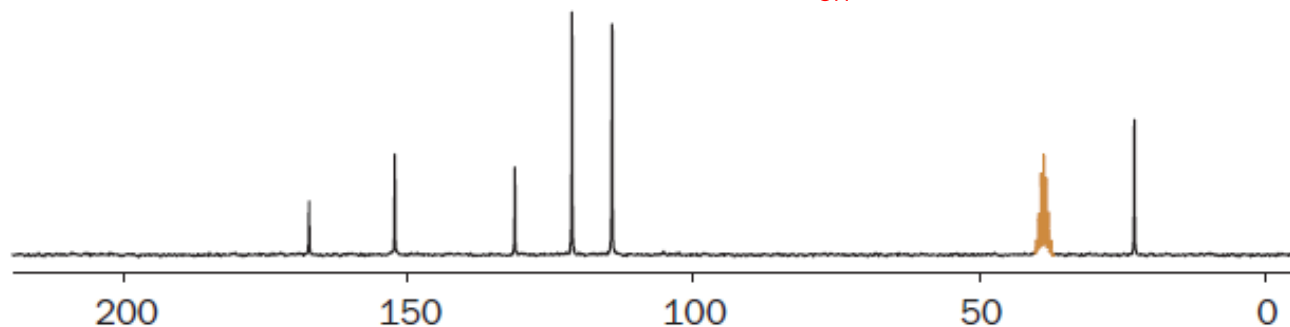
The Number of Signals

Carbon in the same environment are called **chemically equivalent carbon**.

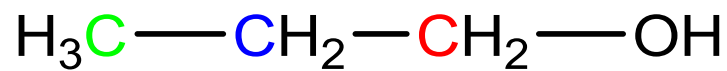
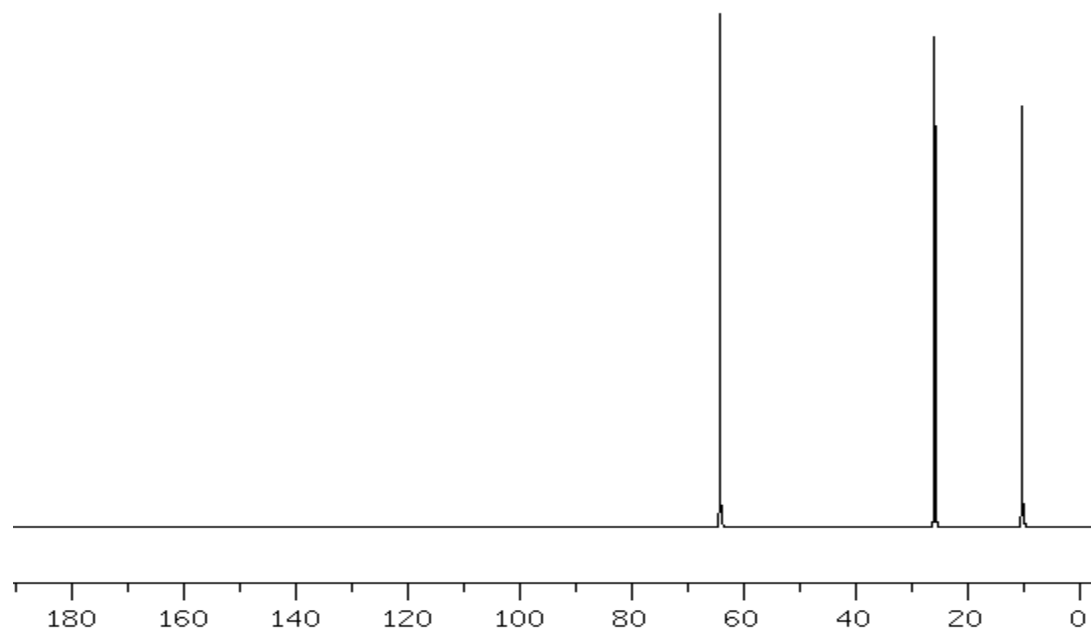
Each set of chemically equivalent carbon in a compound gives rise to a signal in the ^{13}C -NMR spectrum of that compound.



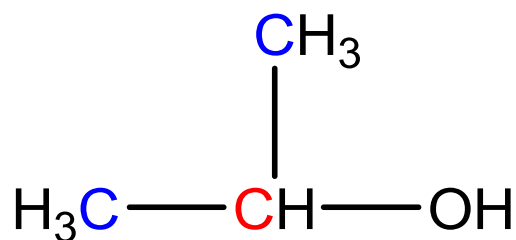
paracetamol



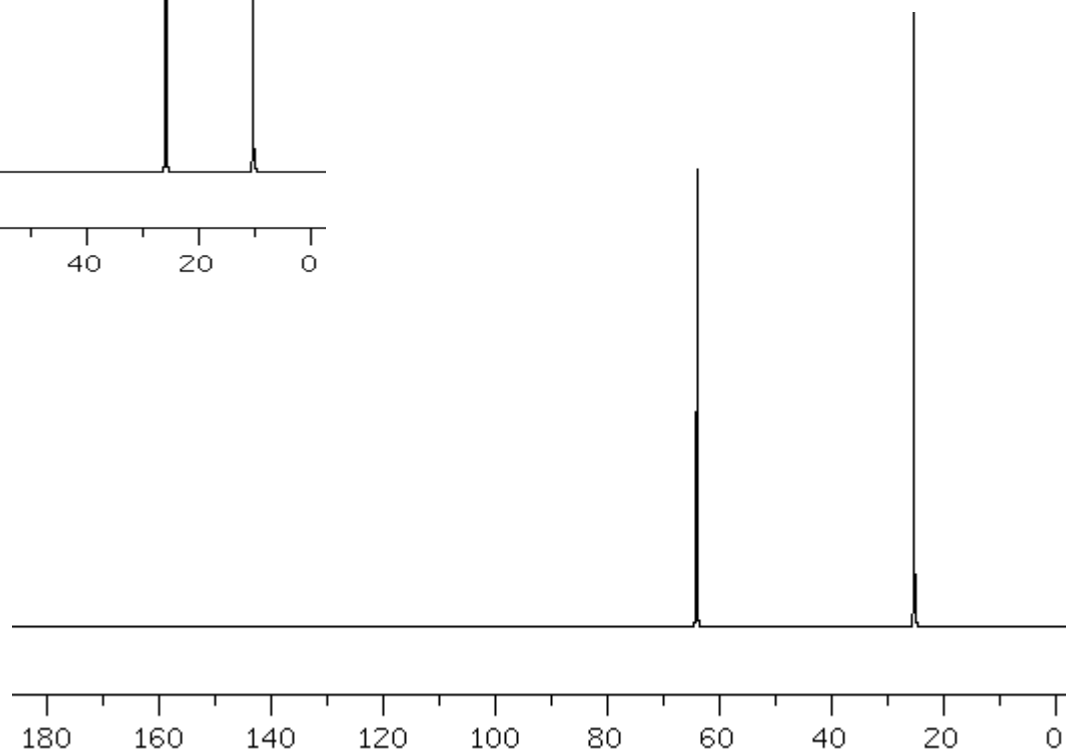
Sometimes the signals are not sufficiently separated and overlap each other



1-propanol (C₃H₈O)



2-propanol (C₃H₈O)



From ¹³C-NMR you can say the alcohol given to you is 2-propanol or 1-propanol

Looking forward

^1H -NMR Spectroscopy