NMR INTRODUCTION.

Technique based on the absorption of EMR in RF region 4-900 MHz by the nuclei of atoms. The quantity of energy involved in RF radiation is too small to rotate, vibrate or excite the atoms (or) molecules. But this energy is sufficient to affect the nuclear spin. ∴ the nuclei of atoms in a molecule may change their direction of spin after absorbing RF radiation.

NMR is most often concerned with nuclei which has $I = 1/2$ i.e odd no. nuclei ex: ^{1}H, ^{31}P, ^{19}F etc.

Spectra can not be obtained for nuclei with even no. of protons (or) even mass no. where $I = 0$.

i.e If $I = 0$ - The spins of all the particles are paired & there will be no net spin & hence $I = 0$.

Ex: ^{12}C, ^{16}O, ^{18}O, ^{32}S etc nuclei have even no. of protons & neutrons & will show zero spin. Particles in such nuclei are paired (spinning in opposite directions) & hence there is no resultant spin. (Zero mag. moment)

If the sum of protons & neutrons is odd, I is $1/2$, $3/2$, $5/2$ etc ^{1}H, ^{19}F, ^{13}C, ^{31}P have $I = 1/2$. there will be mag. moment.

If an ext. mag. field is applied, the no. of possible orientations are calculated by $(2I+1)$

Ex: Hydrogen has the spin quantum no. $I = 1/2$ so the no. of possible orientation is $2 \times 1/2 + 1 = 2$. i.e $+1/2$ & $-1/2$.

The theory behind NMR spectrum comes from the spin of the nucleus and it generates the mag. field. Without an ext. mag. field, the spins of the nuclei are random in direction. But when the ext. mag. field is applied, the nuclei align themselves either with or against the ext. mag. field.

The important application of NMR is the study of hydrogen atoms in organic molecules. H atom is the easiest one to understand from the point of its physical properties. The nuclei of other elements may not behave exactly in the same way as that of hydrogen and ~~may~~ many do not respond to radio waves at all.

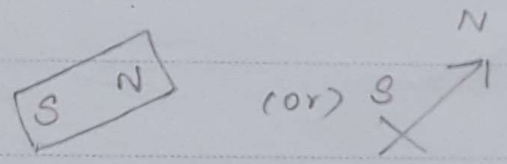
Explanation of Theory of NMR

Nucleus will behave like a magnet, because of its charge & spin. Any atom with odd no. of protons & / or neutrons will behave like a magnet.

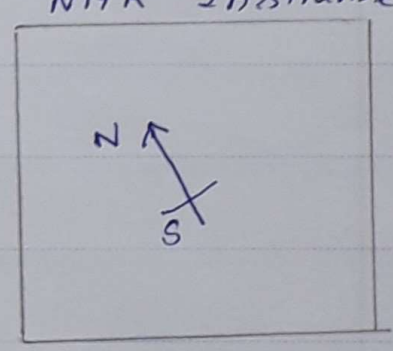
NMR operates by applying magnetic field to the nuclei and measuring the amount of energy necessary to bring the nuclei to resonance.

Nuclei in different electronic environments require different amounts of energy to come to resonance.

If we represent the nucleus as a magnet

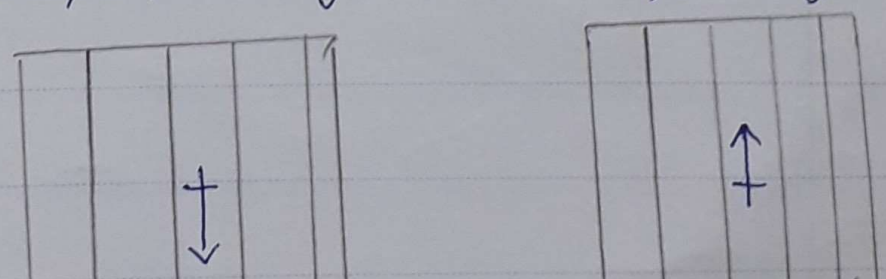


Consider the NMR Instrument and the representation of nuclei as follows.

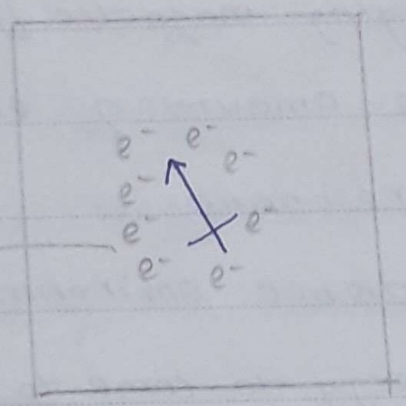


In absence of ext. mag. field, the spins of the nuclei align randomly.

When, the external magnetic field is applied, the spins of the nuclei either align with the app. mag. field (α spin) or against the app. mag. field (β spin).



For NMR to occur, the proton has to flip ~~the~~ its spin from lower energy to higher energy. This depends on the electron environment. Consider the following diagram



ore e⁻s
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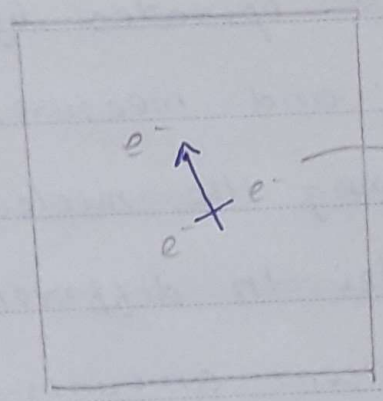
s required to
flip the spin
up field



deshielding
less energy is
needed to flip
the spin
down field.

NUCLEAR MAGNETIC RESONANCE (NMR)

Introduction:

(It is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

Without the magnetic field, the spin states of nuclei are degenerate. i.e possess the same energy and energy level transition is not possible. When a magnetic field is applied, the separate levels and radio frequency radiation can cause transitions between these energy levels.)

NMR spectroscopy is most often concerned with nuclei which has $I = \frac{1}{2}$. i.e odd no/. nuclei ^{1}H, ^{19}F, ^{31}P. Spectra can not be obtained from nuclei with $I = 0$ i.e even no/..

If $I = 0$ - The spins of all the particles are paired, there will be no net spin & and the nuclear spin quantum number I will be zero.

For ex: ^{12}C, ^{16}O, ^{18}O, ^{32}S etc. nuclei have even number of neutrons and even no/.. of protons and will show zero spin.

Particles in such nuclei are paired (spinning in opposite directions) and hence there is no resultant spin and consequently there will be zero magnetic moment.

If the sum of protons & neutrons is odd, I is $\frac{1}{2}$, $\frac{3}{2}$ $\frac{5}{2}$ etc. For ex/. ^{1}H, ^{19}F, ^{13}C & ^{31}P have $I = \frac{1}{2}$

NMR is a powerful tool for investigating nuclear structure. In particular, it reveals the different chemical environments ~~th~~ of various forms of hydrogen present in a molecule.

(NMR is caused by radio frequency waves which are regarded as lowest energy form of EMR that find valid applications in analytical chemistry. The quantity of energy involved in RF radiation is small which is too small to vibrate, rotate or excite an atom or molecule. But this energy is sufficient to affect the nuclear ~~char~~ spin of the atoms of a molecule. Therefore, the nuclei of atoms in a molecule on absorbing RF radiation may change their direction of spin.

The important application of NMR is in the study of hydrogen atoms in organic molecules. The

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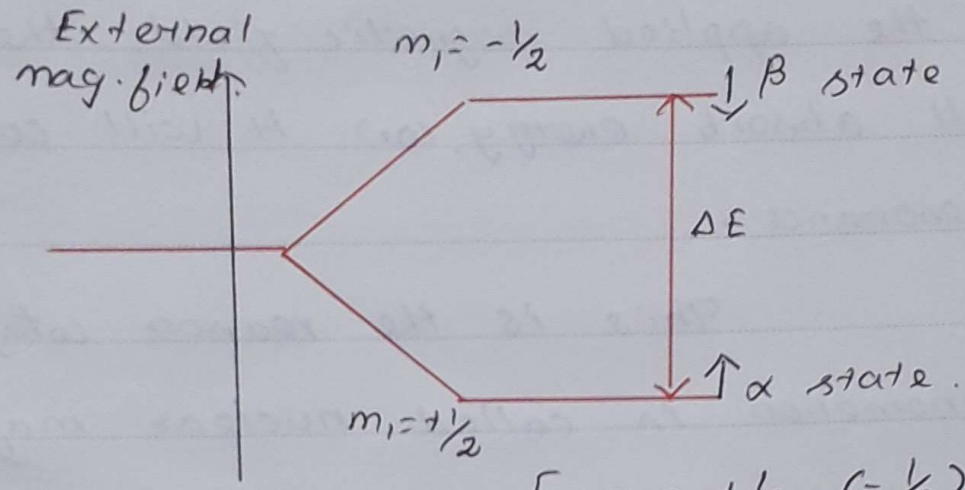
to radio waves at all.)

Resonance Condition :-

If an electromagnetic radiation of frequency ν is allowed to interact with the nuclei, then the nuclei from lower energy level may absorb energy and go to higher energy level.



Splitting of energy levels $[\Delta m = +\frac{1}{2} - (-\frac{1}{2}) = 1]$ of a proton in presence of a magnetic field.

The difference in energy between nuclear spin states in a magnetic field is very small at room temp. and therefore, the population in various states are nearly equal. When the external magnetic field is applied, only the protons in the lower energy state will absorb radiation. In presence of the applied field, the proton will experience torque (a twisting force), which makes the

nuclei to rotate around the direction of the applied field. This precessional frequency is called Larmor frequency. When this Larmor frequency matches with the frequency of the applied magnetic field, the nuclei will absorb energy. (or) it will come to resonance.

This is the reason why this phenomenon is called nuclear magnetic resonance and the condition of resonance is

$$h\nu = g_N \mu_N B_z.$$

g_N - Nuclear 'g' factor which is characteristic of a particular nucleus.

B_z - Strength of the applied magnetic field.

ν - frequency of NMR.

μ_N - Magnetic moment of the nuclei.

Chemical Shift (δ)

We know that in NMR spectrum, the number of signals gives us information about different kinds of protons present in the molecule. Similarly, the position of the signal tells us that what kind of protons they are. That is, whether they are aliphatic, aromatic, primary, secondary or tertiary or adjacent to halogen atom or other atom or group etc. These different kinds of protons have different electronic environments and it is this electronic environment that determines where a proton absorbs in the NMR spectrum.

Different protons have different environment, it means that the electrons present in the bond close to the proton and the electrons present in the neighbouring bonds to the proton show different effects. These e^-s induce their own magnetic field which may reinforce the applied magnetic field or oppose it.

Now inorder for NMR to occur, the proton has to flip its spin from lower energy level to

higher energy level. In other words, it has to change its spin from ↑ to ↓.

If the induced magnetic field reinforces the applied magnetic field, a small external field will be needed for flipping the spin of the proton. Such a proton is said to be deshielded and the absorption is known as downfield.

If the induced magnetic field opposes the external magnetic field, stronger magnetic field will be required to flip the proton. The proton is then said to shielded and the absorption is said to be upfield.

The shift in the positions of NMR absorptions which arise due to shielding and deshielding of protons by the electrons are called Chemical shift. For measuring Chemical shifts of various protons in a molecule, the signal for Tetra methyl silane (TMS) is taken as reference.

Due to low electronegativity of silicon, the shielding of equivalent protons in TMS is greater than most of the compounds. Therefore, NMR signal

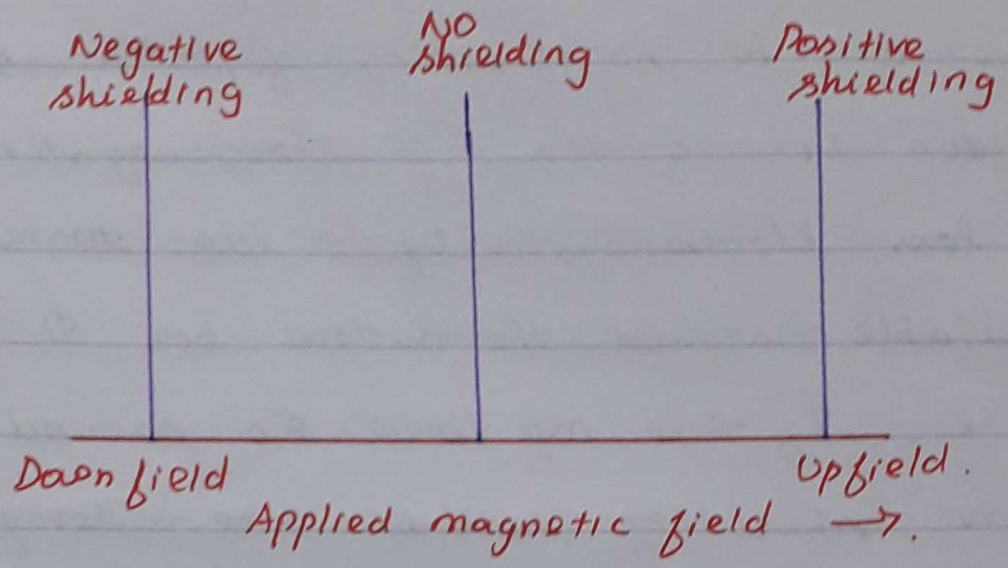
for TMS is taken as a reference and a chemical shift for different kinds of protons are measured relative to it. (In TMS. there are 4 methyl groups and all the protons will be in the same environment. Therefore, there will be shielding of protons by the e's of Silicon bcz of its low electronegativity. If ~~shielding~~ ~~is less~~ Electronegativity is low, more e's will be available around the nucleus bcz Si will not withdraw any e. If there are more e's around the nucleus, more shielding will be there. Therefore applied mag. field should be more to flip the spin of the nucleus. Hence TMS signal in NMR is at 10τ

~~Greater the deshielding of protons larger will be the value of δ.~~

Causes of chemical shift:

When the secondary field produced by the ~~e's~~ circulating e's oppose the applied field at a particular nucleus in the molecule, it means that effective field experienced by the nucleus is less than the applied field. This is known as positive shielding and the resonance position

moves upfield in NMR spectrum because the value of applied field necessary to bring the nucleus into resonance will be greater than that when there were no secondary opposing field.



Effect of shielding and deshielding on position of a resonance of a nucleus.

If the secondary field produced by the circulating e^-, reinforces the applied field, the position of resonance moves down field. This is known as negative shielding.

Spin- Spin Interaction:

In an NMR spectrum, each signal represents one kind or one set of protons in a molecule. It is found that in certain molecules, a single peak (singlet) is not observed,

The distance between the centres of two adjacent peaks in a multiplet is usually stant and is called the coupling constant.

+1) rule: The signal that is being split (n equivalent protons) neighbouring protons which appears as a multiplet with (n+1) peaks. It is called (n+1) rule.

For ex/. in CH_3-CH_2-Br, the signal r CH_3 protons under the influence of $-CH_2$ proto is ~~3~~+1 = ~~4~~. appear as a triplet.

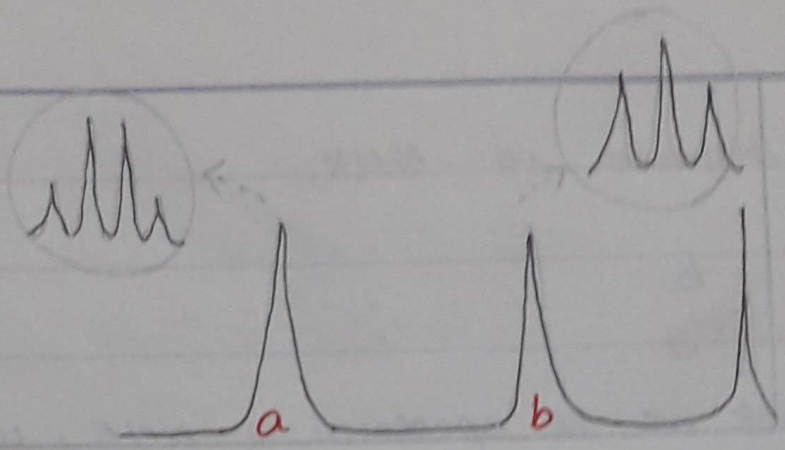
~~n-~~ ~~protons~~ n- split by neighbouring proto

Splitting of signals in NMR.

Ex: $Cl - \overset{a}{CH_2} - \overset{b}{CH_3}$

If we look at the spectrum of NMR, we expects two peaks. One for a & the other for b. If we look at the 'b' peak really close and we focus on a 'b' peak about 10 times zoomed up view of that 'b' peak, looking close into that it is actually not a single peak, it is 3 peaks that are extremely close together i.e the 'b' peak is actually split into 3 peaks. If that happens it will be called as a triplet. The same thing would happen if we look at the 'a' peak. It is actually split up into 4 peaks if it is zoomed up i.e a quartet.

So, what is the reason of its multiplicity? & how they are actually split up upon close examination The peak that is split into something called spin-spin coupling. And a & b hydrogens are called as coupled hydrogens which have a tendency to split each other.



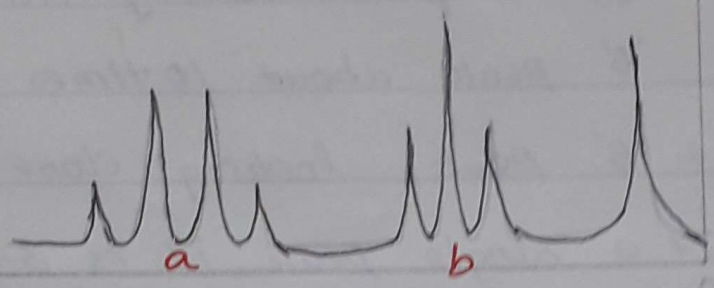
a b.
Cl CH_2 CH_3

a N = 3

N+1 = 3+1 = 4.

b N = 2

(N+1) = 2+1 = 3.



Here, we have to know that splitting follows (n+1) rule. This is ~~the~~ just the simple formula with 'n' representing the no. of neighbouring hydrogens or different hydrogens.

Let us start with 'a' type hydrogen. We want to calculate its 'n' value. If we look at the 'a' hydrogen, those are directly connected to the neighbouring $-CH_3$ carbon. So, those 3 are neighbouring hydrogens to $-CH_2$ protons. So, they are total of 3 hydrogens. Hence, N value for 'a' hydrogen is 3. So, plugging into the formula with the value of N, we will be getting

4 which exactly matches with what we are getting in NMR for 'a'. It is similar for 'b' also. Hence, this is very extremely valid information for predicting NMR.

Sample Problem.

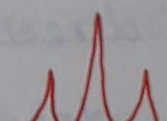
1. $BrCH_2CH_2Br$ - Give the multiplicity of each kind of hydrogen in the following molecule.

i. We have to figure out first how many types of hydrogens are in the sample.

$$\underset{}{Br}\ \underset{a}{CH_2}\ \underset{b}{CH_2}\ Br$$

Hence, there are two types.

a (neighbouring H is 2)



$N = 2$

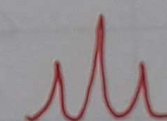
So, we expect that 'a' hydrogen should split into a triplet.

$N+1 = 2+1 = 3$.

b

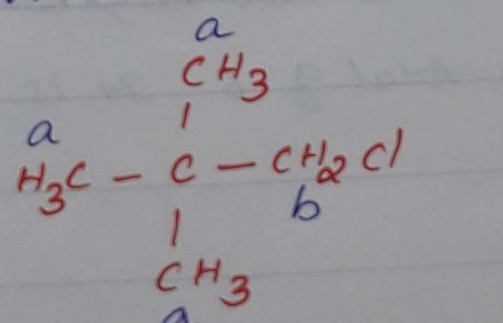
$N = 2$

Again a triplet for 'b'



$N+1 = 2+1 = 3$.

2.



N value for 'a'

$N = 0$

$N+1 = 0+1 = 1$.

singlet

N for b

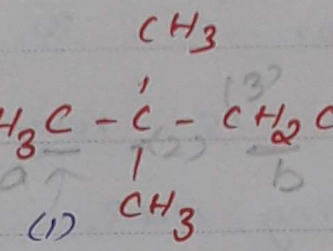
$N = 0$

$N+1 = 0+1 = 1$

singlet

As, all 'a' hydrogens are equivalent, it doesn't matter

matter that which hydrogen we are going to investigate.

For 'a' hydrogen 

, it is connected to this carbon (1) and the neighbouring C is (2) has 0 hydrogen on it. Hence N value is 0. Hence, for (N+1) rule it is (0+0) = 1 which means that, it is a singlet and which is not going to split.

Now for 'b' type hydrogen. 'b' hydrogen is directly connected to C 3 and the neighbouring C 2 does not have any hydrogen. ∴ N value is 0.

N+1 = 0+1 = 1.

3. CH_3 CH_2 CH_3
a b a

a	b
N = 2	N = 6
N+1 = 2+1 = 3.	N+1 = 7

'b' hydrogen is connected to two neighbouring $-CH_3$ carbons. Hence, a total of 6. It is a multiplet.

$$F\overset{a}{CH_2}\ \overset{b}{CH_2}\ \overset{c}{CH_2}\ Cl$$

a	b	c
N = 2	N = X	N = 2 N+1 = 3.

N+1 = 3. N+1 Rule fails. because, If any Hydrogen is connected to two different neighbours, (N+1) Rule fails

$$CH_3 : CH_3$$

a : a These are symmetrical & equivalent.

~~Hence, (N+1) rule does not work out.~~ Because (N+1) rule is N = No. of neighbouring / different H.

As, the two are not different H's.

N value will be zero. Hence (N+1) = 0+1 = 1 singlet. Hence, a peak or signal can not be split by ~~eq~~ its equivalent protons.

Aspects of NMR.

The number of peaks in NMR spectrum is equal the number / type of hydrogens / other atoms in the molecule.

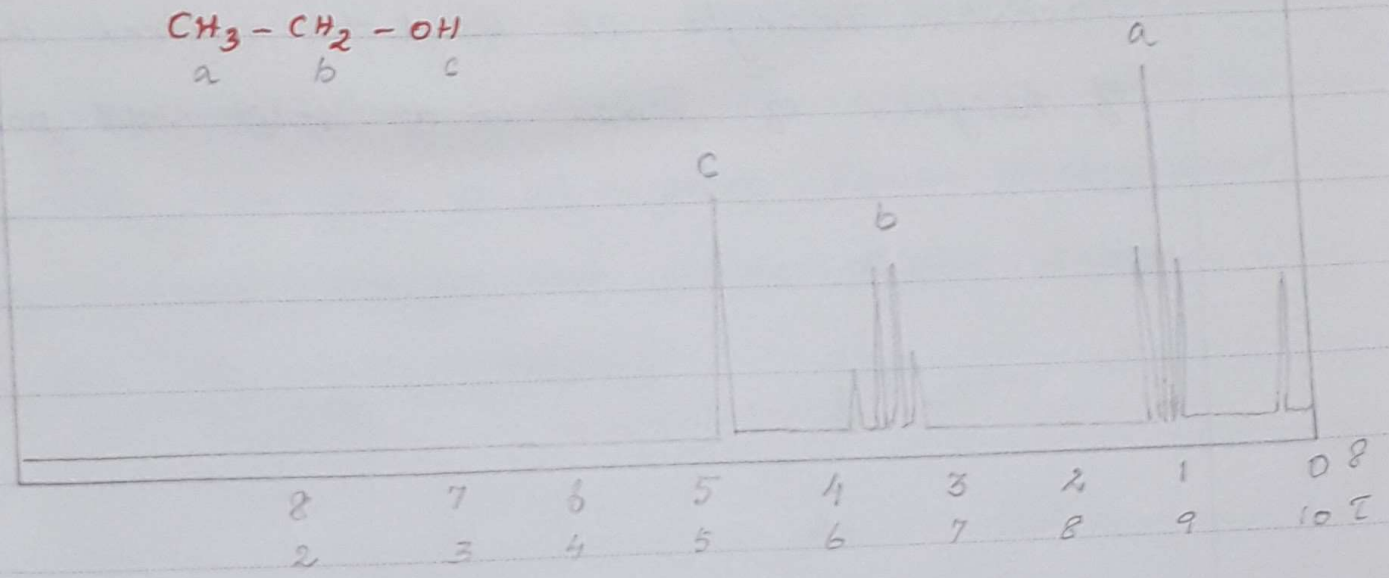
. Proximity to an electronegative atom causes a peak to be shifted downfield

There is a relationship between the area under the peak and the number of hydrogens responsible for the peak.

. Peaks can be split due to neighbouring hydrog

NMR spectrum of Ethanol:

$CH_3 - CH_2 - OH$
a b c



The spectrum of ethanol contains the following peaks.

1) Triplet - δ 1.2 3H (CH_3)
2) Quartet - δ 3.63 2H (CH_2)
3) Singlet - δ 4.8 1H (OH)

Ethanol is having three kinds of protons and consequently exhibits three signals.

The upfield triplet of δ 1.2 is because of the three equivalent methyl protons. Evidently, its splitting is because of two neighbouring protons.

The quartet at δ 3.63 is from two methylene protons. Its multiplicity of four peaks is due to the ~~two~~ three adjuscent methyl protons.

Finally the downfield singlet at δ 4.8 is due to the hydroxyl proton which does not show any coupling with the adjuscent methylene protons. $-CH_3 -CH_2 -OH$

The peaks is 3:2:1