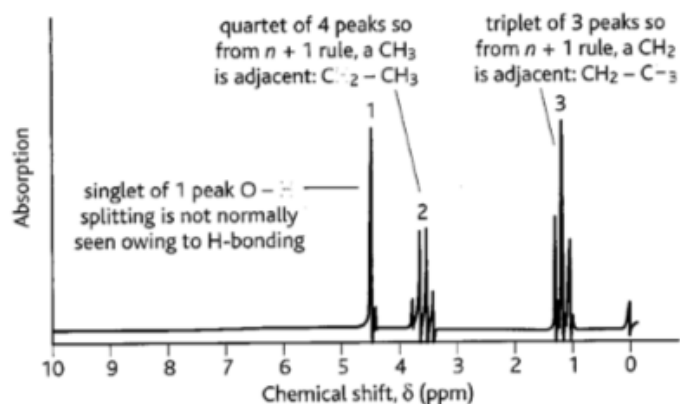


ANALYTICAL TECHNIQUES

PROTON (^1H) NMR SPECTROSCOPY



High-resolution spectrum of ethanol.

First Edition	Jan 2006
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Fourth Edition	Jan 2019 (Revised New Syllabus)

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Proton Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$)

1. Explain how nuclear spin give rise to n.m.r spectroscopy.

Electrons that pair up in atomic orbitals have opposite spin, likewise protons and neutrons in nucleus also have opposite spin. These are said to poses 'spin ', since any spinning electric charge has a magnetic field.

The nuclei will not exhibit any magnetic field if they possess an even mass number (eg: $^{12}_6\text{C}$) their magnetic fields (spins) cancel out hence resulting no overall magnetic field. But if they possess odd mass number ($^{13}_6\text{C}$, ^1_1H) the nucleus will show magnetic properties as their spins do not get cancelled. (1.1% of C atoms are ^{13}C whereas 99.98% of H atoms are ^1H)

If the substance is placed in an external magnetic field, the nuclear magnet lines up with the field. However if the protons are given a little extra energy, their magnetic fields can be made to point in the opposite direction to the field.

It is possible to make it flip from the more stable alignment to the less stable one by supplying energy.

The energy required for this flip depends on the strength of the external magnetic field & it is usually in the range of radio waves in the e.m.r. The flipping of proton due to the radio waves is known as the **resonance condition**.

The precise frequency depends on the environment of the nucleus. Therefore by placing the sample in a strong magnetic field & measuring the frequency of radiation it absorb information can be obtained about the environments of the nuclei in the molecule. This technique is called the nuclear magnetic resonance (n.m.r.)

Since we are focusing on the magnetic behavior of 'H' nuclei - hence the term proton NMR $^1\text{H-NMR}$ is used.

2. Explain the factors which effects the magnetic field of a proton

The electrons, which take part in the bond, which holds the 'H' atom, reduce the external magnetic field, the electrons cut down the size of the external magnetic field felt by the 'H' nucleus. This is referred to as shielding effect.

If 'H' atom is attached to a more electron negative atom the electrons in the bond would be further away from the 'H' nucleus, and so would have less effect on the magnetic field around 'H'. Therefore If 'H' is attached to a more electro negative atom, the external magnetic field which needed to bring 'H' in to resonance will be smaller.

* For a given radio frequency each 'H' atom will need a slightly different magnetic field inorder to achieve the resonance condition, depending the atoms which it is attached to.

3. Describe the patterns in an n.m.r spectrum & explain how to interpret a low resolution n.m.r spectrum

Let us consider the below low resolution nmr spectrum of methanol

The two peaks are due to the 2 different environment of Hydrogen. Three in CH₃ group & one joined to the 'O' atom.

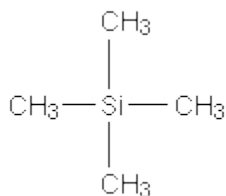
- The above spectrum is a low-resolution n.m.r. which shows the intensity of absorption as a broad peak. This form is no longer used but it helps to understand high resolution n.m.r. Improved technology of high-resolution n.m.r is able to show how the peaks were made up of smaller peaks giving more information of the environment of the proton.
- The sizes of peaks (not the height but the area under the peaks) give important information about the numbers of 'H' atoms in each environment. The area under the peaks gives the ratio of 'H' atom.

Eg: in methanol it is 3:1 this confirms that it has 3 protons on one type (CH₃) & one on the other (OH)

*The horizontal scale is shown as δ (ppm) δ is called as the chemical shift. The difference between the resonant field of a given proton & that of a proton in a fixed molecule is called the chemical shift. The fixed molecule was been assigned zero point. (Chemical Shift 0, $\delta = 0.0$ ppm) This molecule is tetra methyl silane (CH₃)₄ Si commonly called as TMS. Everything is compared with this. TMS is chosen as a standard as there are no carbon and there are 12 'H' atoms in the same environment also it is unreactive.

*The horizontal scale is measure in ppm (parts per million). A peak at a chemical shift 2.0 means that the 'H' atoms, which caused that peak, need a magnetic field two millionths less than the field needed by TMS to produce resonance. (down field)

The weaker the field at which resonance occur, the greater is the chemical shift & the more 'down field' the absorption peak is said to be.


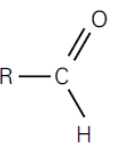
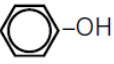
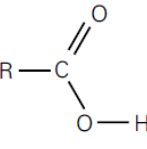
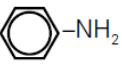
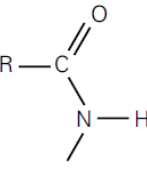


*The compound can be identified by simply matching the chemical shifts given in the data table or by working out the ratio of 'H' atom by the area beneath each peak.

Chemical shift values can slightly vary depending on the solvent, concentration and substituents. In NMR the organic compound to be analyzed is dissolved in a solvent. The commonly used solvent is trichloro methane, CDCl₃. It is a chloroform molecule where the hydrogen atom has been replaced by deuterium, ²H so that it will not produce a signal like ¹H does.

CDCl₃ contains carbon it might sometimes contain ¹³C thus produce a line which is easily recognizable. This produces a small signal near chemical shift 80 ppm which is ignored when interpreting the spectrum.

4. Typical proton (^1H) NMR chemical shift values (δ) relative to TMS = 0

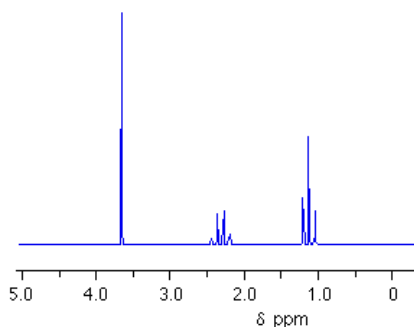
Type of proton	Environment of proton	Example structures	Chemical shift range (δ)
C-H	alkane	$-\text{CH}_3, -\text{CH}_2-, >\text{CH}-$	0.9–1.7
	alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}, -\text{CH}_2-\text{C}=\text{O}, >\text{CH}-\text{C}=\text{O}$	2.2–3.0
	alkyl next to aromatic ring	$\text{CH}_3-\text{Ar}, -\text{CH}_2-\text{Ar}, >\text{CH}-\text{Ar}$	2.3–3.0
	alkyl next to electronegative atom	$\text{CH}_3-\text{O}, -\text{CH}_2-\text{O}, -\text{CH}_2-\text{Cl}, >\text{CH}-\text{Br}$	3.2–4.0
	attached to alkyne	$\equiv\text{C}-\text{H}$	1.8–3.1
	attached to alkene	$=\text{CH}_2, =\text{CH}-$	4.5–6.0
	attached to aromatic ring		6.0–9.0
	aldehyde		9.3–10.5
O-H (see note below)	alcohol	$\text{RO}-\text{H}$	0.5–6.0
	phenol		4.5–7.0
	carboxylic acid		9.0–13.0
N-H (see note below)	alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
	aryl amine		3.0–6.0
	amide		5.0–12.0

Note: δ values for O-H and N-H protons can vary depending on solvent and concentration.

(Quoted from the data booklet)

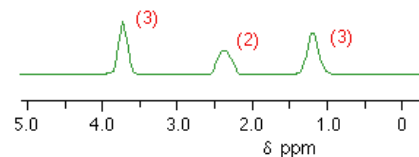
5. The difference between high & low-resolution spectra.

High resolution spectrum for methyl propanoate



Improved technologies of high-resolution n.m.r are able to show how peaks were made of smaller peaks providing more information of the environment of the protons.

Low-resolution spectrum for methyl propanoate



Low resolution spectrum is much simpler, it cannot distinguish the individual peaks of various groups. The relative area of the peak provide information about the no. of 'C' atoms in each environment.

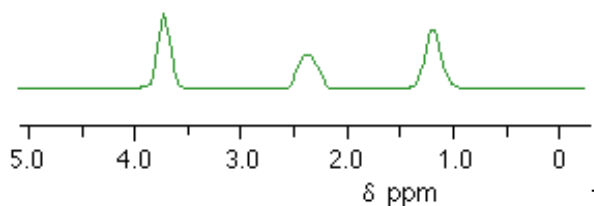
6. Interpret the above low-resolution spectrum of methyl propanoate ($\text{CH}_3\text{CH}_2\text{COOCH}_3$) using the total number of peaks & areas under the peaks

The 3 peaks represent that there are 3 different environments for the 'H'. The CH_2 group is in different environment from CH_3 groups. Also the 2 $-\text{CH}_3$ groups are in different environments. One is attached to a CH_2 & the other to oxygen.

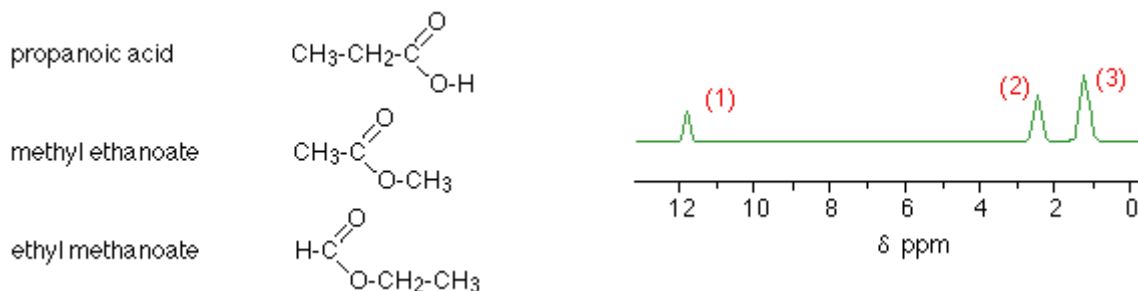
The ratio of the areas will provide information on the ratio of no of 'H' atoms in each environment. The areas are in the ratio of 3:2:3 in methyl propanoate.

7. Interpret the below low-resolution spectrum of methyl propanoate ($\text{CH}_3\text{CH}_2\text{COOCH}_3$) using the provided range of chemical shift data.

	chemical shift, δ
$\text{R}-\text{CH}_3$	0.7 - 1.6
$\text{R}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$	2.0 - 2.9
$-\text{O}-\text{CH}_3$ or $-\text{O}-\text{CH}_2-\text{R}$	3.3 - 4.3
$\overset{\text{O}}{\parallel}{\text{H}}-\text{C}-$	9.0 - 10.0
$-\text{COOH}$	11.0 - 12.0



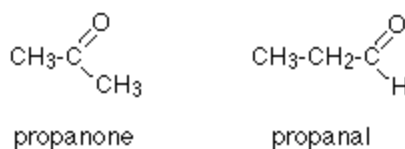
8. The below low-resolution n.m.r spectrum belongs to one of the below given molecule. Assign the correct molecule using range of chemical shift data in the previous question hence explain the species responsible for each chemical shift.



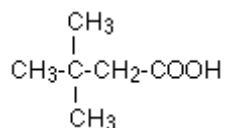
As there are 3 peaks the molecule should have the 'H' at 3 different environments. Therefore this eliminates methyl ethanoate, as it contains the 'H' in 2 different environments.

By analyzing the chemical shift data for the rest of the molecule proves that the molecule is propanoic acid.

9. How would you use low resolution NMR to distinguish between the isomers propanone and propanal?



10. 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?



Splitting of signals in high resolution n.m.r

1. Describe the spin-spin coupling & how it is used to identify the number of protons adjacent to a given proton.

The splitting of peaks in a high resolution spectrometer arises due to the magnetic environment of the proton in one group is effected by the magnetic field of a proton in the adjacent group. This splitting is caused by spins of protons on adjacent 'C' atoms coupling with each other. The difference in the magnetic field of a proton & the adjacent proton depends on whether the spin of the adjacent proton is parallel or anti parallel to the applied magnetic field.

Eg: Consider the arrangements of spin for the $-CH_3$ protons in ethanol CH_3CH_2OH the adjacent $-CH_2$ has two 'H' atoms & there are 4 ways in which their spins can be aligned.

The effect of $\uparrow\downarrow$ is the same as $\downarrow\uparrow$ therefore they produce one peak twice as high as others. Thus the $-CH_3$ peak splits in to triplet in the ratio of 1:2:1

The above process of splitting due to adjacent protons is called spin coupling or spin-spin splitting or spin-spin coupling.

If we consider the $-CH_2$ group the adjacent $-CH_3$ group has 3 protons hence there are 8 ways in which their spins can be aligned.

Thus the $-CH_2$ peak splits into 4 (quartet) in the ratio of 1:3:3:1

2. State the N+1 rule which is used to describe the splitting of the signals.

The splitting of a signal is described by the **N+1 rule**, where **N** is the number of equivalent protons bonded to an adjacent carbon. Equivalent protons are the protons bonded to an adjacent carbon are equivalent to each other but not equivalent to the proton giving rise to the signal.

For example in 1-bromo-2,2-dimethylpropane the signal of the methyl groups are singlets (no splitting) as the adjacent carbon is not bonded to any hydrogen. ($N + 1 = 0 + 1 = 1$)

In contrast, the carbon adjacent to the methyl group in 1,1-dichloroethane is bonded to one proton, therefore the signal for the methyl protons is split in to a doublet ($N + 1 = 1 + 1 = 2$)

Number of equivalent protons causing splitting	Multiplicity of the signal	Relative peak intensities
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	sextet	1:5:10:10:5:1
6	septet	1:6:15:20:15:6:1

- The only exception to this rule is that the 'H' atom on -OH & -NH₂ group does not cause any splitting.
- If a peak is split into 2, the adjacent 'C' atom has one 'H', likewise if a peak is split into 4 the adjacent 'C' has 3 'H' atoms.
- This does not apply for molecules which are symmetrical. If the environment is same then we do not add the hydrogen atoms. i.e CH₃CH₂CH₂CH₃ the CH₃ peak will split into triplet as adjacent 2H are in the same environment. (2+2= 2 not 4) likewise, the CH₂ peak will split in to Quartet as adjacent 3H are in same environment. (3+3 = 3 not 6)

3. State the uses of Magnetic Resonance Imaging (MRI)

Nuclear Magnetic Resonance is the principle behind Magnetic Resonance Imaging (MRI) body scanners, which detect protons in water molecules in the body. Unlike X- Rays this technique is completely harmless to the patient.

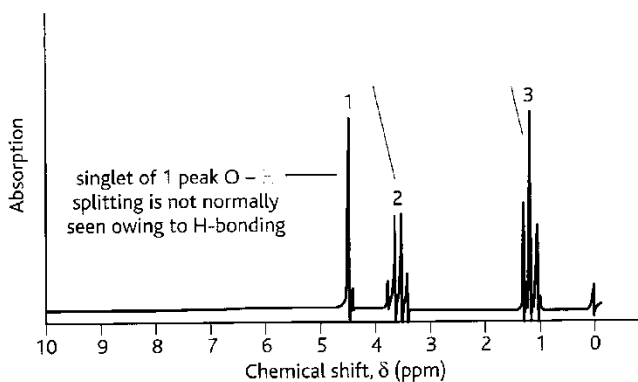
MRI is used as a diagnostic tool for the detection of problems in soft tissues. The patient is placed inside an extremely powerful electromagnet & kept for about 20 minutes till the scanning is done.

Protons in water, carbohydrates, proteins & lipids give different signals as they possess protons in different environment. Thus produce different signals which enables different organs to be distinguished.

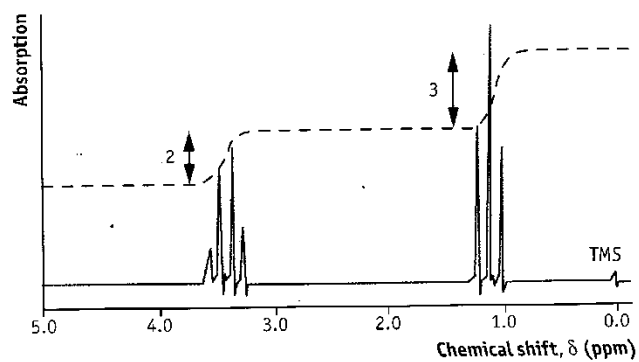
The 'H' nuclei in soft tissues possess different chemical shifts hence computers can generate pictures of slices through the part of the body to be investigated. This can be used to diagnose cancer, various brain & nerve related & other diseases.

4. Identify the peaks & suggest the formula of the compounds which give rise to each peak.

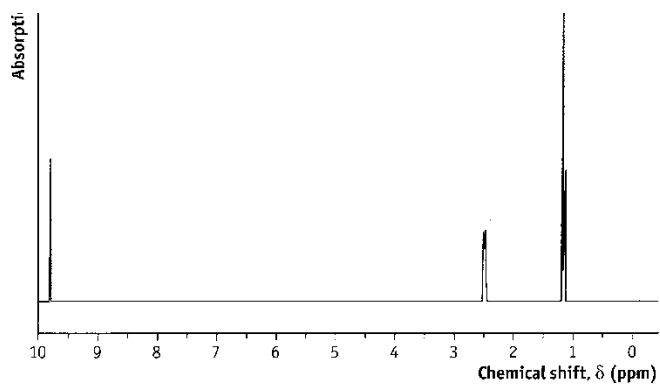
NMR Spectrum of Ethanol



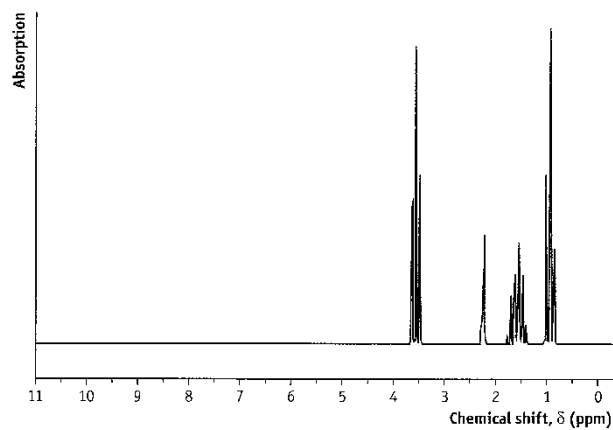
NMR Spectrum of Ethoxyethane



NMR Spectrum of Propanal



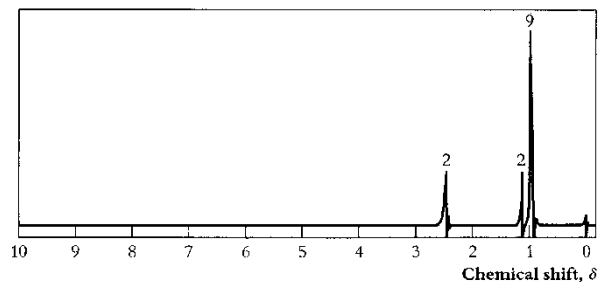
NMR Spectrum of Propanol



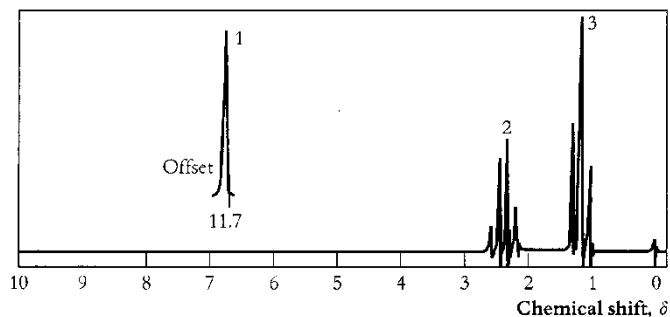
5. With the help of the chemical shift values given in the table below identify the peaks in the NMR spectrums below & suggest the identity of the compound which give rise to each peak with the help of N+1 rule.

Group	Chemical shift, δ
R-CH ₃	0.85-0.95
R-NH ₂	1.0
R-CH ₂ -R	1.3
R ₃ C-H	2.0
CH ₃ -CO ₂ R	2.0
R-COCH ₃	2.1
C ₆ H ₅ -CH ₃	2.3
R-C≡C-H	2.6
R-CH ₂ -Ial	3.2-3.7
R-O-CH ₃	3.8
R-O-CH ₂ R	4.0
R-O-H	3.5-5.5
RCH=CH ₂	4.9-5.9
C ₆ H ₅ -OH	7.0
C ₆ H ₅ -H	7.3
R-CHO	9.7
R-CO ₂ H	11.0-11.7

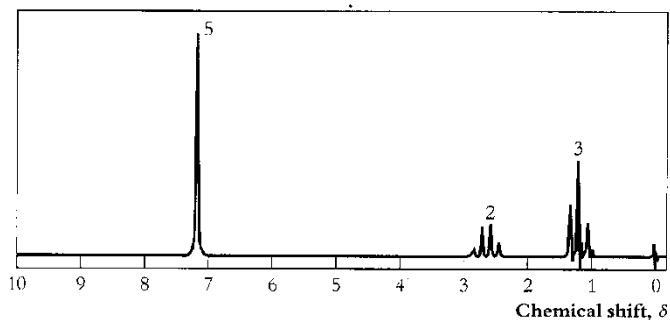
(a) This molecule is consist of 'C', 'N' & 'H'



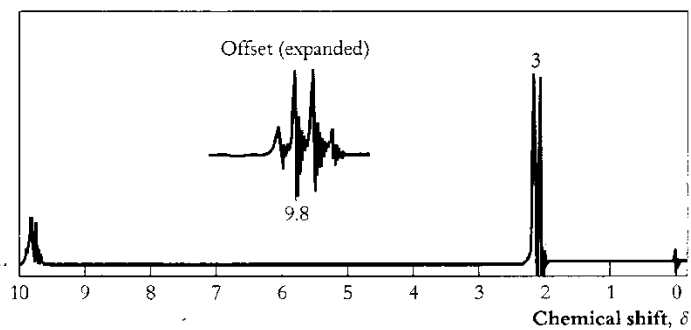
(b)



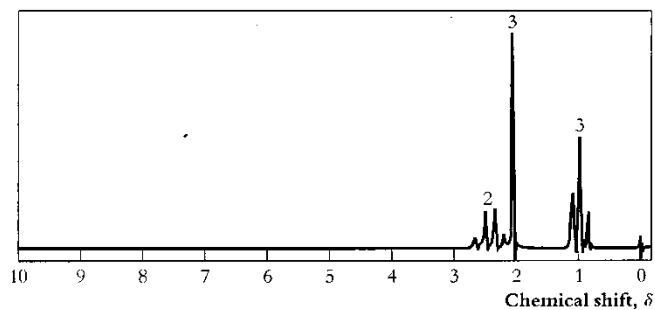
(c)



(d)

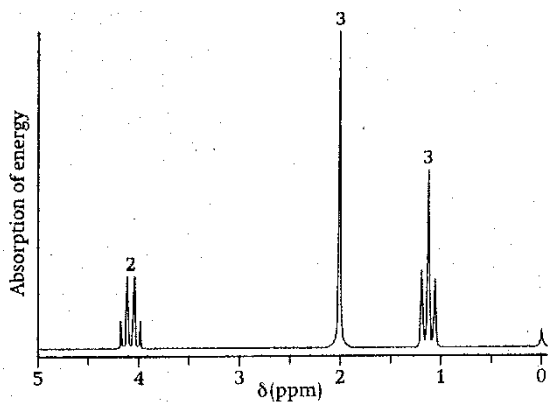


(e)



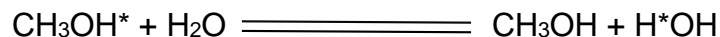
6. A compound has the molecular formula $C_4H_8O_2$. The n.m.r spectrum of this compound is shown below. The compound shows strong absorption in its I.R. spectrum at 1720cm^{-1} .

- From the splitting patterns, deduce which protons are on adjacent carbon atoms.
- Deduce the structural formula of the compound.



- State and explain the effect of adding D₂O in the identification of O-H & N-H protons.

The reason why the O-H proton or the N-H proton does not split is that those protons exchange rapidly with the protons of water / acid present as shown below:



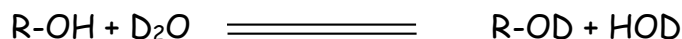
Due to this rapid exchange the signal of the -OH protons becomes a single peak. Similar takes place in -NH group in amines and amides.

When chemical shift values for OH & NH is observed it covers a wide range as the molecular environment changes.

<u>Different environment</u>	<u>Chemical Shift</u>
Aliphatic Amines -NH ₂ / -NH-	1.0 - 5.5
Aromatic Amnies -NH ₂	3.0 - 6.0
Amides -CONH ₂	5.0 - 12.0
Aliphatic Alcohols -OH	1.0 - 5.5
Phenol, Arenes -OH	6.5 - 7.0
Carboxylic -OH	11.0 - 11.7

In most cases these ranges overlap with the chemical shift of many proton environments. However with the help of deuterium oxide, D₂O we can positively identify the presence of the NH or OH groups.

The peaks due to OH / NH disappear from the spectra when a small amount of D₂O is added. D₂O also known as 'heavy water', where ²H (deuterium) exchange reversibly with the protons of OH / NH.



²H do not absorb NMR as ¹H does due to the even mass number. As a result when D₂O is added the OH / NH peaks disappear from the NMR spectrum. By comparing the peaks of the original NMR spectrum the presence of OH / NH groups can be identified.