Anderson Serangoon Junior College
2025 H3 Chemistry
Nuclear Magnetic Resonance (NMR)

Learning Outcomes:

(a) outline the principles of NMR with reference to:
- (i) nuclear spin
- (ii) the process of absorption energy

[quantitative calculations of transitional energy are **not** required; detailed knowledge of instrumentation is **not** required]

(b) understand the following features and use them in the interpretation and prediction of ^{1}H NMR spectra:
- (i) chemical shift
- (ii) deuterated solvents in the identification of labile protons
- (iii) the number of ^{1}H NMR signals: equivalent and non-equivalent protons
- (iv) peak area (integration) and proton counting
- (v) spin-spin splitting: first order spin-spin coupling; multiplicity

(c) explain the use of the δ scale with tetramethylsilane (TMS) as the reference

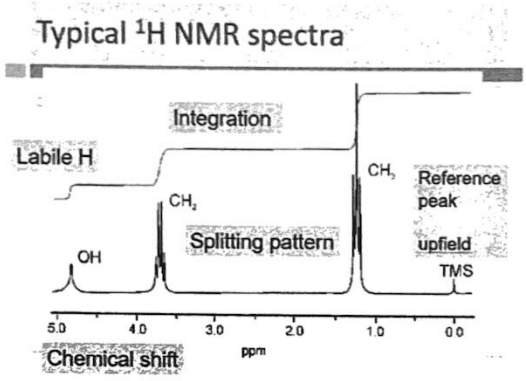
(d) explain the factors affecting chemical shift
- (i) electronegativity: inductive effect of substituents, including shielding and deshielding effects
- (ii) anisotropic effects
- (iii) hydrogen bonding

App to generate ^{1}H NMR spectra of organic compounds

^{1}H NMR Spectroscopy

- NMR (nuclear magnetic resonance) spectroscopy is an analytical technique used to determine the structure and properties of molecules by analyzing the interaction of atomic nuclei with an external magnetic field. It is widely used in chemistry to identify and quantify organic compounds.
    - **N**uclear – Involves spin of electron
    - **M**agnetic – "Spinning nucleus" behaves like a tiny nuclear magnet which interacts with the external magnetic field.
    - **R**esonance – Involves nuclei resonating at appropriate radio frequency.

- Nuclear Magnetic Resonance (NMR) spectra are presented as a graph of *absorbance* against *change of frequency* in parts per million (symbol δ).

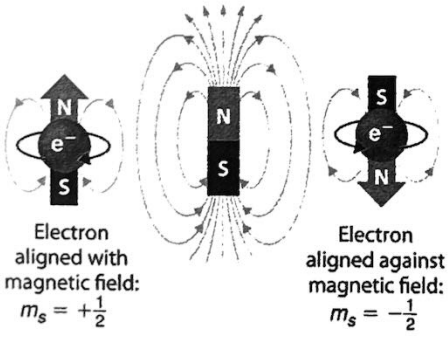


- It uilitizes the radiowaves of the EM.

- NMR allows us to detect atomic nuclei and what sort of environment they are in, within the molecules.

Magnetic properties of the nucleus

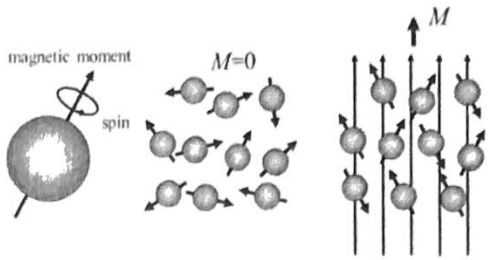
- In atomic structure, we have seen that electrons possesses "spin".



1s

- When elements have at least one isotope with nuclei with an odd atomic mass or odd/even atomic number, they are NMR active. Examples: ^1_1H (proton), $^{13}_6C$.

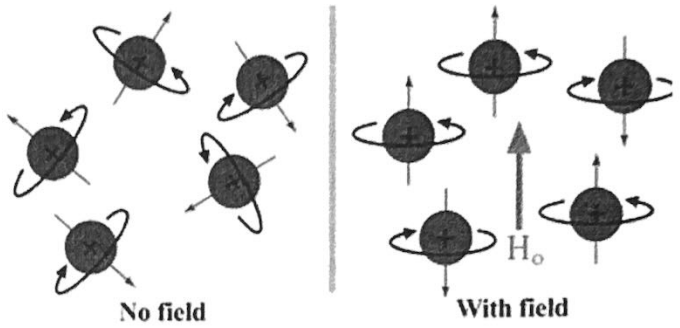
- The nuclei of hydrogen atoms spin about an axis. Since the nuclei are positively charged, the spinning is associated with a circulation of electric charge giving rise to magnetic fields. Hence, the spinning ^{1}H nucleus has a magnetic moment, like the magnet of a compass needle.



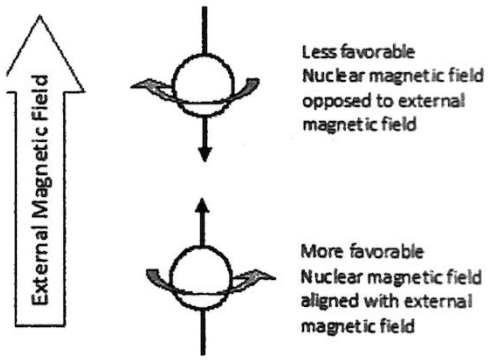
If a nucleus has an unpaired proton it will have spin and it will have a net magnetic moment or field

- Nuclei obey the laws of quantum mechanics. Hence, there are only two orientations allowed for the ^1H nuclei: a clockwise (+ ½) or counter clockwise (- ½) spin. In the absence of an external magnetic field, these spin states are of equal energy.

- In the *absence* of a magnetic field, nuclei's spins are orientated randomly and the 2 spin states are of the same energy.



- In the *presence* of a magnetic field, nuclear spins become parallel to the direction of the field.
  - The spins may be parallel or anti-parallel to the magnetic field
  - The two spin states occupy two different energy levels.
  - Nuclei whose spin are in the same direction as the magnetic field (like a compass needle does in the Earth's magnetic field) occupy a *lower* energy state.

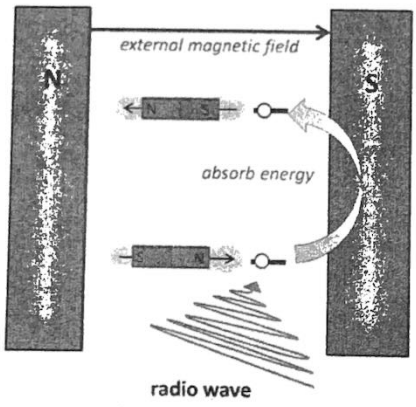


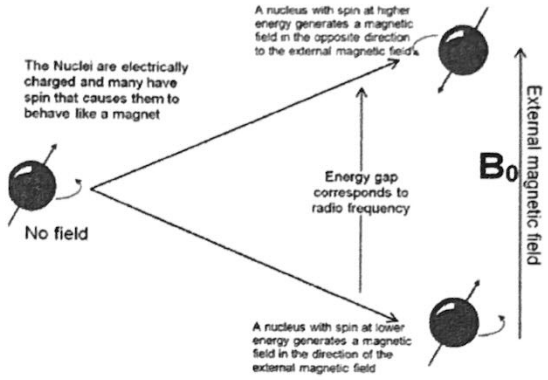
  - There are many more nuclei in the *lower* energy state (preferred orientation) than the *higher* energy state (opposite to the field's direction)

- The phenomenon of nuclear magnetic resonance occurs when nuclei aligned with the applied field absorb energy from electromagnetic radiation and change their spin orientation with respect to the field, by going to a higher energy level.

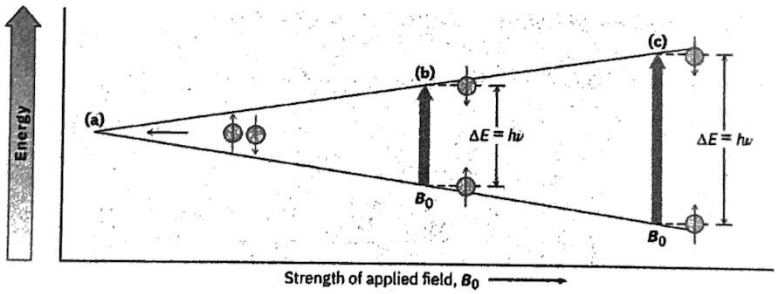
- When the nuclei absorb energy at a certain frequency ($E = h\frac{c}{\lambda}$), it is said to **resonate,** giving an NMR signal. Hence the term Nuclear Magnetic *Resonance.*

- The excited nuclei may relax by emitting energy in the radiation, returning to the ground state.





- The energy gap separating the two levels increases as the strength of the external field increases. The frequency of absorption is, in fact, directly proportional to the strength of the magnetic field and it also depends on the properties of the nuclei itself.



For your information:

- The energy difference between the nuclear spin being aligned with the magnetic field and against it is very very small.
- It is so small that a very very strong magnetic field is needed to see any difference at all. Hence NMR machines contain very strong electromagnet.
- The earth magnetic field is 2×10^{-5} tesla and the magnets used in NMR machines are between 2 amd 10 tesla which is about 10^5 time stronger.
- Since the energy difference is very small, the amount of energy needed to flip the nucleus can be provided by electromagnetic radiation of radio wave frequency.

Outline of the Principle of NMR spectroscopy

In absence of magnetic field, the spin of the nucleus with odd proton number will oriented randomly. Once an **external magnetic field** is applied, they reorient their spin either **aligned with the field** or **against the field**. Orientation parallel to alignment of applied field is lower in energy that the one against the field.

When nuclei are irradiated with radiowave, the lower energy nuclei absorbed the photon and **flip to** the orientation with a **higher energy state**. These nuclei are said to be in resonance.

Nuclei in **different chemical environment** will have **different energy gap** between the two spin states and hence they will absorb the **radiowave** radiation at **different frequency**.

Why do chemically distinct nuclei absorb energy at different frequencies?

- The variation in frequency for different hydrogen atoms mean the energy jump from nucleus-aligned-with to nucleus-aligned-against applied magnetic field must be different for each type of hydrogen atom.
- The nuclei of different types of hydrogen atom experience a magnetic field that is not quite the same as the magnetic field that is applied.
- Each nuclei 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 is applied.
- The electrons are said to **shield** the nucleus from the external magnetic field.
- If the electron distribution varied from ^1H atom to ^1H atom, so does the local magnetic field and so does the resonating frequency of the ^1H nuclei.

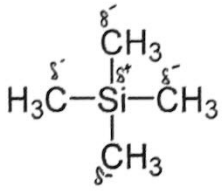
For your information:

- The exact frequency at which the nucleus resonates depends on the external applied magnetic field.
- If the sample is run on different machines with different magnetic fields, it will resonate at different frequencies.
- It will be difficult to say exactly where the signal was on different machines.
- All protons resonate at approximately the same frequency is a given magnetic field and that the exact frequency depends on the sort of chemical environment it is in, which in turn depends on its electron.
- This approximate frequency is the operating frequency of the machine and simply depends on the strength of the magnet – the stronger the magnet, the larger the operating frequency.
- The precise value of the operating frequency is simply the frequency at which a standard reference sample resonates.

The internal standard and the solvents used

- Solvent used to dissolve the sample should contains no protons.
  E.g. tetrachloromethane, CCl_4, or deuterochloroform, $CDCl_3$, or heavy water, D_2O.

- Reference sample used is usually tetramethylsilane (TMS), $(CH_3)_4Si$.



Reason:

(i) TMS is volatile and inert.

(ii) The four carbon atoms attached to silicon are all equivalent. Hence, all 12 hydrogen atoms are equivalent.

(iii) Silicon is more electropositive than carbon. Hence, the carbon are fairly electron-rich (or **shielded**), which means they resonate at frequency a little less than that of most organic compounds.

(iv) Hence, it produces a strong singlet peak at a lower frequency than most ^1H absorptions in organic molecules, so its peak does not interfere with the other peaks.

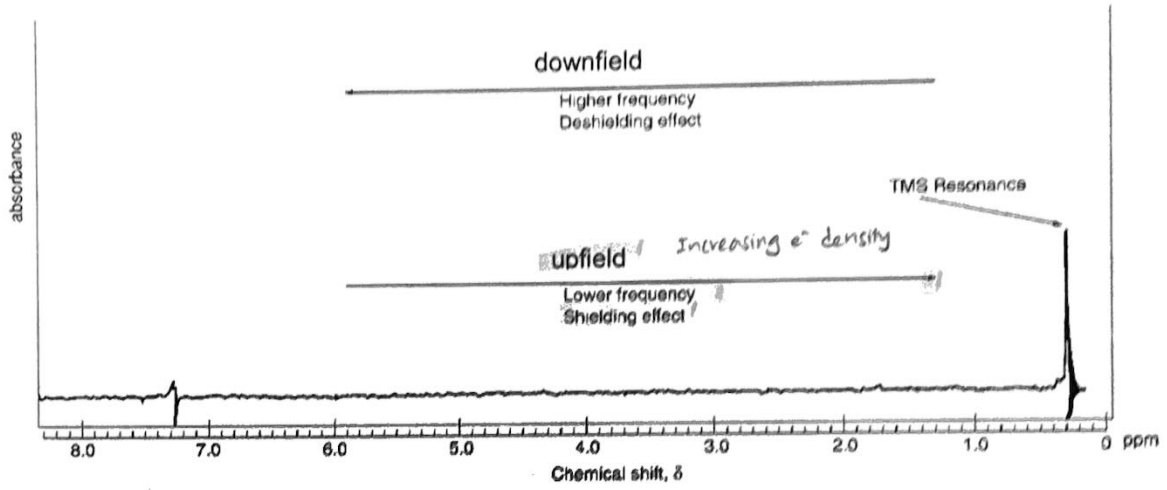
The ^{1}H NMR spectra of organic compounds

- An NMR spectrum consists of a graph of **absorbance** against **chemical shift** (symbol δ). The chemical shift of a proton, in parts per million (p.p.m.), is the difference between its absorption frequency and that of TMS, divided by the irradiating frequency in MHz).

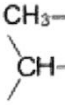
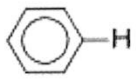
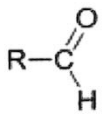
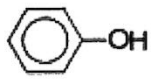
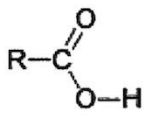
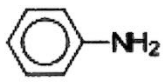
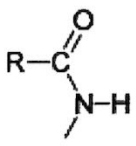
$$\delta_x = \frac{(frequency_x(Hz) - frequency_{TMS}(Hz))}{frequency_{TMS}(MHz)}$$

where δ_x = chemical shift of proton x
$frequency_x$ = frequency of absorption of proton x
$frequency_{TMS}$ = frequency of absorption of the protons in TMS

- No matter what the operating frequency of the NMR machine, the signals in a given sample will always occur at the same chemical shifts. By definition, TMS itself resonates at 0 p.p.m.
- Most protons in organic molecules resonate within 10 ppm of TMS, and by convention, the zero point of the scale (TMS) is on the right hand side.
- The chemical shift scale runs to the left from zero (where TMS resonates).
- Most protons in actual chemical compounds resonate at different frequencies.



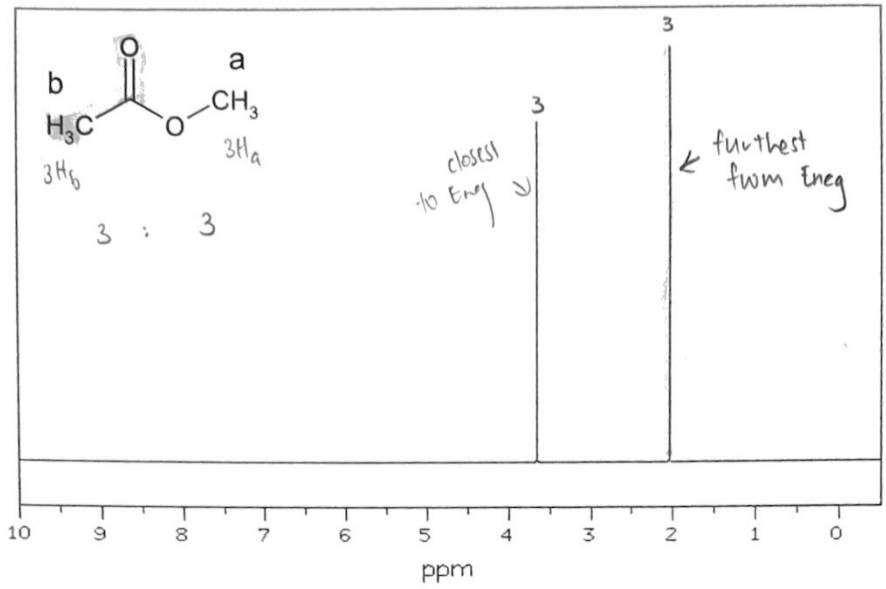
6 Typical proton (^{1}H) chemical shift values (δ) relative to TMS = 0

Type of proton	Environment of proton	Structural unit	Chemical shift range (δ)
C–H	alkane	–CH_3, –CH_2–, 	0.9–1.7
	alkyl next to C=O	CH_3–C=O, –CH_2–C=O, 	2.2–3.0
	alkyl next to aromatic ring	CH_3–Ar, –CH_2–Ar, 	2.3–3.0
	alkyl next to electronegative atom	CH_3–O, –CH_2–O, –CH_2–Cl, 	3.2–4.0
	attached to alkyne	≡C–H	1.8–3.1
	attached to alkene	=CH_2, =CH–	4.5–6.0
	attached to aromatic ring		6.0–9.0
	aldehyde		9.3–10.5
O–H (see note below)	alcohol	R–O–H	0.5–6.0
	phenol		4.5–7.0
	carboxylic acid		9.0–13.0
N–H (see note below)	alkyl amine	R–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.

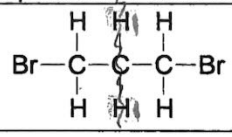
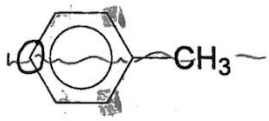
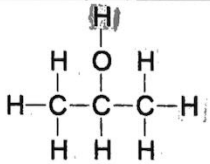
Chemically Equivalent Protons

- Frequency at which a proton absorbs radiation depends on the strength of the **local** magnetic field around it.
- Protons in different chemical environments within a molecule absorb at different frequencies. This is because the local magnetic field they experience depends on the electrical and magnetic environment around them despite in the same external magnetic field.
- For example, the ^1H NMR spectra of methyl acetate shows 2 distinct proton environments.
- Area under the peaks is exactly proportional to the number of protons. Protons spectra are normally integrated. The area under the peaks is computed and recorded as a line with steps corresponding to the area.



Exercise 5.1:

Identify the protons that are chemically equivalent in each of the following molecules:

(i)	1,3-dibromopropane		2
(ii)	methylbenzene		4
(iii)	propan-2-ol		3

Factors Affecting the Chemical Shift of a Proton

- When a molecule is placed in an external field, the electron pairs within their molecules rotate in their orbits in such a way that they *produce a magnetic field which opposes the external field.*
- This phenomenon is called **diamagnetism**. The effect is to 'shield' nearby protons from the external field.
- This reduces the frequency at which they absorb energy when they flip from their lower to their higher energy state.

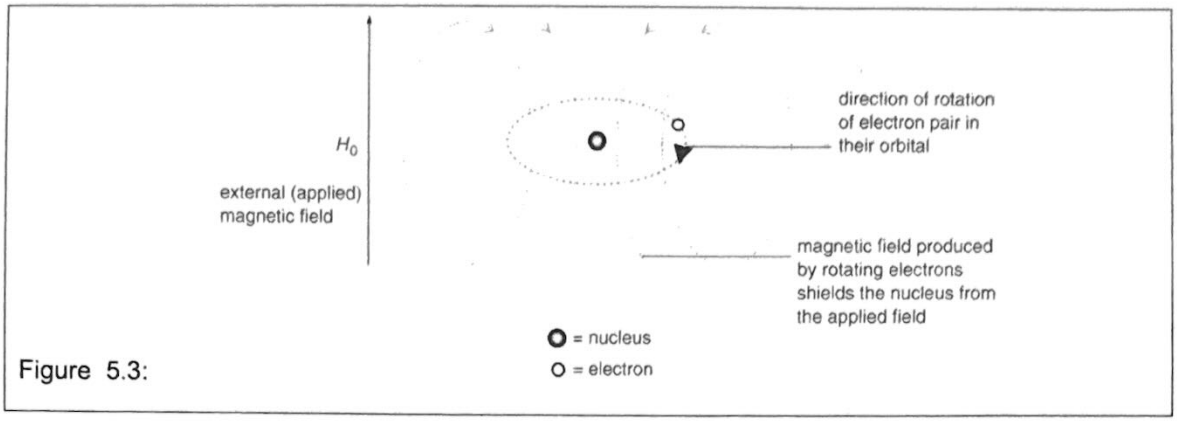
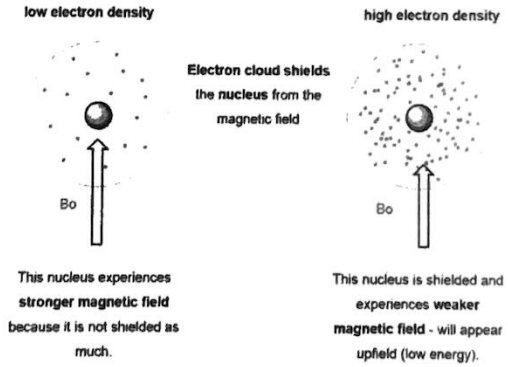


Figure 5.3:

1. **The inductive effect** of electronegative atoms

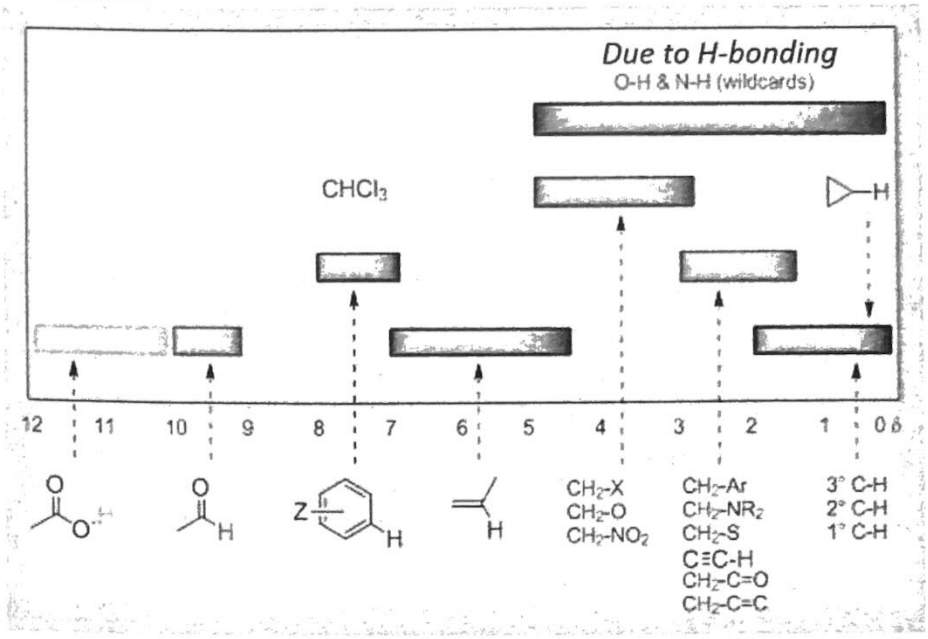
- When a proton is near an electronegative atom within a molecule, the bonding electrons are drawn away from the proton to the electronegative atom. This proton is less shielded or deshielded from the external magnetic field, and hence it absorbs radiation at a higher frequency. Thus the *chemical shift increases.*



- NOTE: The closer the proton is to the electronegative atom, the larger the increase.

proton environment	$-CH_2-C-C$	$-CH_2-C-O$	$-CH_2-N<$	$-CH_2-O-$
δ	1.3	1.9	2.5	3.4

← More deshielded More shielded →



2. **The magnetic anisotropic effect** associated with some π-bonded systems.

- Magnetic anisotropy means that there is a "non-uniform magnetic field".
- Electrons in π systems (*e.g.* aromatics, alkenes, alkynes, carbonyls *etc.*) interact with the applied field which induces a magnetic field that causes the anisotropy.
- As a result, the nearby protons will experience 3 fields: the applied field, the shielding field of the valence electrons and the field due to the π system.
- Depending on the position of the proton in this third field, it can be either shielded or deshielded.
- π-bonded electrons are further away from the nuclei of atoms than σ-bonded electrons, so they are more influenced by the external magnetic field. As can be seen from Figure 5.4, the electrons in the π-bond circulate in a diamagnetic way to produce a magnetic field that opposes the external field.
- But this opposing magnetic field is in the **middle** of the π-bond. Because of the closed circular nature of the magnetic lines of force, the hydrogen atoms joined to the C=C double bond will experience a stronger field (i.e. external field + local field caused by circulating π-electrons).
- NOTE: This causes a **deshielding effect** on the protons in the plane of the atoms joined to the π-bond.
- The anisotropic effect is **very** apparent for the aldehydic proton in aldehydes.
- However, the proton attached to an alkyne absorbs at a **lower** frequency than expected, because the proton is in line with the axis of the triple bond's cylinder of π electron density, so the induced field will oppose the applied field.

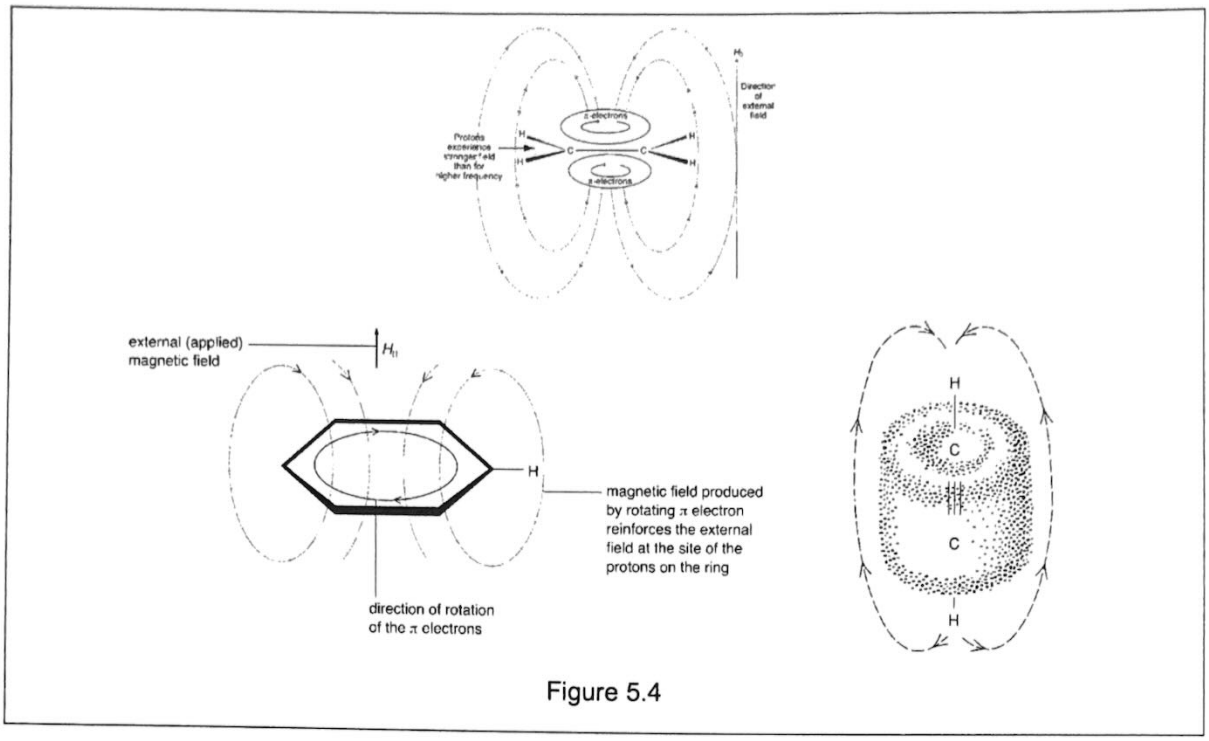
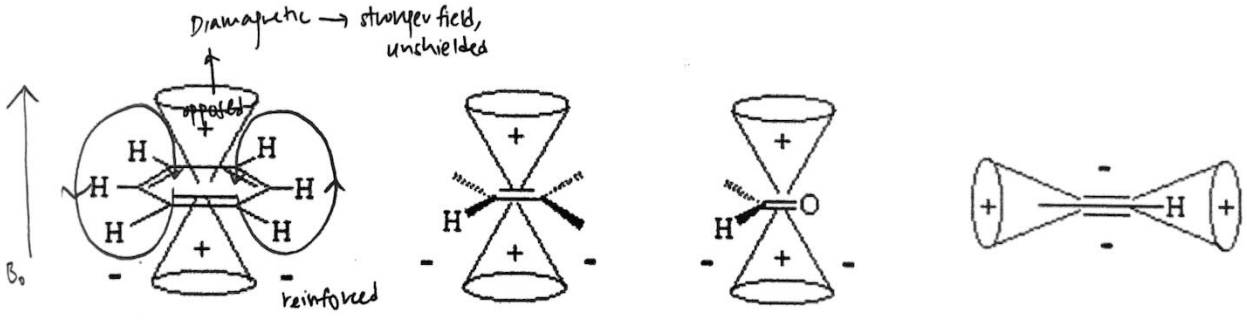


Figure 5.4

- The following table shows some examples of the anisotropic effect.

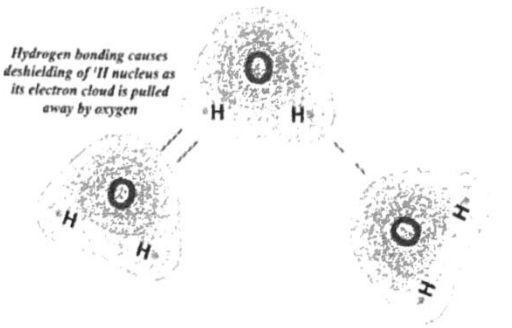
proton environment	>CH-C-	-C≡C-H	>C=CH-C	benzene (C_6H_6)	O=CH-
δ	1.5	2.5	5.5	7.3	9.7



Schematic diagram of shielding cones for common pi systems. The + denotes shielding areas and - denotes deshielding areas. Remember shielding lowers the chemical shift, δ and deshielding increases δ. Typical H δ values are also shown.

3. Hydrogen Bonding

When the proton is involved in the hydrogen bonding, a larger downfield shift occurs than when it is not involved. This is because the density of proton decreases due to close approach of an electronegative atom. The greater the degree of hydrogen bonding, the more deshielded a proton becomes, the larger is the downfield shift.



Effects of hydrogen-bonding on local magnetic fields due to relative shielding of ^1H nuclei by electron clouds.

Spin-spin coupling

- The low resolution NMR spectrum of ethanol contains three different absorption peaks occurring at slightly different values of the applied field (Figure 5.5).
- The areas under these peaks are found to be in the ratio 1:2:3.
- These different peaks are due to the fact that the single -OH proton, the two $-CH_2-$ protons and the three $-CH_3$ absorb at different frequencies.

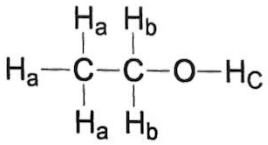
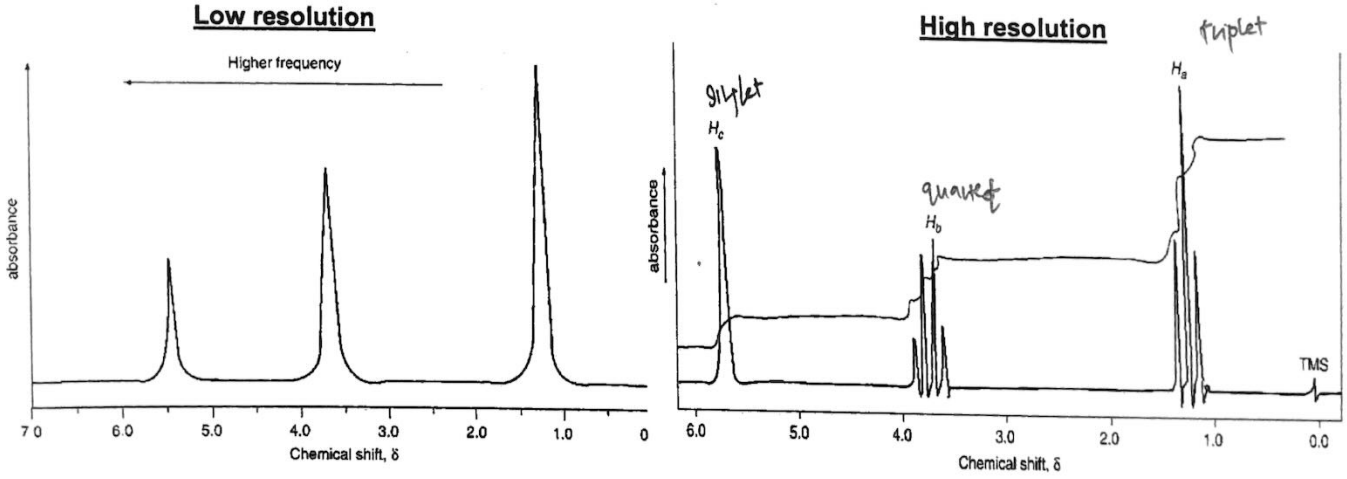


Figure 5.6

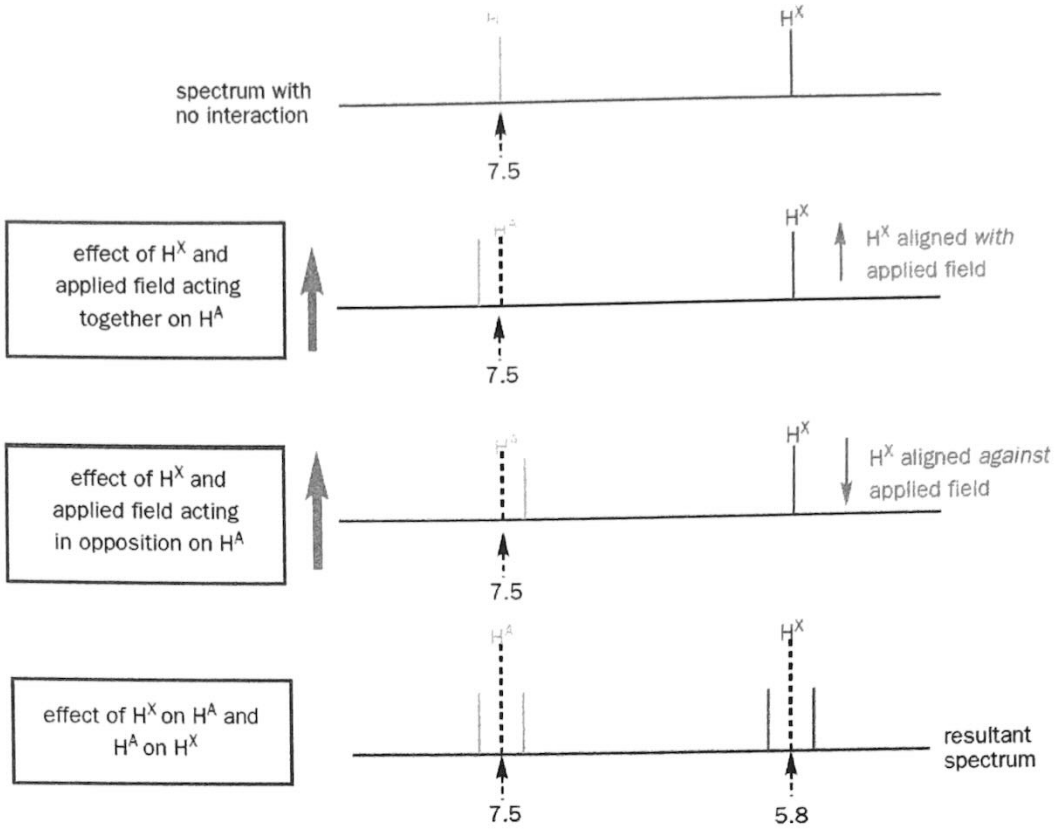
Figure 5.5



- A high resolution spectrum of ethanol (Figure 5.6) shows the same three peaks, but this time the peak at δ 1.2 is split into three peaks, and that at δ 3.7 is split into four.
- Nearby protons can interact with each other and the result of this is known as **coupling.**
- A proton can be near enough to experience the small magnetic field other protons as well as the field of the magnet itself.

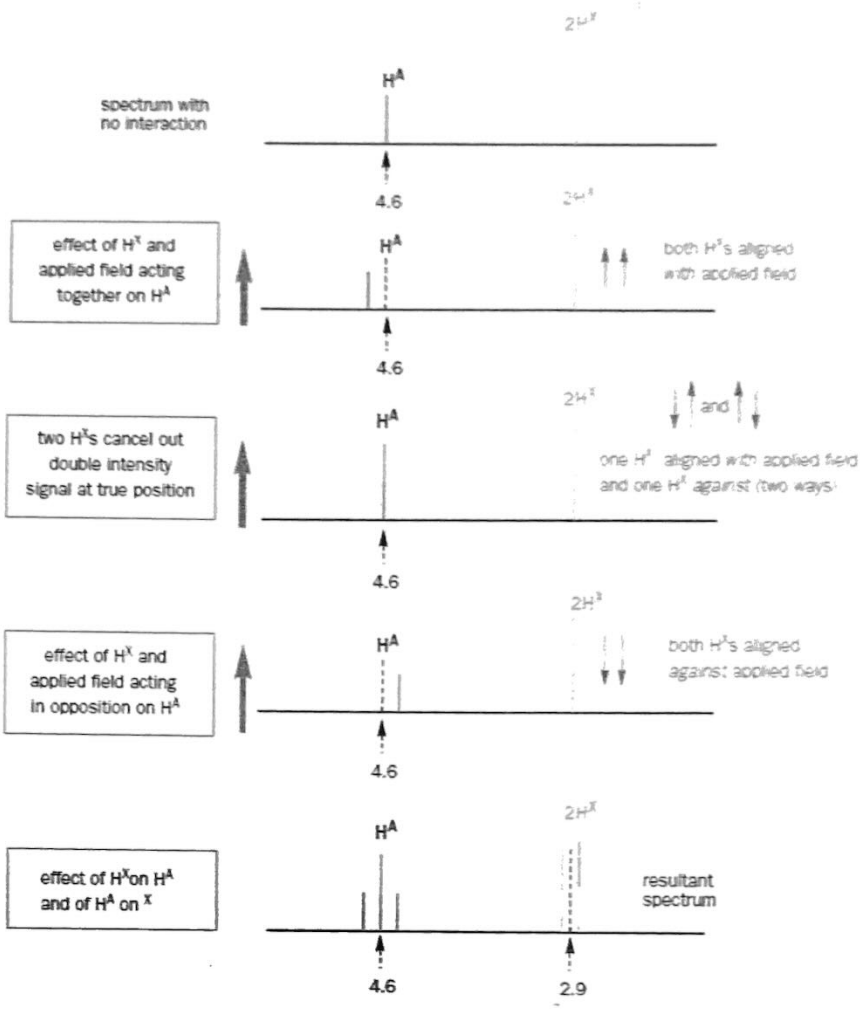
For your information:

- The following diagram shows an example where one proton is affected by another proton:



- H^A experience two different fields : The applied field plus the field of H^x or the applied field minus the field of H^x.
- H^x acts either to increase or to decrease the field experience by H^A. The position of a resonance depends on the field experienced by the proton as these two situations give rise to two slightly different peak – a **doublet.**
- The same situation apply for H^x as well.
- The field of the proton is very small compared to the field of the magnet and the separation between the lines of a doublet is very small.

- The following diagram shows an example where one proton is affected by two another protons:



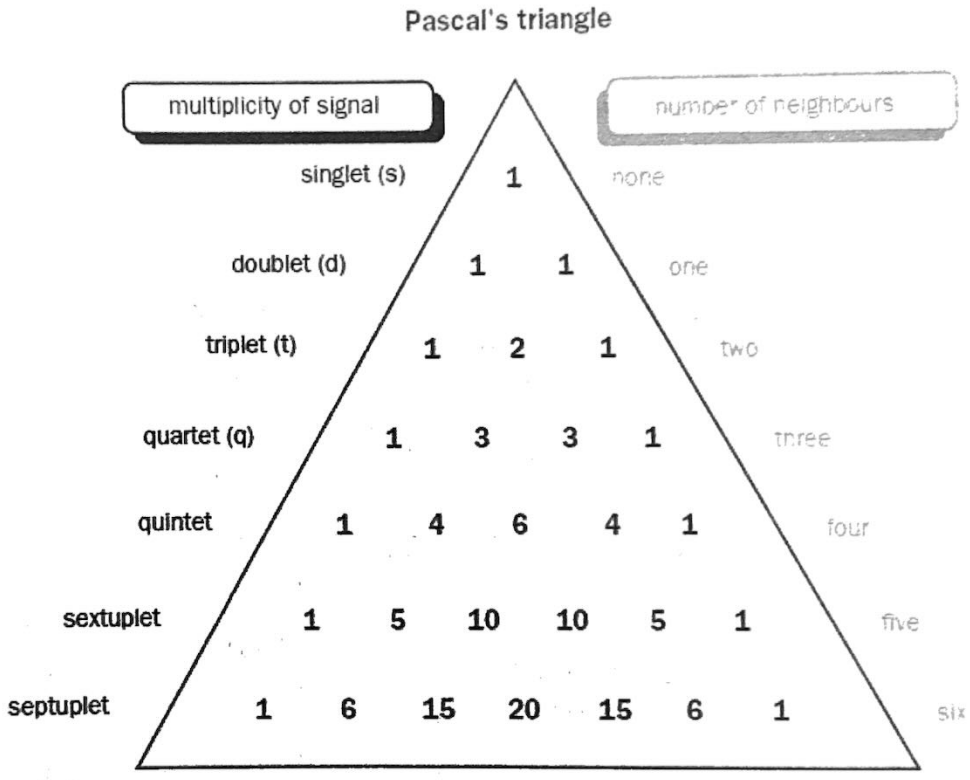
- H^A interact with two other protons H^x and it can experience three states of protons H^x.
- Both H^x can be aligned with the magnet or both against. These states can increase or decrease the applied field as before.
- However, if one proton H^x is aligned with and one against the applied field, there is no net change to the field experienced by H^A and there are two possibilities for this (see diagram).
- This will cause a signal of double intensity for H^A at the correct chemical shift, one signal at higher chemical shift and one at lower chemical shift.

The general rules governing splitting patterns are as follows:

1. Protons in identical chemical environments (e.g. the three H atoms in the $-CH_3$ group) do not split their own absorption peak.
2. The absorption peak of resonating protons is only split by nearby protons on the **adjacent** carbon atom – protons further away (usually) have little effect
3. The resonance peak of a proton adjacent to *n* protons is split into $(n + 1)$ peaks.
4. The intensities of the peaks in a multiplet are as in the following table.

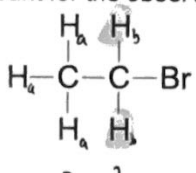
number of protons adjacent to the resonating proton, *n*	number of lines in multiplet, *n* + 1 (multiplicity)	relative intensities of lines	multiplet name
0	1	-	Singlet (s)
1	2	1:1	Doublet(d)
2	3	1:2:1	Triplet (t)
3	4	1:3:3:1	Quartet (q)
4	5	1:4:6:4:1	Quintet (Qt)

Or the Pascal's triangle:



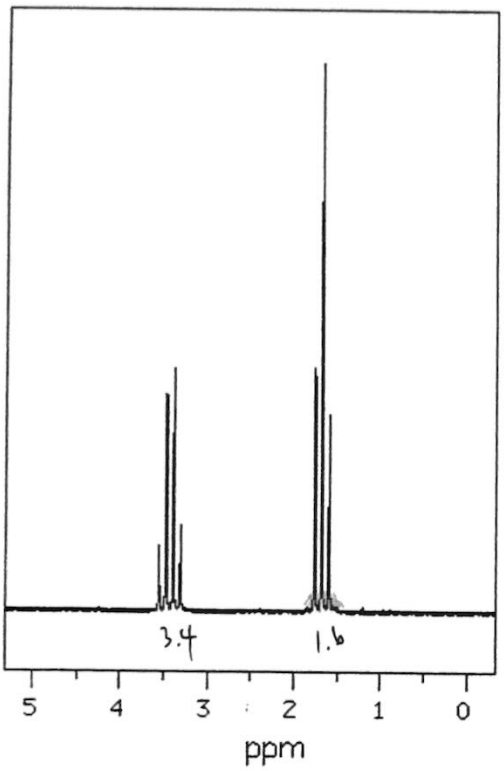
Exercise 5.2: Account for the observed splitting pattern in the ^{1}H NMR spectra of the following compounds.

(a) Bromoethane



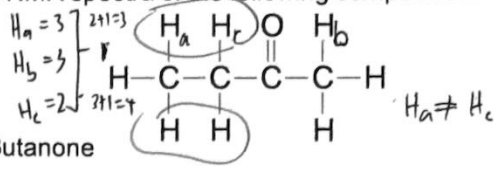
$H_a \neq H_b$

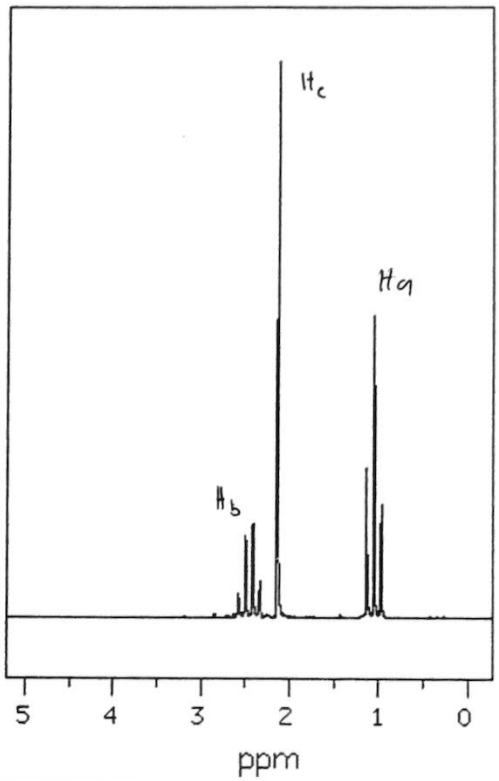
3 : 2



δ / ppm	Multiplicity	Deductions
	s / d / t / q	___ *protons adj to* ___ *(group)*
1.6	Triplet	$-CH_3$ adjacent to $-CH_2-$
3.4	quartet	$-CH_2$ adjacent to $-CH_3-$ Deshielded by electronegative Br

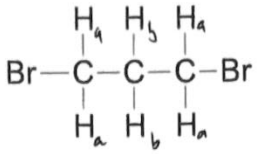
(b) Butanone



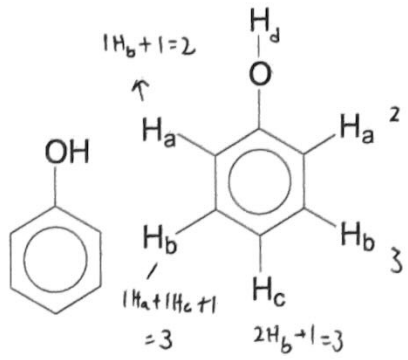


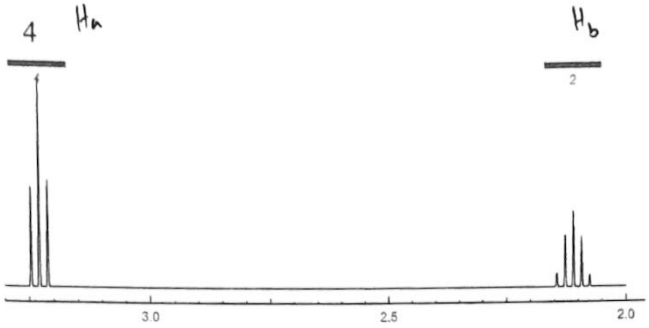
δ / ppm	Multiplicity	Deductions
	s / d / t / q	___ *protons adj to* ___ *(group)*
1.1	Triplet	$-CH_3$ adjacent to $-CH_2-$
2.1	Singlet	$-CH_3$ without protons on adjacent C atom. Deshielded by adj C=O
2.4	Quartet	$-CH_2$ adj to $-CH_3$ adjacent C atom. Deshielded by adj C=O

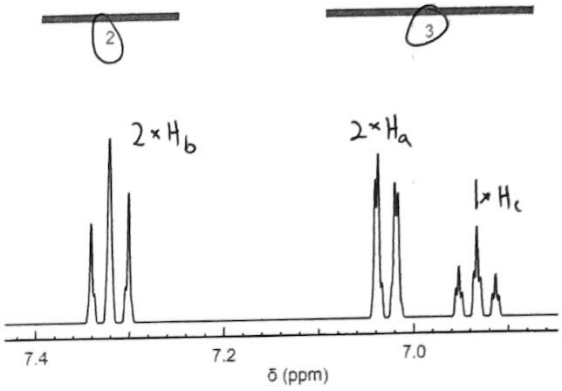
(c) 1,3-dibrompropane



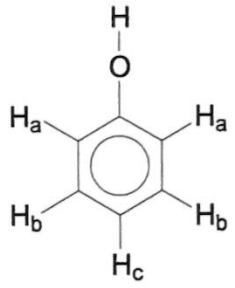
(d) phenol







δ / ppm	Multiplicity	Deductions
	s / d / t / q	___ *protons adj to* ___ *(group)*
2.1	~~Triplet~~ Quintet	-CH_2- adjacent to $-CH_2Br$
3.3	Triplet	-CH_2- adjacent to $-CH_2$ AND Br, deshielded by electronegative Br

δ / ppm	Multiplicity	Deductions
	s / d / t / q	___ *protons adj to* ___ *(group)*
7.1	Duplet	
7.3	Triplet	

Effect of adding D_2O

- No splitting is observed between the protons on –OH groups and adjacent protons on the carbon skeleton.
- This is due to rapid exchange with protons on other –OH groups such as those in water (most samples contain small amounts of impurities that catalyse the exchange).

$$CH_3CH_2O\mathbf{H} + H_2O \rightleftharpoons CH_3CH_2OH + HO\mathbf{H}$$

- These protons are called **labile protons**.
- This means that adjacent protons only experience an averaged-out field of all the exchanging protons rather than the local field caused by the two possible orientations of the OH proton. ____(The –OH absorption in **ultra-dry** ethanol does in fact appear as a triplet).
- **A useful application**: The disappearance of absorption peak of labile proton when an NMR sample is shaken with D_2O (D is deuterium, ^2H).

$$CH_3CH_2O\mathbf{H} + \mathbf{D}_2O \rightleftharpoons CH_3CH_2O\mathbf{D} + HO\mathbf{D}$$

Examples of labile protons: $-NH_2$, -COOH, $-CONH_2$

Integration of peak areas

- The area under each peak is proportional to the number of protons responsible for that absorption.
- Thus from the left hand side, the areas of the peaks are in the ratio 1:2:3. (Fig 5.5)
- This is also true for the high resolution spectrum, but in this case the sum of the areas underneath *all* the split peaks in a group is proportional to the number of protons.

Intrepretation of NMR spectrum

The following information can be derived from a ^1H NMR spectrum:

- chemical shift => Types of H in each environment
- no. of signals => no. of types of H in the molecule
- ratio of the signal areas => no. of equivalent protons in each type
- splitting pattern => The no. of equivalent adjacent protons hence reveal the structure neighbouring groups $(n+1)$
- A signal that disappears when using solvent containing D_2O => labile proton

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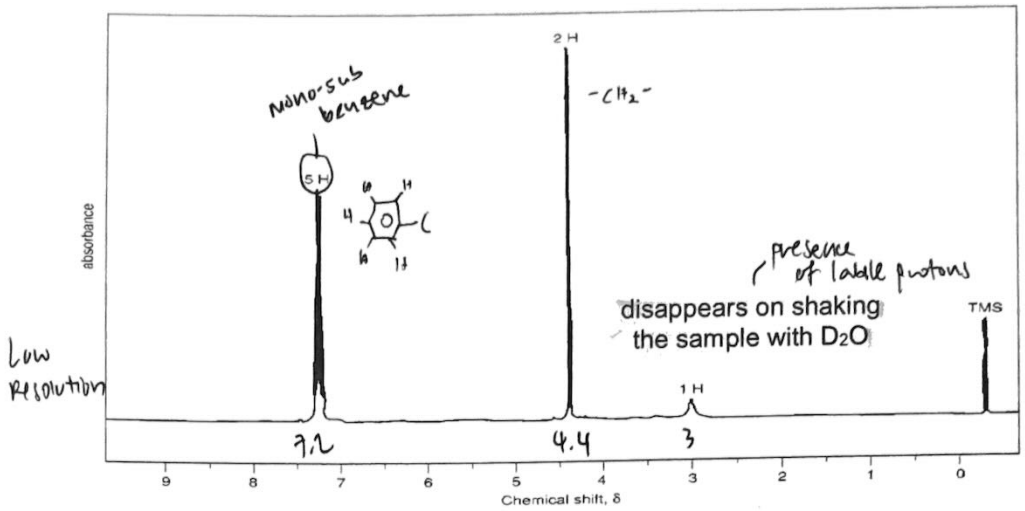
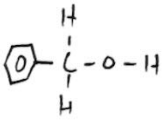
Exercise 5.3:
Deduce the structure of unknown compound **X** and **Y** from their ^{1}H NMR spectrum given below.

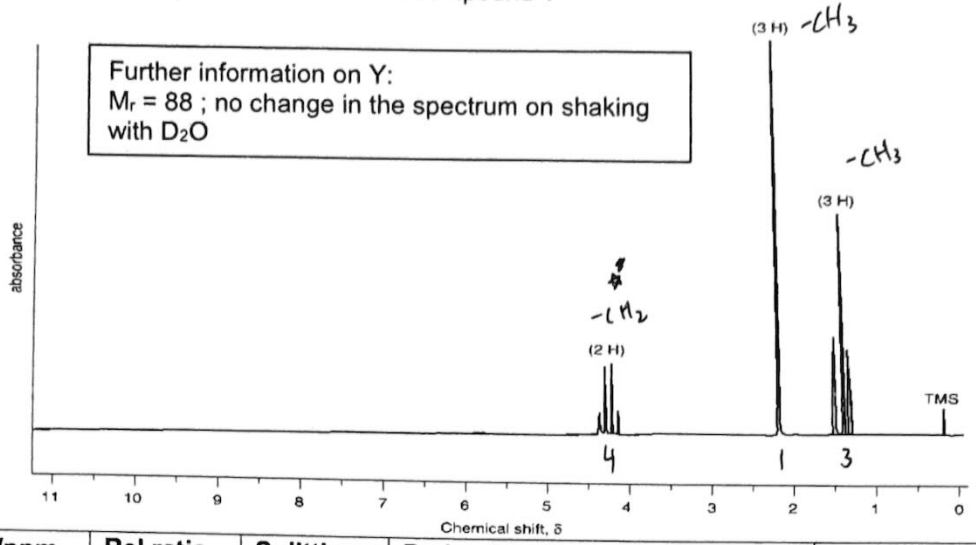
(a) ^{1}H NMR spectrum of unknown compound **X** (M_r = 108)



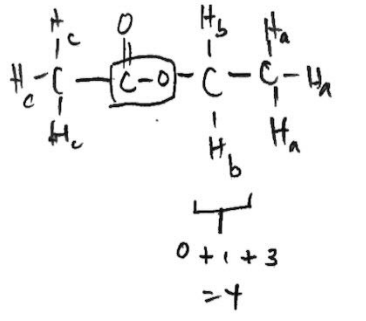
δ/ppm	Rel ratio	Splitting	Deduction	Structure of X
3.0	1	s (disappears with D_2O)	Labile -OH proton	
4.4	2	s	$-CH_2-$ deshielded by adj phenyl ring and Eneg O atom No proton on adj C atom	
7.2 – 7.3	5	m	$-C_6H_5$ · aromatic protons from mono-substituted phenyl ring	

(b) ^{1}H NMR spectrum of unknown compound **Y**

Further information on Y:
M_r = 88 ; no change in the spectrum on shaking with D_2O



	δ/ppm	Rel ratio	Splitting	Deduction	Structure of Y
H_a	1.4	3 (2H)	t	$-CH_3$ adjacent to $-CH_2$	$H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$
H_b	2.2	3	s	$-CH_3$ adj to C atom w/o proton Deshielded by adj C=O	
H_c	4.3	2	q	$-CH_2-$ adj to $-CH_3$ Deshielded by adj O atom	



88
- 15×2
- 14
44
- 16 (O)
28 (C=O)

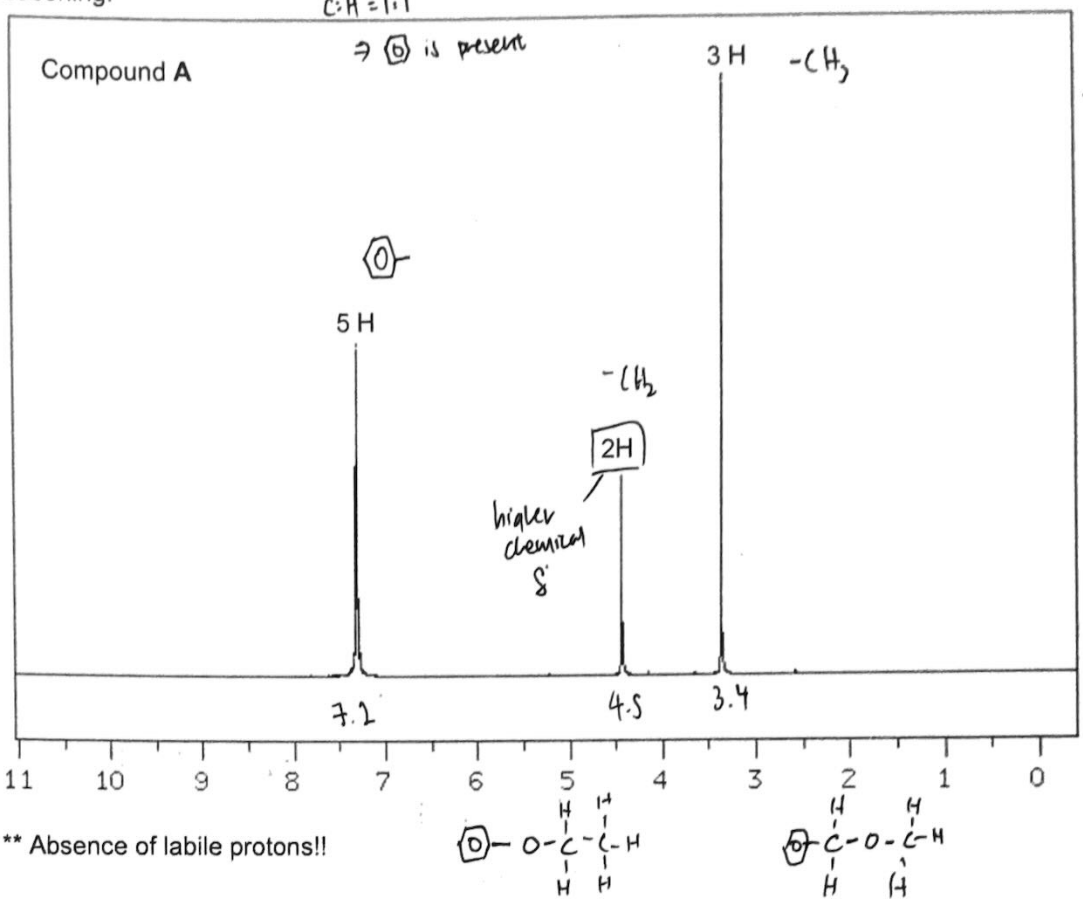
Exercise 5.4:

The two ^{1}H NMR spectra shown below were obtained from compounds **A** and **B** which have the same molecular formula $C_8H_{10}O$. Deduce the structures of both compounds, explaining your reasoning.

C:H = 1:1

⇒ ⓑ is present

Compound **A**



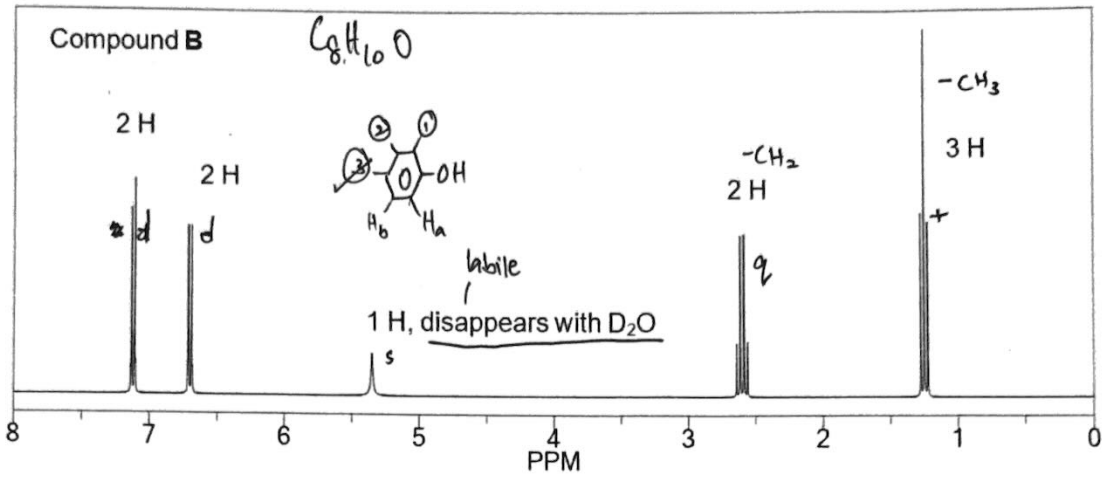
8C

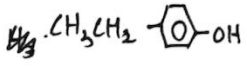
5+2+3 H = 10 H

1 x O

** Absence of labile protons!!

δ/ppm	Rel ratio	Splitting	Deduction	Structure of A
7.2	5	M	$-C_6H_5$ aromatic protons from mono-substituted phenyl ring	ⓑ-CH_2-O-CH_3
4.5	2	S	$-CH_2$ w/o protons on adj C atom; deshielded by adj O atom	
3.5	3	S	$-CH_3$ w/o protons on adj. C atom; deshielded by adj O atom	



δ/ppm	Rel ratio	Splitting	Deduction	Structure of B
6.8 7.2	2 2	Duplet	$-C_6H_4$ aromatic proton from di-substituted phenyl ring ∵ 2 types of proton	
5.3	1	singlet	labile -OH proton on phenol group as H disappears with D_2O	
2.6	2	quartet	$-CH_2-$ adj to $-CH_3$ Next to phenyl ring	
1.3	3	triplet	$-CH_3$ adj to $-CH_2$	