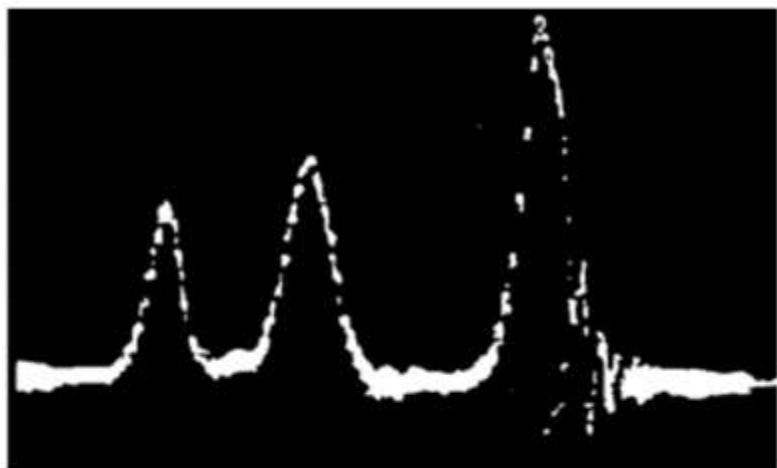# ^{1}H NMR Spectroscopy

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First reported proton NMR spectrum of ethyl alcohol.

Reference books: Pavia, Lampman, Kriz and Vyvyan
William Kemp and Silverstein

NMR SPECTROSCOPY: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Introduction:

- Spectroscopy is the study of **interaction of electromagnetic radiation** with the **matter** (**compounds**)

- **Spectroscopic techniques** have been successfully used to **determine the structure** and **functional groups** of the **organic compounds**

- Light is a form of energy, described by two complimentary theories;

  ➢ Wave theory, and

  ➢ Corpuscular theory

- Neither of these theories alone can completely account for all the properties of light

- Most of the spectroscopic studies account for the **wave theory**

- The propagation of light by waves involves both **electric** and **magnetic forces**, which give rise to their common class name *electromagnetic radiation*

Electromagnetic radiation is characterized by;

- **Wavelength (λ)** in meters, centimetres, millimetres

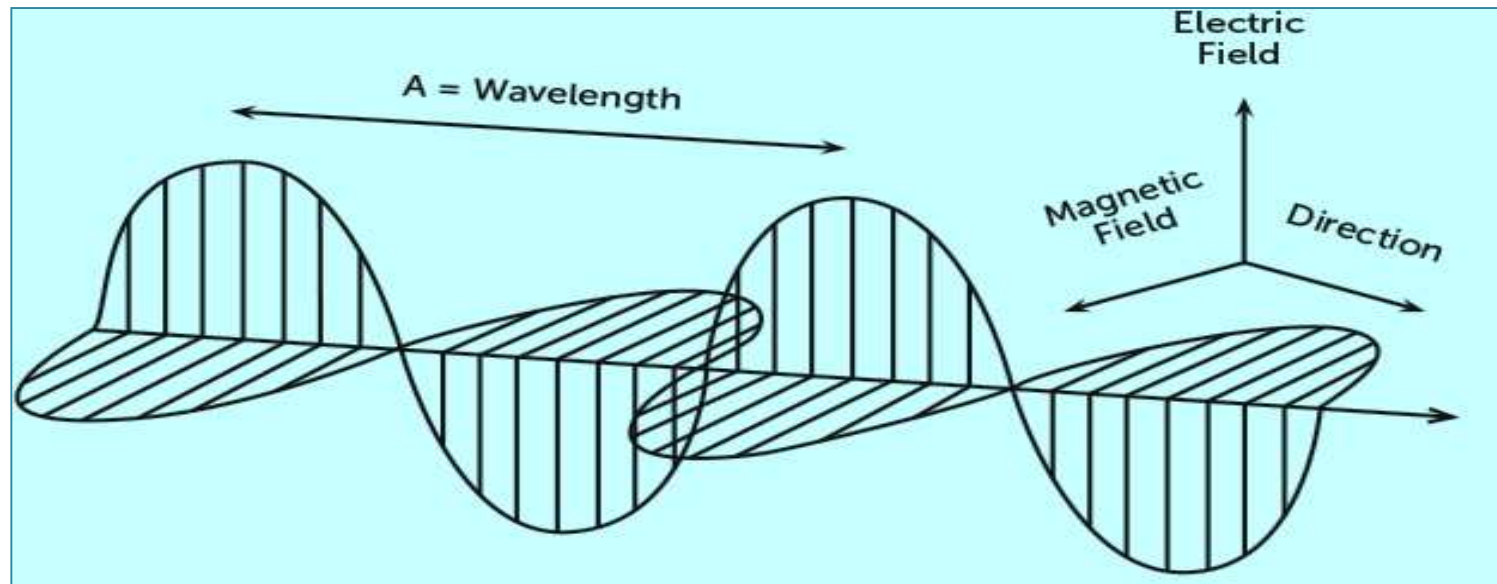- **Frequency (v)** in reciprocal seconds (s^{-1}, or Hz ($1s^{-1}$ = 1Hz)

Figure 1 *Propagation of electromagnetic radiation (alternating electric and magnetic forces)*

Electromagnetic spectrum

| Radiation type | Radio waves | Microwaves | Infrared | | Ultraviolet | X-rays | Gamma rays |

Wavelength (approximate): 30 mm — 1 mm — 10 nm — 0.01 nm

Visible light
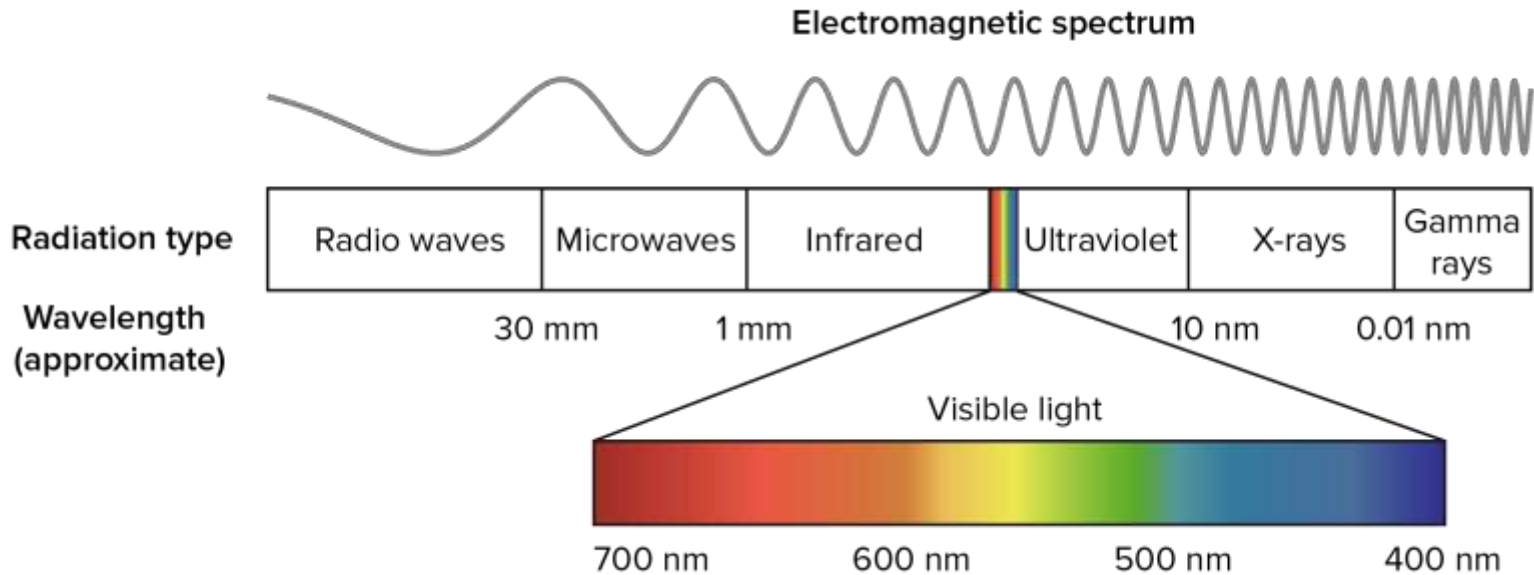
700 nm — 600 nm — 500 nm — 400 nm

Figure 2 *Electromagnetic spectrum*

$$E = h\nu$$

$$\nu = c/\lambda$$

$$E = hc/\lambda$$

Higher the frequency, higher the energy and **lower the frequency, lesser the energy**

Longer the wavelength, lesser the energy and **shorter the wavelength, higher the energy**

Comparative Analogy

Electromagnetic Spectrum
(longest wavelength to shortest wavelength)

1. Radio and TV
2. Microwaves
3. Infrared
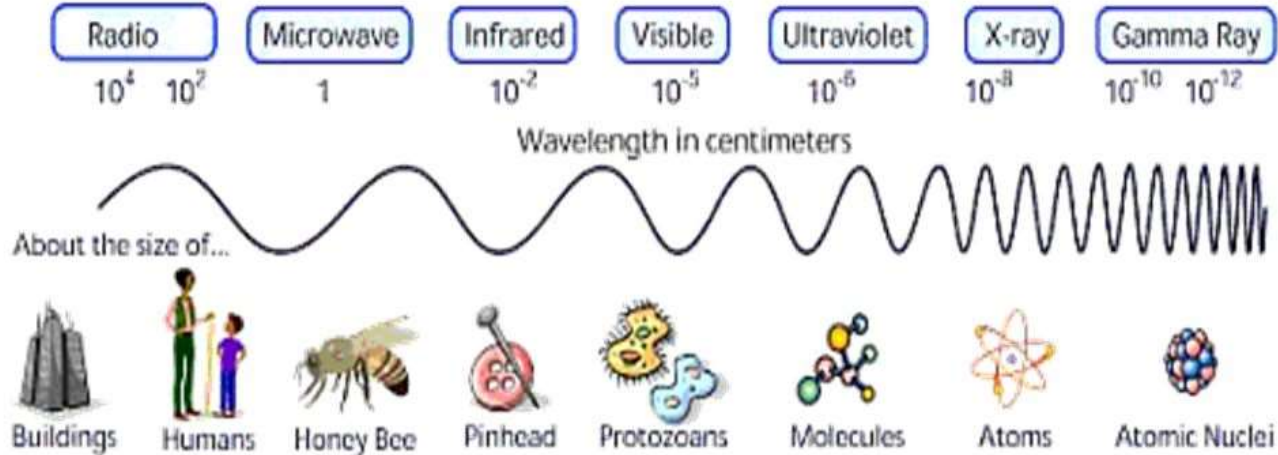4. Visible

5. Ultraviolet
6. X-rays
7. Gamma Rays

Radio		Microwave	Infrared	Visible	Ultraviolet	X-ray	Gamma Ray
10^4 10^2		1	10^{-2}	10^{-5}	10^{-6}	10^{-8}	10^{-10} 10^{-12}

Wavelength in centimeters

About the size of...

Buildings | Humans | Honey Bee | Pinhead | Protozoans | Molecules | Atoms | Atomic Nuclei

Table 1 *Spectroscopic techniques, purpose of study and their applications*

Sl. No.	Name of the technique	Radiation used	Wave Length	Purpose of study	Application
1	X-Ray diffraction	X-rays	0.01 - 10nm	*Inter-atomic distance*	skeletal structure
2	UV-Visible spectroscopy	UV-visible radiations	10 - 700 nm	*electronic transitions*	conjugation
3	IR spectroscopy	IR radiation	700 nm - 1mm	*bending and stretching vibrations of covalent bonds*	functional groups
4	Microwave spectroscopy	Microwaves	1 mm-30 mm	*rotational transitions*	rotational transitions of molecules
5	**NMR spectroscopy (^{1}H NMR)**	**Radiowaves**	**> 1 mm**	***nuclear spin transitions***	**Number of different types of hydrogens in a molecule**

Discoveries in NMR

Name of the Discovery	Discoverer/s
Nuclear Magnetic Resonance (NMR)	F. M. Bloch & E. M. Purcell
Fourier Transform Nuclear Magnetic Resonance (FT- NMR)	Richard Ernst
Two Dimensional NMR (2D - NMR)	J. Jeener
Magnetic Resonance Imaging (MRI)	Paul Lauterbur

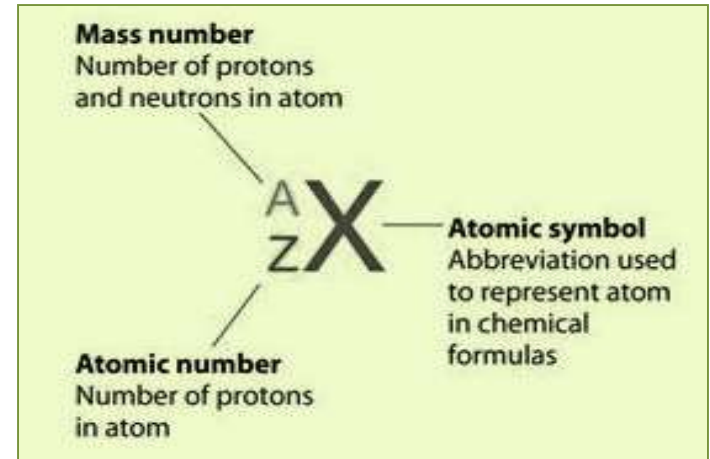# Proton magnetic resonance (PMR) / ^{1}H NMR spectroscopy

➢ **Nuclear Magnetic Resonance** (or NMR) is concerned with the **magnetic properties** of certain **atomic nuclei**

➢ Typically, the nucleus of the hydrogen atom-the **proton** (**^{1}H NMR**) and that of the **carbon-13 isotope** (**^{13}C NMR**) of carbon

➢ Studying **^{1}H NMR spectroscopy** enables us to know the **different types of hydrogen** present in the organic molecule.

The spinning nucleus

▪Many atomic nuclei have a property called **spin**; the nuclei behave as if they were **spinning**

▪In fact, any atomic nucleus that possesses either *odd mass*, *odd atomic number*, or *both* (odd mass & odd atomic number) has a property called **spin**

▪This spin is referred as magnetic moment denoted by symbol *μ* (mu)

spinning nucleus
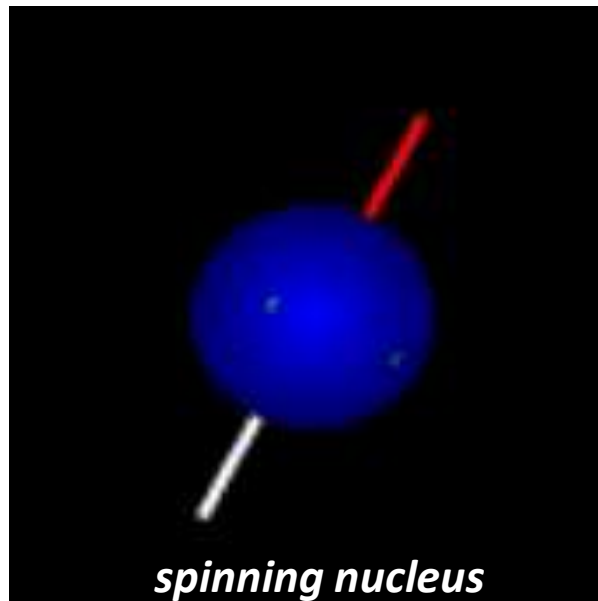
- **Nuclei** that possess **spin** include $^1H_1$, $^2H_1$, $^{13}C_6$, $^{14}N_7$, $^{17}O_8$ and $^{19}F_9$ which possess **either odd mass**, **odd atomic number** or **both** (odd mass & odd atomic number)

- The nuclei of the most abundant isotopes of carbon ($^{12}C_6$) and oxygen ($^{16}O_8$) do **not possess magnetic moment** as these nuclei do not have **odd mass** or **odd atomic number**

Mass number
Number of protons and neutrons in atom

$_Z^A X$

Atomic symbol
Abbreviation used to represent atom in chemical formulas

Atomic number
Number of protons in atom

➤ Nucleus of the **hydrogen atom** (**proton** or ^1H) does have *spin* since it has **odd mass** and **odd atomic number**

➤ For each nucleus, the **number of allowed spin states** it may adopt is determined by its *nuclear spin quantum number* $\mathbf{I}$

➤ For each nucleus, there are **2I + 1 allowed spin states**

➤ A **proton** (hydrogen nucleus) has the **spin quantum number $\mathbf{I} = 1/2$** and has **two allowed spin states [2(1/2) + 1 = 2]** for its nucleus i.e., **-1/2 and +1/2**

➤ For **chlorine nucleus $\mathbf{I} = 3/2$** and there are **four allowed spin states [2(3/2) + 1 = 4]** i.e., **-3/2, -1/2, +1/2 and +3/2**
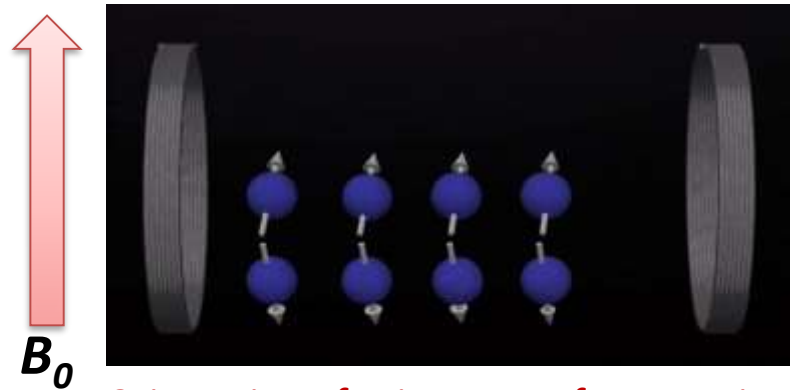
The effect of an external magnetic field B_0

✓ Any **charged particle** under **motion** generates **magnetic field** of its own

✓ The **proton** behaves as a **tiny spinning bar magnet**

✓ All the **spin states** of a proton are of **equivalent energy** (degenerate) in the **absence of the external magnetic field** (**B_0**)

✓ However, the **spin states** are **not of equivalent energy** in an **applied magnetic field** or **external magnetic field** (**B_0**)

✓ A **proton** can have **two allowed spin states -1/2 and +1/2**

✓ Consequently in an **external magnetic field B_0**, the **protons** can **only adopt two orientations** with respect to an external magnetic field *i.e.,*

1) *aligned with the external magnetic field B_0* (+1/2, the lower energy state)

2) *opposed to the external magnetic field B_0* (-1/2, the higher energy state)
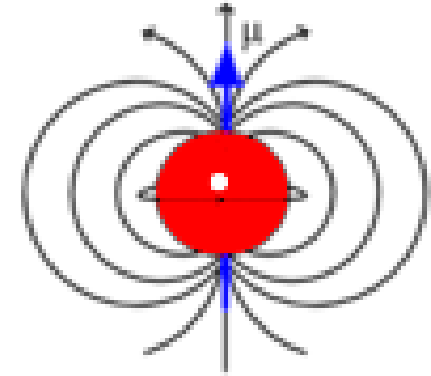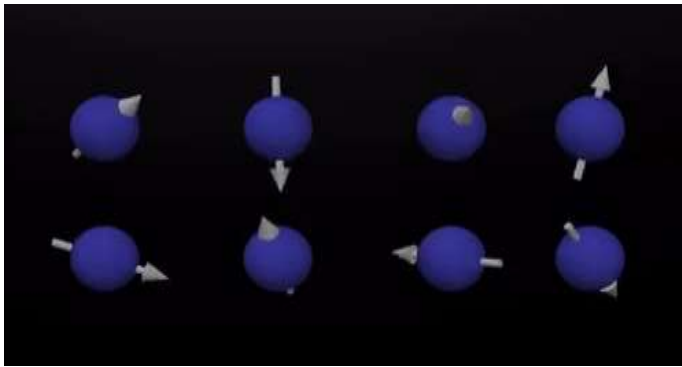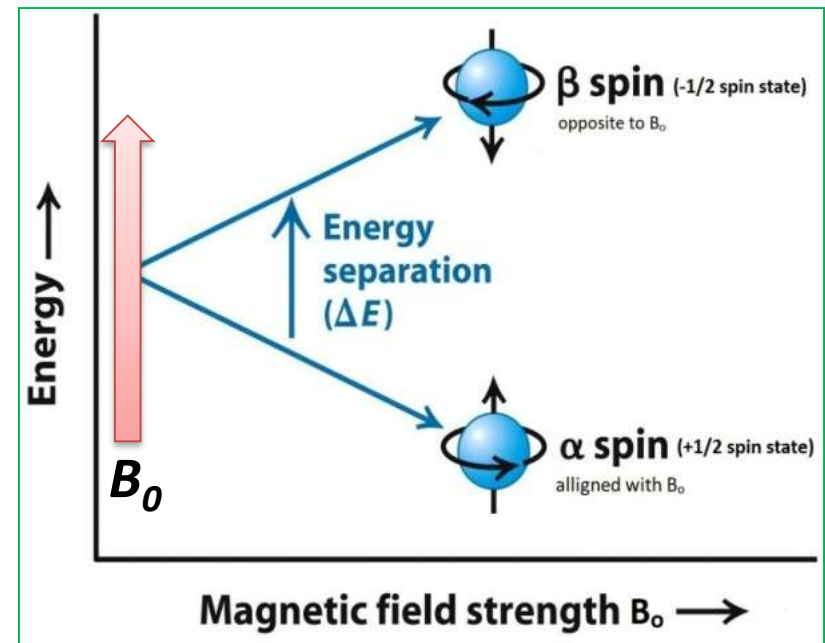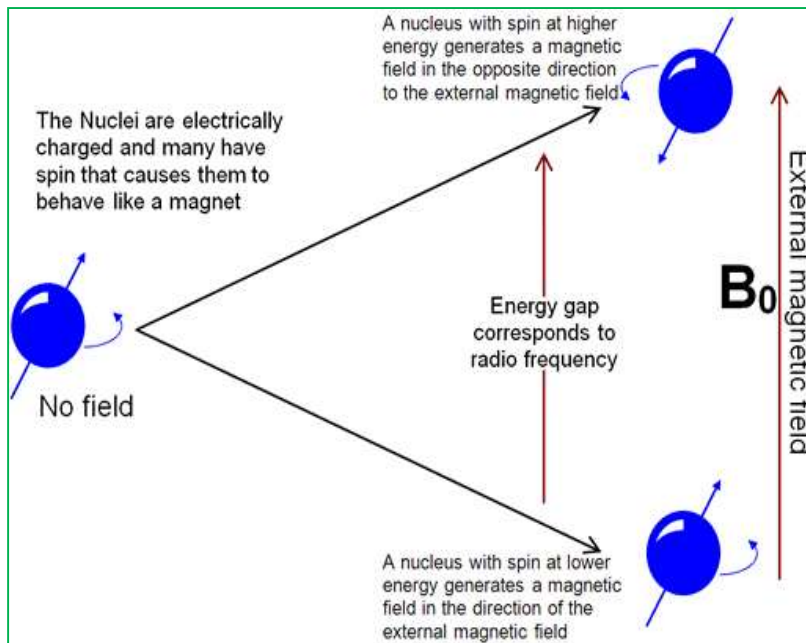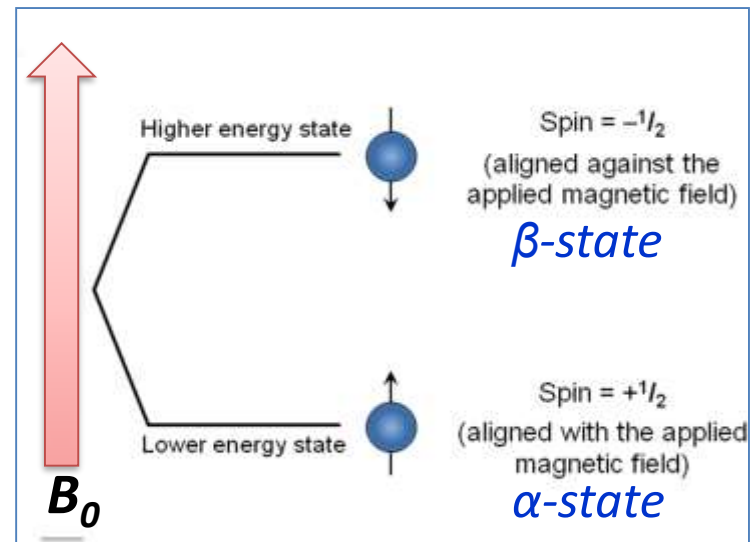
Degenerate spin states of protons in the absence of B_0

B_0

Orientation of spin states of protons in the presence of B_0

The Nuclei are electrically charged and many have spin that causes them to behave like a magnet

No field

A nucleus with spin at higher energy generates a magnetic field in the opposite direction to the external magnetic field

A nucleus with spin at lower energy generates a magnetic field in the direction of the external magnetic field

Energy gap corresponds to radio frequency

B_0

External magnetic field

Energy

B_0

Magnetic field strength B_o →

β spin (-1/2 spin state) opposite to B_o

Energy separation (ΔE)

α spin (+1/2 spin state) alligned with B_o

Spin states of a proton in presence of external magnetic field B_o

No field   With field B_0

Energy

No Field

Applied Magnetic Field

m = -1/2
β-state

m = +1/2
α-state

B_0

Higher energy state

Lower energy state

Spin = −1/2
(aligned against the applied magnetic field)
β-state

Spin = +1/2
(aligned with the applied magnetic field)
α-state
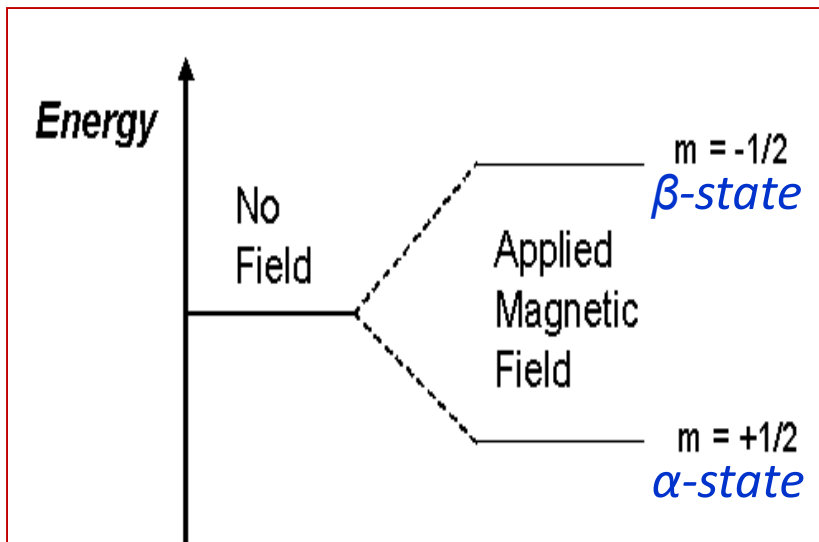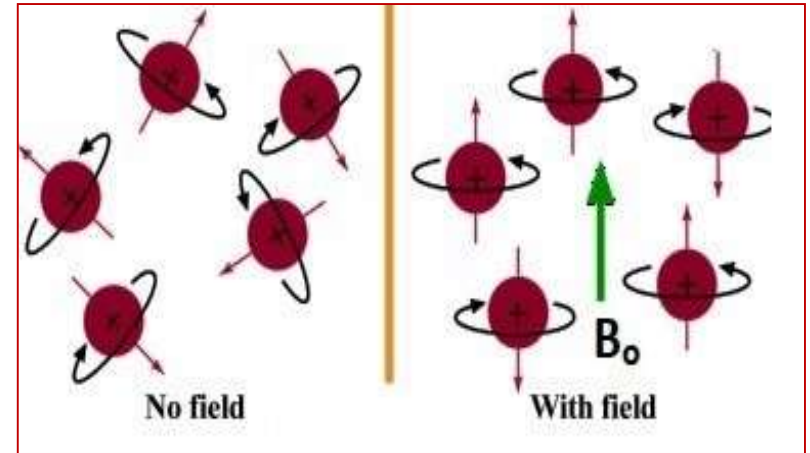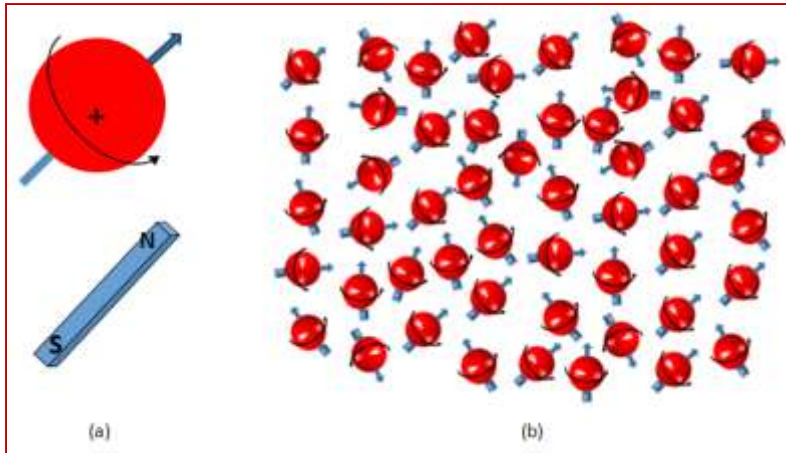
Absorption of energy (electromagnetic radiation)

The nuclear magnetic resonance phenomenon occurs when nuclei aligned

with an applied field are induced to absorb energy (hv) and change their spin

orientation with respect to the applied field
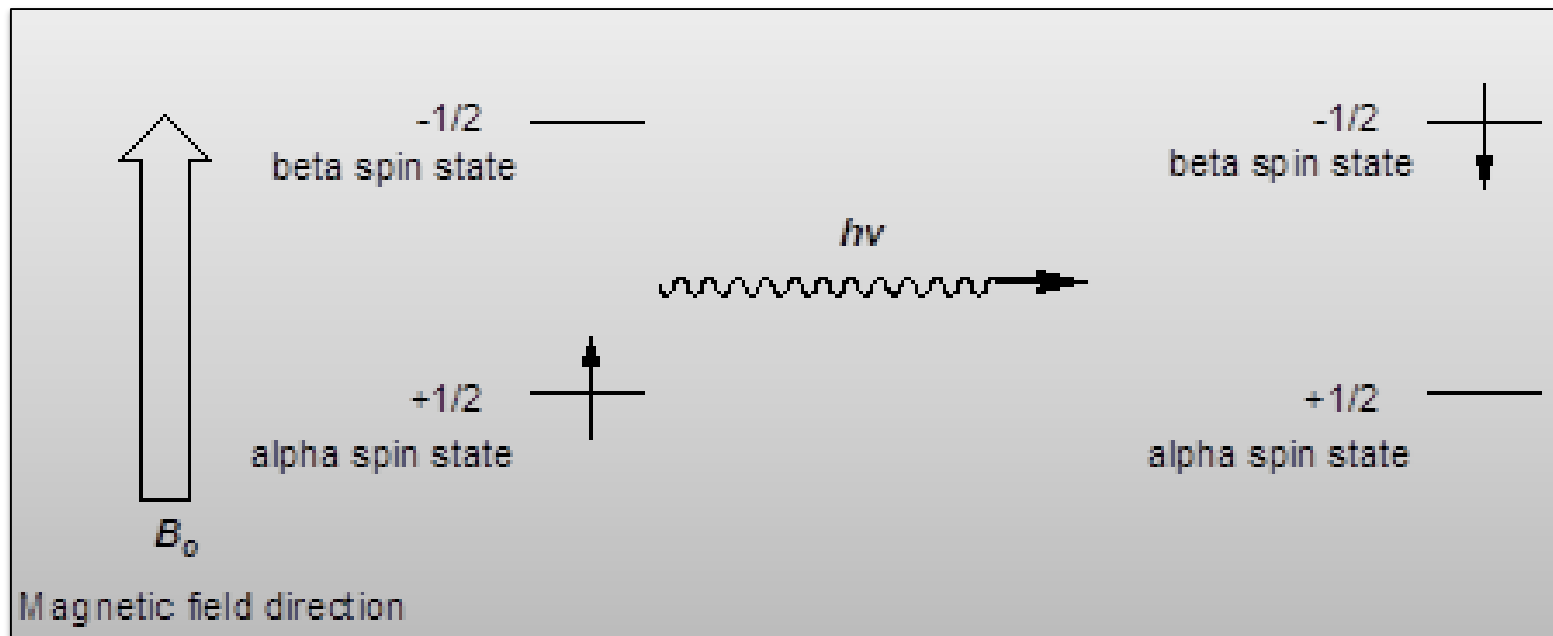
The NMR absorption process for a proton

➢ The energy absorption is a quantised process, and the energy absorbed (**ΔE**) must equal the energy difference between the two spin states

$$E_{absorbed} (\Delta E) = (E_{-1/2\ spin\ state} - E_{+1/2\ spin\ state}) = h\nu$$

➢ **ΔE** depends upon the strength of the external magnetic field B_0

➢ **The stronger the applied magnetic field B_0, the greater the energy difference (ΔE) between the two spin states**
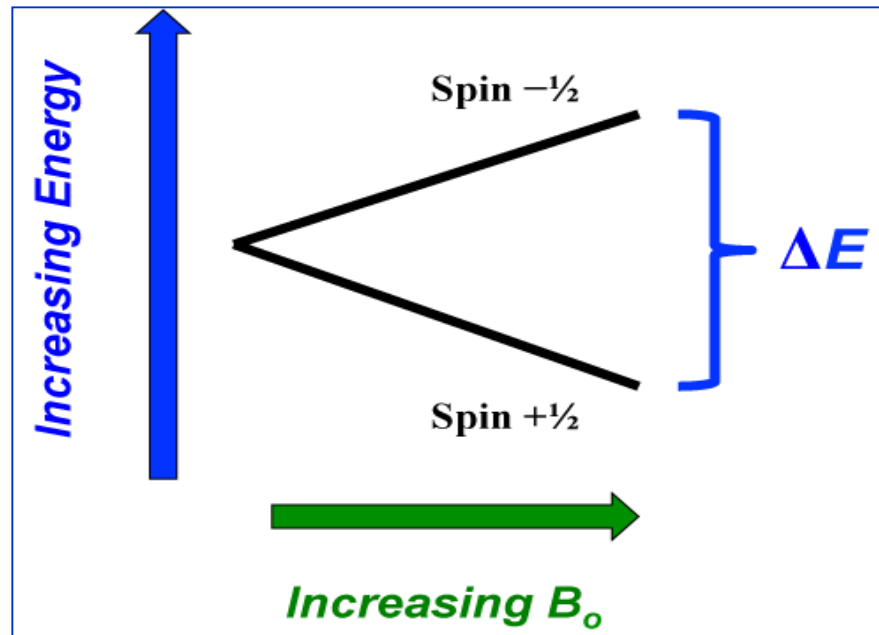
Spin state energy separation as a function of the strength of the applied magnetic field B_0

Frequencies and field strengths at which proton has its resonance
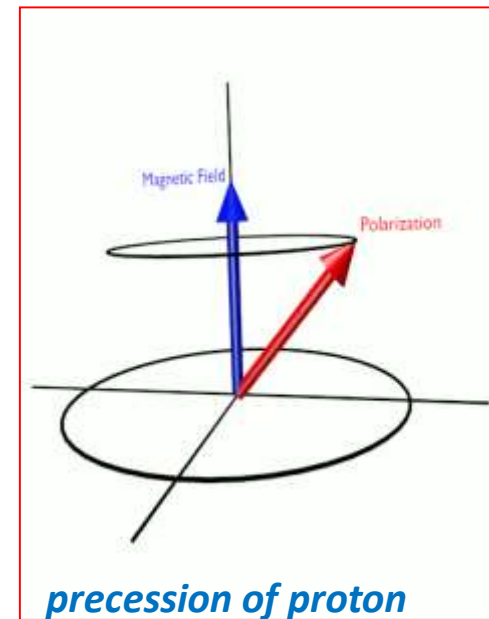
➤ For a proton, if the applied magnetic field B_0 has strength of approximately **1.41 Tesla**, the **difference in energy between the two spin states** (**+1/2 and -1/2**) of the proton is about **2.39 X 10^{-5} kJ/mole**

➤ This energy difference corresponds to the **energy of radiofrequency** (RF) or **radiowaves** of the electromagnetic spectrum

➤ **Radiowave** with a frequency of about **60 MHz** (M = mega = 10^6 or 60,000,000 Hz) is used if the applied magnetic field has strength of approximately **1.41 Tesla**

Nuclei	Field strength, B_0 (Tesla)	Frequency, v (MHz)
¹H (proton)	1.00	42.6
	1.41	60.0
	2.35	100.0
	4.70	200.0
	7.05	400.0
1 Tesla = 10,000 Gauss		

The mechanism of absorption of radiofrequency (resonance)

❖ To understand the nature of nuclear spin transition, the analogy of a **child's spinning top** is useful

❖ Under the influence of earth's gravitational field, the spinning top begins to precess about its axis

❖ Similarly, a **proton** begins to **precess** under the **influence** of an **applied magnetic field B_0.** This phenomenon is called ***precession***

precession of proton

precession of proton
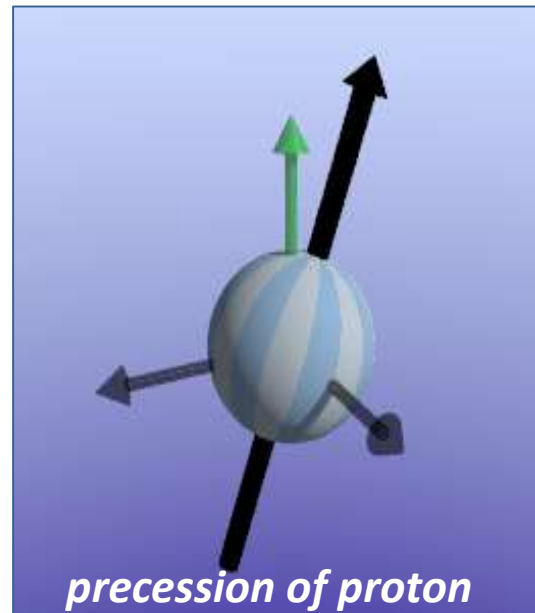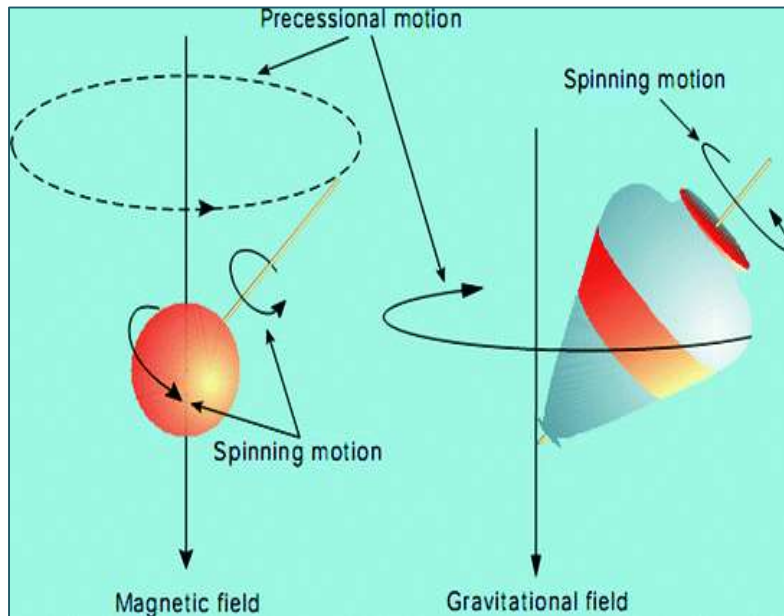
The precessional frequencies of a proton at different field strengths

- In the presence of an applied magnetic field B_0, the proton begins to **precess** about its own axis with **angular frequency ω** (omega)

- This frequency, at which a proton **precesses** is called '*precessional frequency*' or '*Larmor frequency*'

- **The precessional frequency of a proton is directly proportional to the strength of an applied field** *i.e., $\omega \propto B_0$*

- *The stronger the applied field, the higher the rate of precessional frequency (ω) of a proton*

Field strength, B_0 (Tesla)	Precession frequency, ω (MHz)
1.41	60.0
2.35	100.0
7.05	400.0
14.1	600.0

The mechanism of absorption of radiofrequency (resonance)

- Since the **proton** is **positively charged**, the precession generates both **magnetic field** and **electric field** of a particular **frequency**

- If the **radiofrequency waves** (**hv**) of this **frequency** are supplied to the **precessing proton**, the **energy** can be **absorbed**

- When the **frequency** of the oscillating electric field component of a **precessing proton matches** the **frequency** of the **oscillating electric field** component of the incoming **radiofrequency**, the two fields can **couple**

- **Energy** can be **transferred** from the incoming **radiation** to the **proton**, thus causing a **spin change** (+1/2 spin state to -1/2 spin state). This condition is called **resonance**
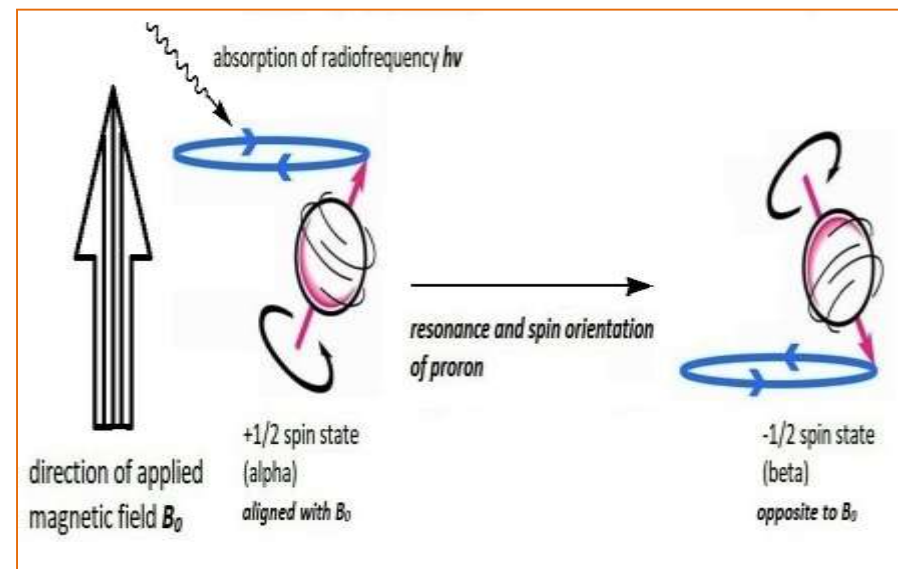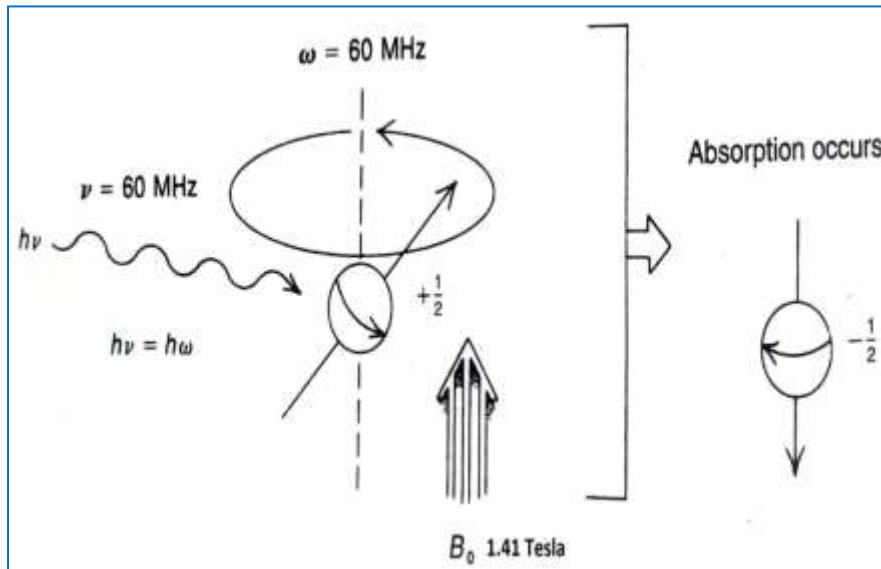
The nuclear magnetic resonance process; absorption occurs when v = ω

Population of nuclei in spin states

▪For a **proton**, if the **applied magnetic field** has a **strength** of **1.41 Tesla**, **resonance** occurs at about **60 MHz** of **radiofrequency**

▪Using $\Delta E = h\nu$, the difference in energy (ΔE) between the two spin states (+1/2 and -1/2) of the proton is found to be around 2.39 x 10^{-5} kJ/mole

▪Since this energy difference (ΔE) between the two levels is small, thermal energy resulting from room temperature is sufficient to populate both of these energy levels

▪However, there is a **slight excess of protons** in the **α-spin state** (**lower energy level**)

▪The **excess nuclei** are the ones that allow us to observe **resonance**

▪When the radiofrequency is applied, it not only induces transitions upward (from **α-spin state** to **β-spin sate**) but also stimulates transitions downward (from **β-spin state** to **α-spin state**)

▪The **population of spin states** is dependent on the **field strength B_o**

▪ **If the strength of applied magnetic field is increased, the energy difference between the two states also increases, which cause an increase in excess population**

Chemical shift and shielding

➢ For a magnetic field strength of **1.41 Tesla**, we have seen that protons have **precessional frequency** of approximately **60 MHz**

➢ However, the **pecessional frequency** of **all the protons** in the same external magnetic field is **not the same**

➢ The precession frequency of any proton depends on a number of factors and this was first observed by **J. T. Arnold**, **S. S. Dharmatti** and **M. E. Packard** in 1951

➢ They were able to detect **three different values** for the **precessional frequencies** of the protons in **ethanol** (CH_3, CH_2 and OH)

➢ These values corresponded to **three different chemical environments** for the protons in ethanol which marked the **beginning of NMR** as a tool of the **organic chemist**

➢ Because the **shift** in **precessional frequency** is **depended** on **chemical environment**, this gave rise to the term *chemical shift*

Chemical shift and shielding

✓ The **protons** in a molecule are **surrounded** by **electrons**

✓ The **valence shell electron densities** surrounding the proton **vary** from one proton to another in a molecule

✓ In an applied magnetic field B_0, the **valence electrons surrounding the protons** are caused to **circulate**

✓ Since **electrons** are **charged**, this circulation of electrons called a *local diamagnetic current* generates a *counter magnetic field* that *opposes the applied field B_0* (because any charged particle under motion generates electric and magnetic fields)

✓ Thus, the protons are *shielded* from the applied magnetic field B_0 by the *electrons* surrounding them. **Figure 9** illustrates this effect, which is called *diamagnetic shielding* or *diamagnetic anisotropy* (anisotropy = non uniform).
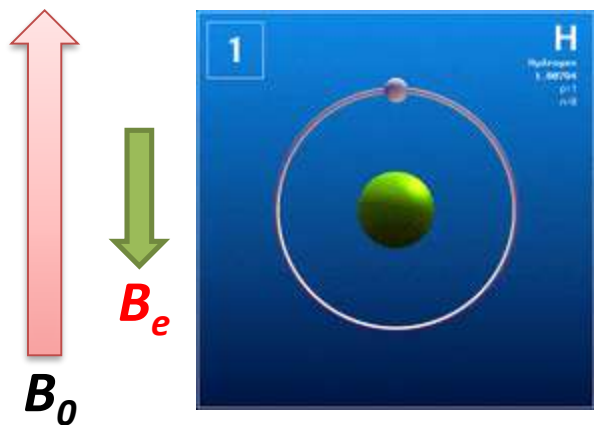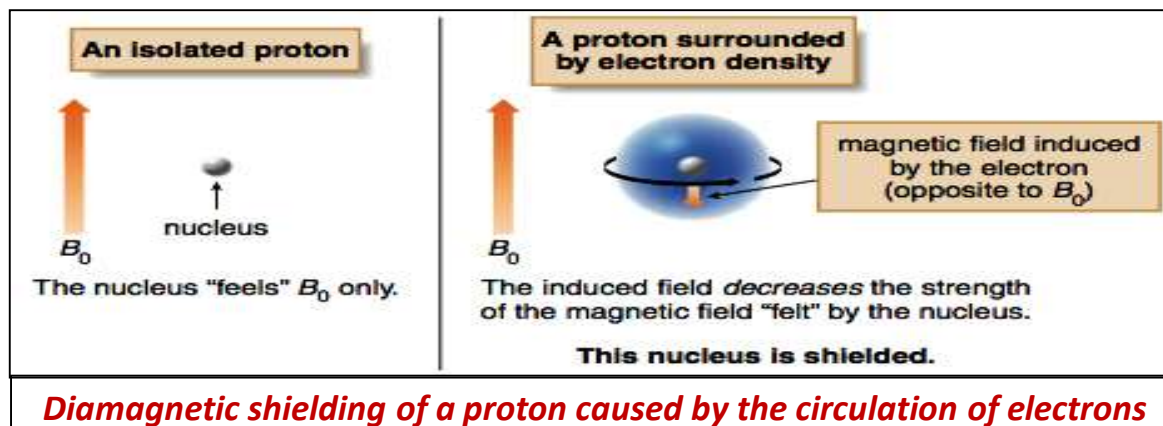

B_0 = Applied magnetic field

B_e = Magnetic field exhibited by the circulation of electron surrounding the proton

B_e opposes B_0

B_e shields the proton from the B_0

Chemical shift and shielding

An isolated proton	A proton surrounded by electron density
↑ nucleus B_0 The nucleus "feels" B_0 only.	magnetic field induced by the electron (opposite to B_0) B_0 The induced field *decreases* the strength of the magnetic field "felt" by the nucleus. **This nucleus is shielded.**

Diamagnetic shielding of a proton caused by the circulation of electrons

✓ The circulation of electrons called a local diamagnetic current generates a secondary, induced magnetic field B_e that opposes the applied magnetic field B_0

✓ The **shielding** from the **applied magnetic field** for **each proton** in a molecule **depends** on the **electron density** surrounding it

✓ *The greater the electron density around a proton, the greater the induced counter magnetic field B_e that opposes the applied field B_0*

✓ **The counter magnetic field B_e that shields a proton decreases the net applied magnetic field that the proton experiences. As a result, the proton precesses at a lower frequency**

✓ Each **proton** in a molecule is in a **slightly different chemical environment** (electron density around a proton) and consequently has a slightly different amount of electron shielding

✓ *Since each proton has different electron density, each proton experiences slightly difference in the B_0, hence each proton precesses at slightly different precessional frequency (ω) and each proton has its resonance at slightly different radiofrequency*

Precessional frequencies of the protons of ethanol at 1.41 T B_0 (60 MHz)

CH₃-CH₂-OH
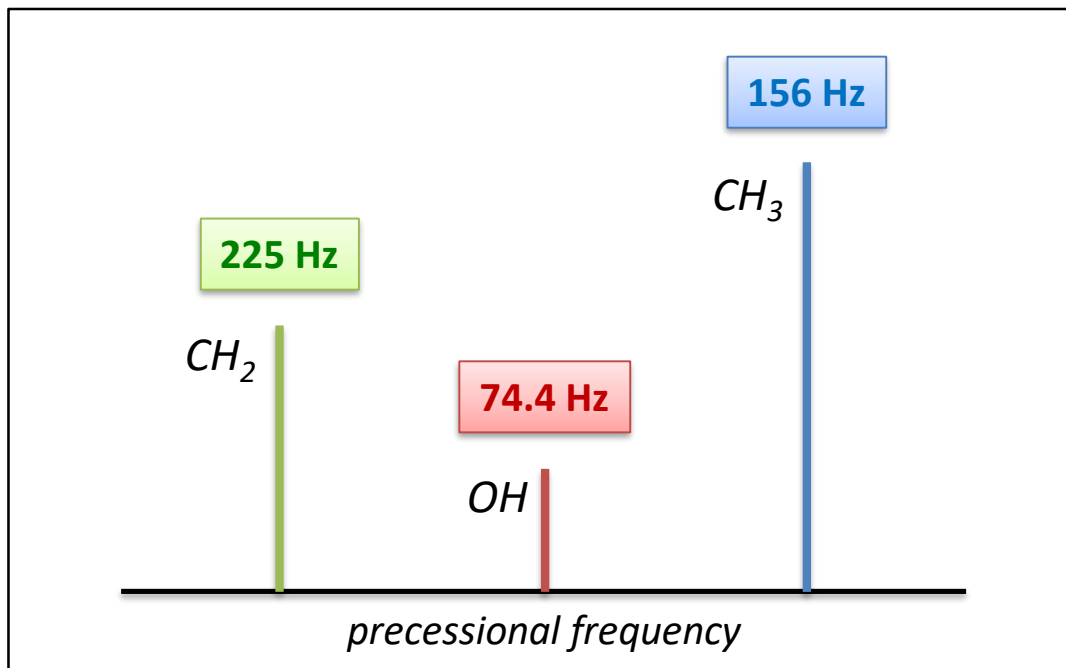
TMS (tetramethylsilane) as an internal standard

- In a molecule each proton has a different resonating frequency since each proton has a different chemical environment and has a different amount of electron shielding

- However, these differences in resonance are very small

- For example, the difference between the resonance frequencies of the protons in chloromethane (CH_3Cl) and those in fluoromethane ((CH_3F) is only 72 Hz when the applied field is 1.41 Tesla and the radiation used to induce spin transitions is of 60 MHz

- The difference between chloromethane and fluoromethane represents a change in frequency of only slightly more than one part per million (**ppm**) (1 ppm for 60 MHz = 60,000,000 Hz; 2 ppm for 60 Hz = 120,000,000 Hz)

- **It is very difficult to measure exact frequencies to that precision**

- Hence, no attempt is made to measure the exact resonance frequency of any proton

- Instead, a **reference compound** is used and the resonance frequency of each proton in a molecule is measured relative to the resonance of the protons of the reference compound.

- In other words, *frequency difference* is measured directly

➢ The standard reference compound that is used universally is **tetramethylsilane**, **(CH₃)₄Si**, also called **TMS**

➢ Thus, when an organic compound is measured, the resonances of its protons are reported in terms of how far (in Hz) they are shifted from those of TMS.

$$CH_3 \\ | \\ H_3C - Si - CH_3 \\ | \\ CH_3$$ tetramethylsilane (TMS)
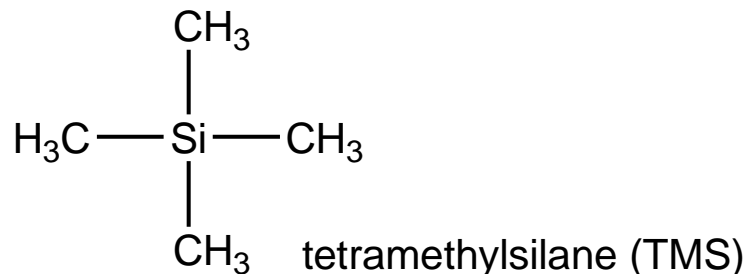
Advantages of TMS as an internal standard reference compound:

1) The protons of TMS are more shielded

2) TMS gives an intense sharp signal even at low concentrations (12 protons)

3) It is chemically inert and has a low boiling point, so that is easily removed from a recoverable sample

4) It is soluble in most organic solvents

➢ The shift form TMS for a given proton depends on the strength of the applied magnetic field

➢ In an applied magnetic field of 1.41 Tesla the resonance of a proton is approximately 60 MHz, whereas in an applied field of 2.35 Tesla the resonance appears to approximately 100 MHz

➢ This results in confusion for the workers trying to compare data if they have spectrometers that differ in the strength of the applied magnetic field

➢ This is overcome by a new parameter that is independent of field strength B_0

➢ It is determined by dividing the shift in Hz of a given proton by the frequency in MHz of the spectrometer with which the shift value was obtained

➢ In this manner, a field independent measure called the **chemical shift** (**δ** = *delta*) is obtained

$$\delta = \frac{\text{shift in Hz}}{\text{spectrometer frequency in MHz}}$$

Definition of chemical shift: The chemical shift in δ units is the amount by which a proton resonance is shifted from TMS, in parts per million (ppm), of the spectrometer's basic operating frequency

- Values of δ for a given proton are always the same irrespective of whether the measurement was made at 60 MHz (1.41 Tesla) or at 100 MHz (2.35 Tesla)

- For example, at 60 MHz the shift of the protons in CH_3Br is 162 Hz from TMS, while at 100 MHz the shift is 270 MHz. However, both of these correspond to the same value of δ i.e., **2.70 ppm**;

$$\delta = \frac{162\ Hz}{60\ MHz} = \frac{270\ Hz}{100\ MHz} = 2.70\ ppm$$

- Most of the workers report chemical shifts in **delta (δ) units** or **parts per million (ppm)**, of the main spectrometer frequency. On this scale, the resonance of the protons in TMS comes at exactly 0.00 ppm

- The NMR spectrometer actually scans from high δ values to low ones. **Figure 10** is the typical chemical shift scale with the sequence of δ values that would be found on a typical NMR spectrum.

Direction of scan ⇒   TMS

12 11   10   9   8   7   6   5   4.   3   2   1   0 δ scale
   (ppm)
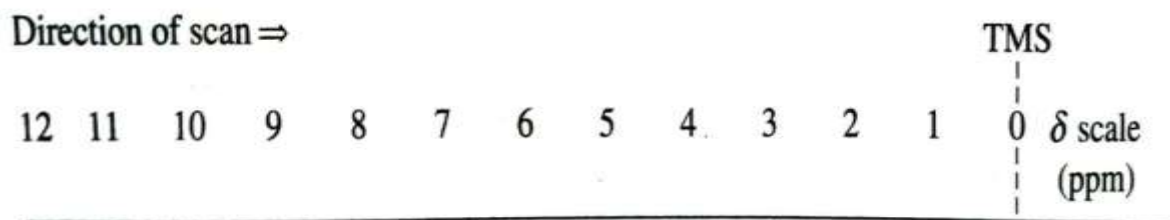
A typical NMR spectrum

Chemical equivalence

➢ All the protons found in chemically identical environments within a molecule are **chemically equivalent**, and they often exhibit the same chemical shift

➢ Thus, all the protons in TMS or all the protons in benzene, cyclopentane or acetone have protons that are equivalent and have resonance at a single value of $\boldsymbol{\delta}$

➢ Each such compound gives rise to a single absorption peak (signal) in its NMR spectrum. Such protons are said to be chemically equivalent

➢ Whereas, a molecule that has different sets of protons that are chemically distinct from one another may give rise to a different absorption peak from each set, in which case the different sets of protons are chemically non-equivalent

➢ The following examples show the number of sets of chemically equivalent and non-equivalent protons and number of NMR absorption peaks (signals)
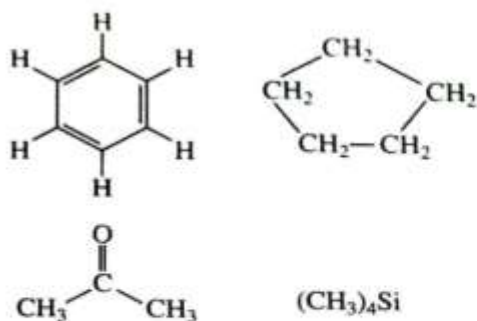
Molecules giving rise to one NMR absorption peak—all protons chemically equivalent
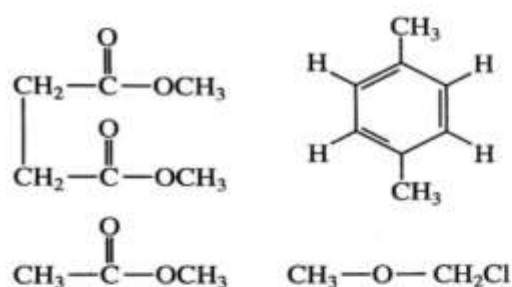
Molecules giving rise to two NMR absorption peaks—two different sets of chemically equivalent protons
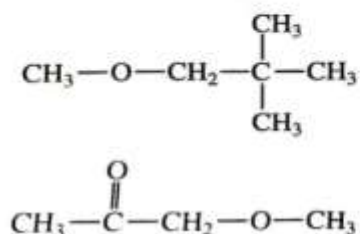
Molecules giving rise to three NMR absorption peaks—three different sets of chemically equivalent protons
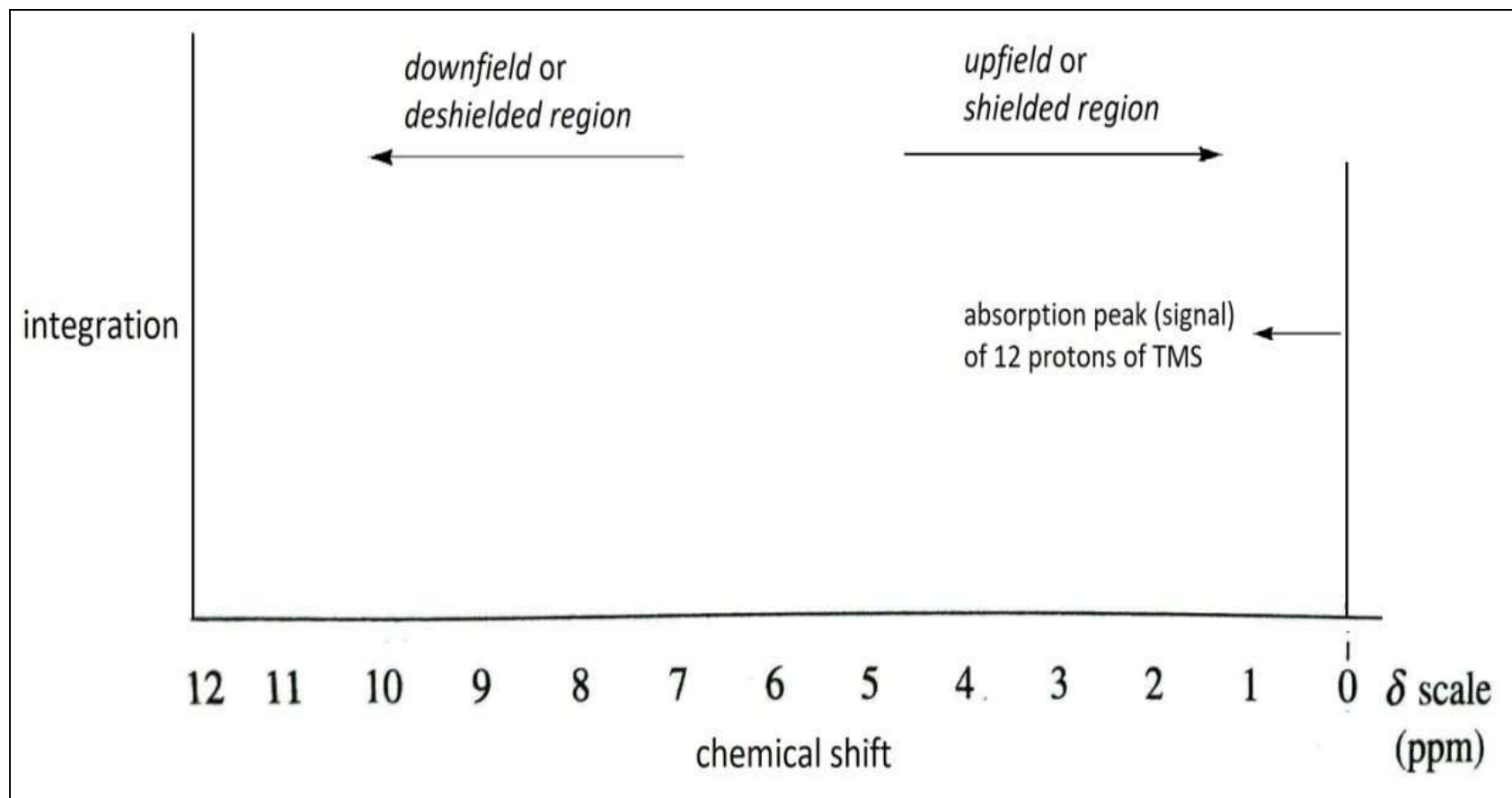
On the basis of chemical equivalence, we can see that, NMR spectrum furnishes valuable information regarding the number of different sets of protons present in a molecule

Reference: Pavia, Lampman, Kriz and Vyvyan

Intensity (height) of the signal or integration

- The NMR spectrum not only distinguishes how many different types of protons a molecule has, but also reveals how many of each type are contained within the molecule

- In the NMR spectrum, **the area under each peak is proportional to the number of hydrogens (protons) generating that peak**

NMR spectrum

- *It is the plot of chemical shift in δ units or ppm against integration of the absorption peaks (signals)*

- For hydrogen nucleus, the NMR spectrum ranges from 0 ppm to 12 ppm

- The NMR spectrum starts from the right side at 0 ppm, the signal for TMS (internal standard)

- The right part of the NMR spectrum is called '*upfield region*' or '*shielded region*' because the protons in this range are greatly shielded which experiences lesser applied magnetic field strength B_0 and precesses at lower frequency

- As a result of which the protons in this range requires increased field strength B_0 to come into resonance.

- The left part of the NMR spectrum is called '*downfield region*' or '*deshielded region*' because the protons in this range are less shielded which experiences greater applied magnetic field strength B_0 and precesses at higher frequency. As a result of which the protons in this range requires less field strength B_0 to come into resonance

downfield or
deshielded region

upfield or
shielded region

integration

absorption peak (signal)
of 12 protons of TMS

12 11   10   9   8   7   6   5   4.   3   2   1   0 δ scale
(ppm)

chemical shift

The ^{1}H NMR spectrum

Reference: Pavia, Lampman, Kriz and Vyvyan

Nuclear shielding and deshielding

✓ If the resonance frequencies of all protons in a molecule were the same, NMR would be of little use to the organic chemist

✓ The protons in the molecule will have different resonance frequencies (chemical shifts) due to **nuclear shielding and deshielding** effects

✓ Not only do different types of protons have different chemical shifts, buy each also has a characteristic value of chemical shift

Factors influencing chemical shift

1) Electronegativity effects

2) Hybridization effects

3) Magnetic anisotropy or diamagnetic anisotropy

1) Electronegativity effects:

- The chemical shift increases as the electronegativity of the attached element increases
- Electronegativity is a tendency of atom to pull the bonding electrons toward it

- Previously, you have studied that the electrons around the proton shield it from the applied magnetic field B_0

- **The shielding of a proton depends on the electron density surrounding it. The greater the electron density around a proton, the greater the proton is shielded.**

- Electronegative substituents on the carbon reduce the shielding effect in the vicinity of the attached protons because electronegative substituents reduce the electron density around the protons

- As a result of which such protons will experience greater magnetic field and have high precessional frequency, and show resonance at higher δ values

electronegativity effects continued.....

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ	4.26	3.40	3.05	2.68	2.16	0.23	0

- For example, in case of methyl haides (CH_3F, CH_3Cl, CH_3Br and CH_3I), fluorine is more electronegative compared to other halogens

- Hence, the protons in CH_3F are more deshielded which show higher **δ** values

- Compared to fluorine, iodine is less electronegative, hence the protons in CH_3I are shielded and show lower **δ** values

- In case of TMS silicon is electropositive i.e., it donates electrons to the carbon of methyl group

- Hence, the protons in TMS are greatly shielded and show resonance at very low **δ** values

2) Hybridization effects:

- The chemical shift is also dependent on the hybridization of the carbon to which hydrogen is attached

- As the **s** character in the hybridization increases, electronegativity of the carbon atom also increases

$$sp^3 \quad < \quad sp^2 \quad < \quad sp$$

Increasing electronegativity
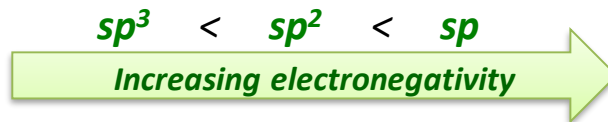
(i) sp³ hydrogens (alkanes):

- All the hydrogens attached to purely sp^3 carbon atoms ($C-CH_3$, $C-CH_2-C$) have resonance in the range from 1-2 ppm provided no electronegative elements are nearby

(ii) sp² hydrogens (alkenes):

- Simple vinyl hydrogens (-C=C-H) have resonance in the range from 4.5 to 7 ppm

- Since **sp²** hybridized carbon is more electronegative than **sp³** hybridized carbon, vinyl hydrogens have a greater chemical shift than aliphatic hydrogens on **sp³** carbons

- Aromatic hydrogens (attached to **sp²** hybridized carbon) appear in a range further downfield around 7 to 8 ppm.

- The downfield shift of vinyl and aromatic protons are however, greater than one would expect based on the hybridization effects

- Another effect, called **anisotropy**, is responsible for the largest part of these shifts

- Aldehyde proton which is also attached to the **sp²** hybridized carbon show chemical shift even downfield around 9 to 10 ppm. This shift is again due to **anisotropy**

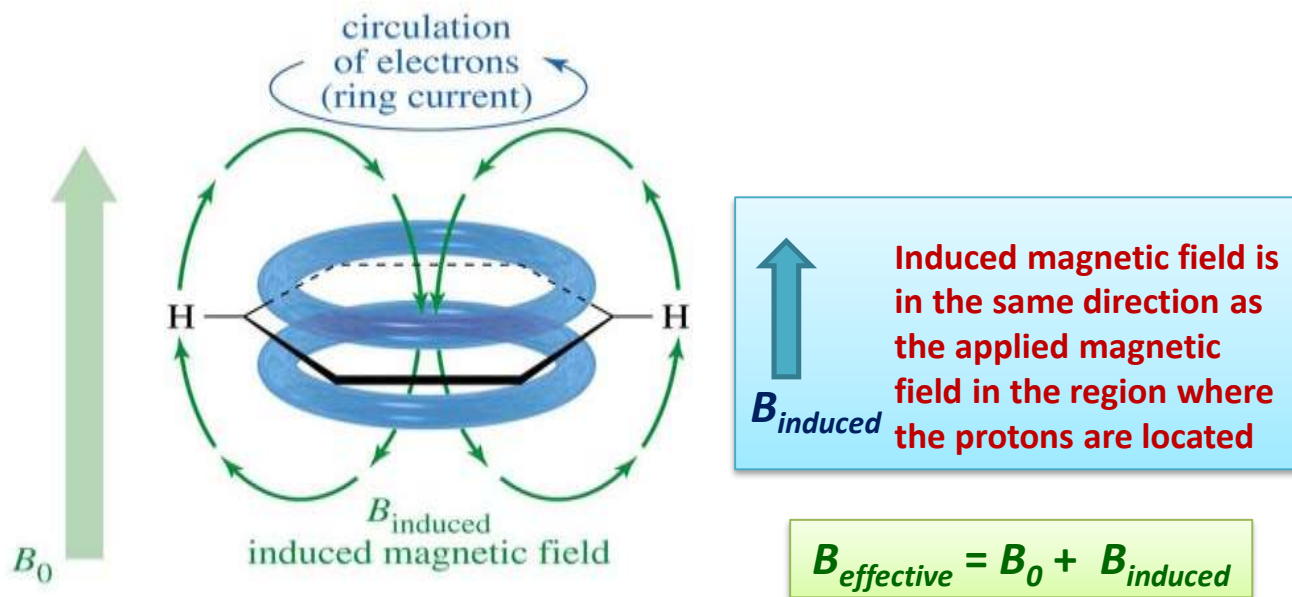**(iii)** *sp hydrogens (alkynes):*

- Acetylene protons (-C≡C-H) appear surprisingly at 2 to 3 ppm

- On the basis of hybridization, one would expect the acetylenic proton to have a chemical shift greater than that of the vinylic proton, because *sp* carbon is more electronegative than *sp²* carbon

- But this is the opposite of what is actually observed due to **anisotropy**

3) Magnetic anisotropy or diamagnetic anisotropy:

- The anomalous (unexpected) values for the protons of alkenes, aromatic, aldehyde and acetylene can be explained on the basis of magnetic anisotropy

- Magnetic anisotropy – non-uniform magnetic moment

- That is, in one direction the magnetic moment (**generated by the circulation electrons**) is aligned to the applied magnetic field B_0 and in other direction it is opposite

- In case of alkenes, benzene, aldehyde and acetylene, each of these compounds have π-electrons in the vicinity (nearby) of the proton in question

(a) Benzene:

- When it is placed in the applied magnetic field, the π-electrons in the benzene ring are induced to circulate around the ring.

- This circulation is called a ring current

- The moving π-electrons generate a magnetic field called **diamagnetic anisotropy**

- This induced magnetic field is said to be aligned with the applied magnetic field B_0

- The benzene protons (hydrogens) lie in this deshielding zone and are said to be deshielded by this magnetic anisotropy
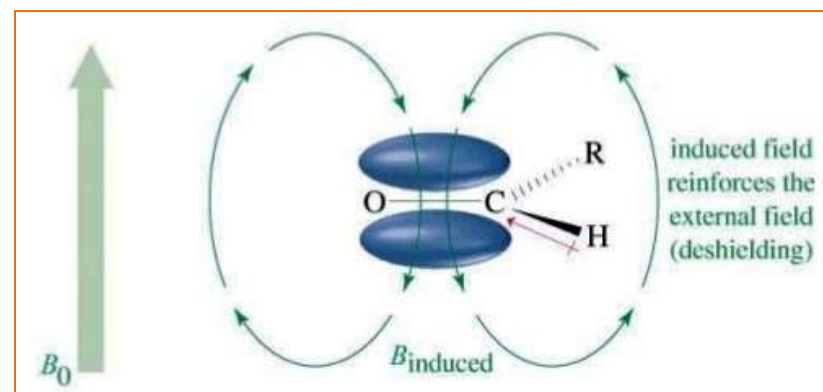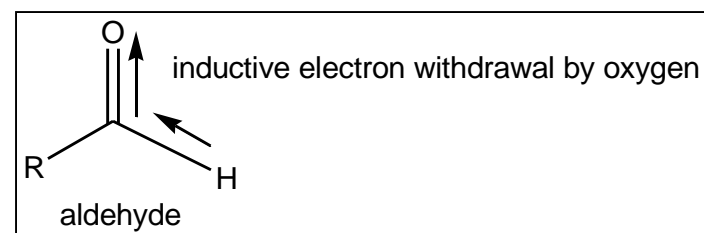

circulation of electrons (ring current)

$B_{induced}$
induced magnetic field

B_0

$B_{induced}$

Induced magnetic field is in the same direction as the applied magnetic field in the region where the protons are located

$$B_{effective} = B_0 + B_{induced}$$

(b) Alkenes and aldehydes:

- In presence of an applied magnetic field, the π-electrons are induced to circulate which generates an induced magnetic field called diamagnetic anisotropy

- The protons of alkene and aldehyde fall in the deshielding zone and are said to be deshielded protons

- Hence alkene show downfield shifts around 4.5 to 7 ppm

- Whereas, aldehydic proton appears even far downfield (9 to 10 ppm) than alkene and aromatic protons, because of carbonyl group which has electronegative oxygen atom that will pull the bonding electrons and make lesser electron density around this proton
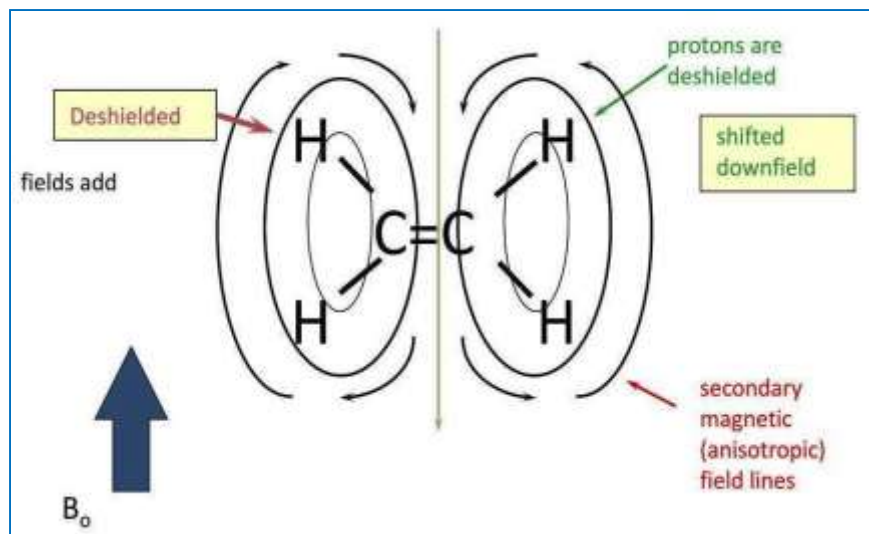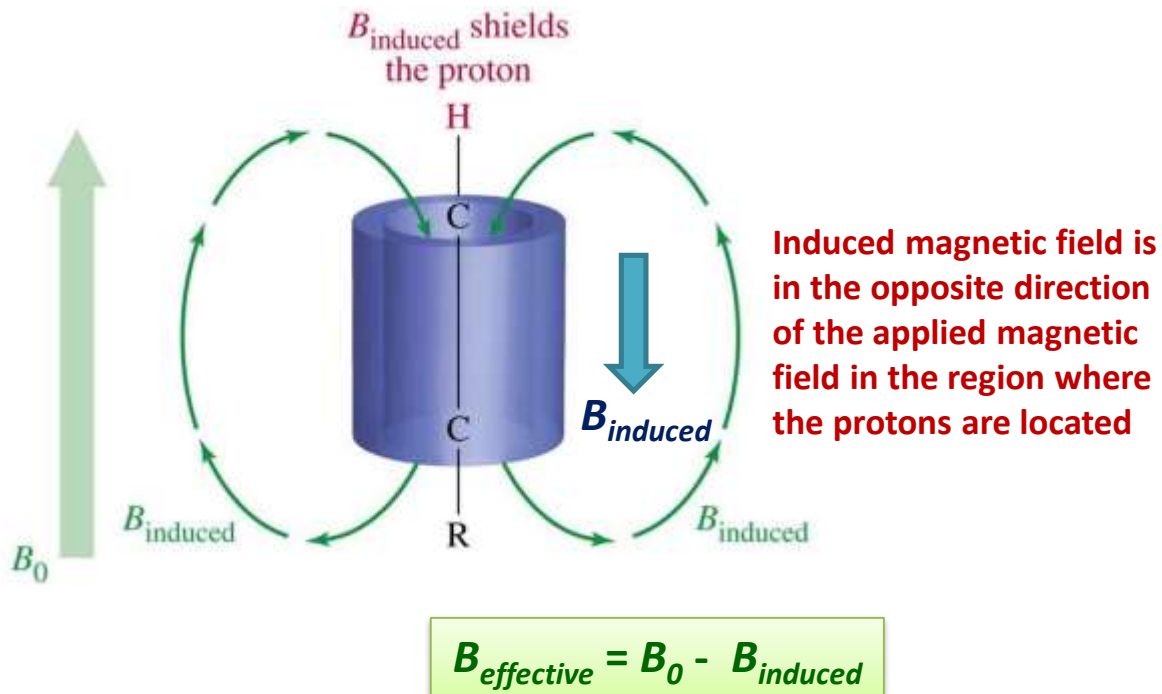

$$B_{effective} = B_0 + B_{induced}$$

(c) Alkynes:

- In acetylene, the magnetic field generated by induced circulation of π-electrons has geometry such that the acetylenic hydrogens are shielded

$B_{induced}$ shields
the proton

Induced magnetic field is in the opposite direction of the applied magnetic field in the region where the protons are located

$$B_{effective} = B_0 - B_{induced}$$

The shielding and deshielding regions due to the presence of π-electrons have characteristics shapes and directions

**benzene**   **alkene**   **aldehyde**   **acetylene**
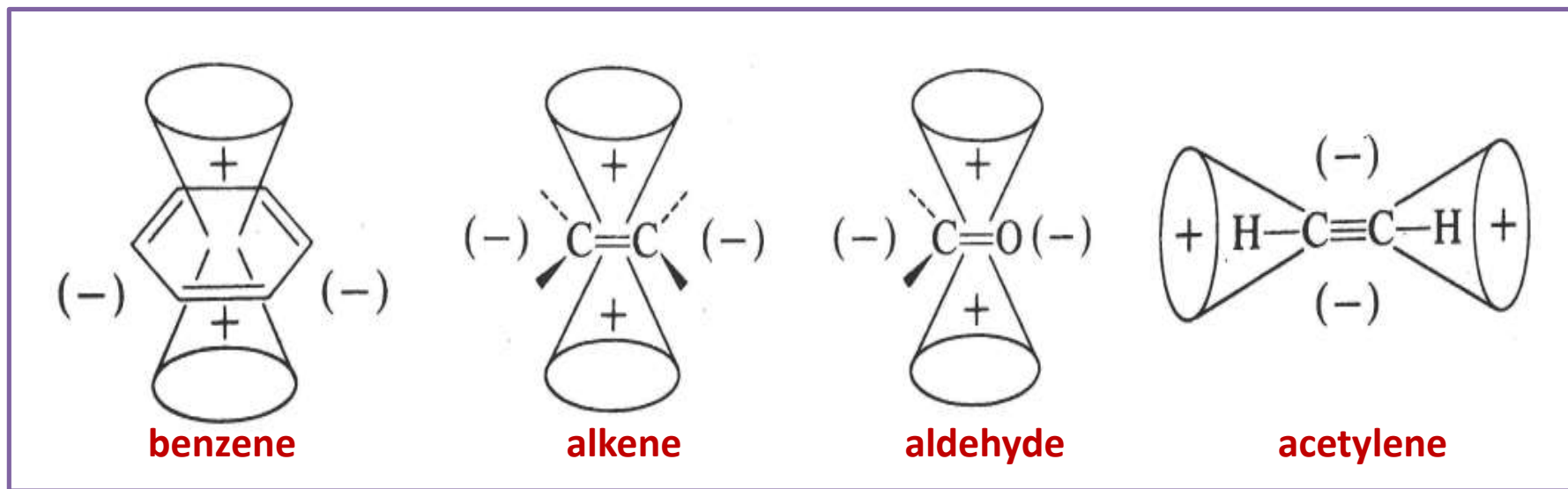
Anisotropy caused by the presence of the π-electrons

Shielding (+) and deshielding regions (-)

Reference: Pavia, Lampman, Kriz and Vyvyan

Spin-spin coupling **(n+1)** rule / spin-spin splitting

- The chemical shift and integration (peak area) can give information about the number and types of hydrogens contained in a molecule

- A third type of information to be found in the NMR spectrum is derived from spin-spin coupling phenomenon

- Even in simple molecules, one finds that each type of proton rarely gives a single resonance peak

- The NMR spectrum of 1,1,2-tribromoethane shows two peaks as it has two chemically distinct types of hydrogens

$$H_a \quad H_b$$

$$Br - C - C - Br$$

$$Br \quad H_b$$
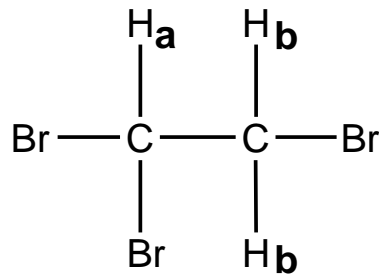
1,1,2-tribromoethane

- 1,1,2-Tribromoethane has two sets of protons, H_a and H_b

- From our previous studies information, one would predict two absorption peaks (two signals) in the NMR spectrum (one signal for H_a and the other for H_b protons)

- However, 1,1,2-tribromoethane shows five absorption peaks: a group of three peaks (called a **triplet**) at 5.78 ppm and a group of two peaks (called a **doublet**) at 4.15 ppm

- The **methine** (**CH**) resonance is said to be split into a **triplet**, and the **methylene** (**CH$_2$**) resonance is said to be split into a **doublet**

- The integration of triplet and doublet peaks is 1:2
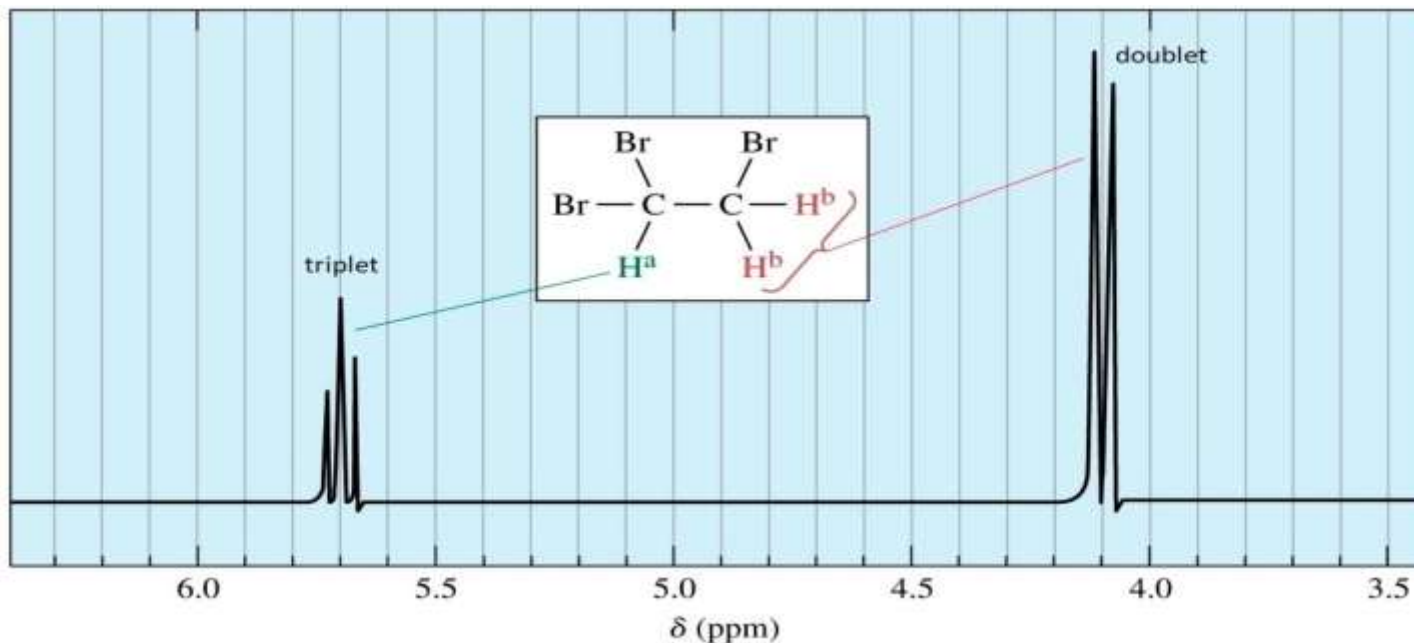
- This phenomenon of splitting the signals is called **spin-spin coupling**, which can be explained by $n + 1$ **rule**

- Where, 'n' is number of equivalent protons on the adjacent carbon atom(s)

- The absorption peak of a proton splits into $n + 1$ components
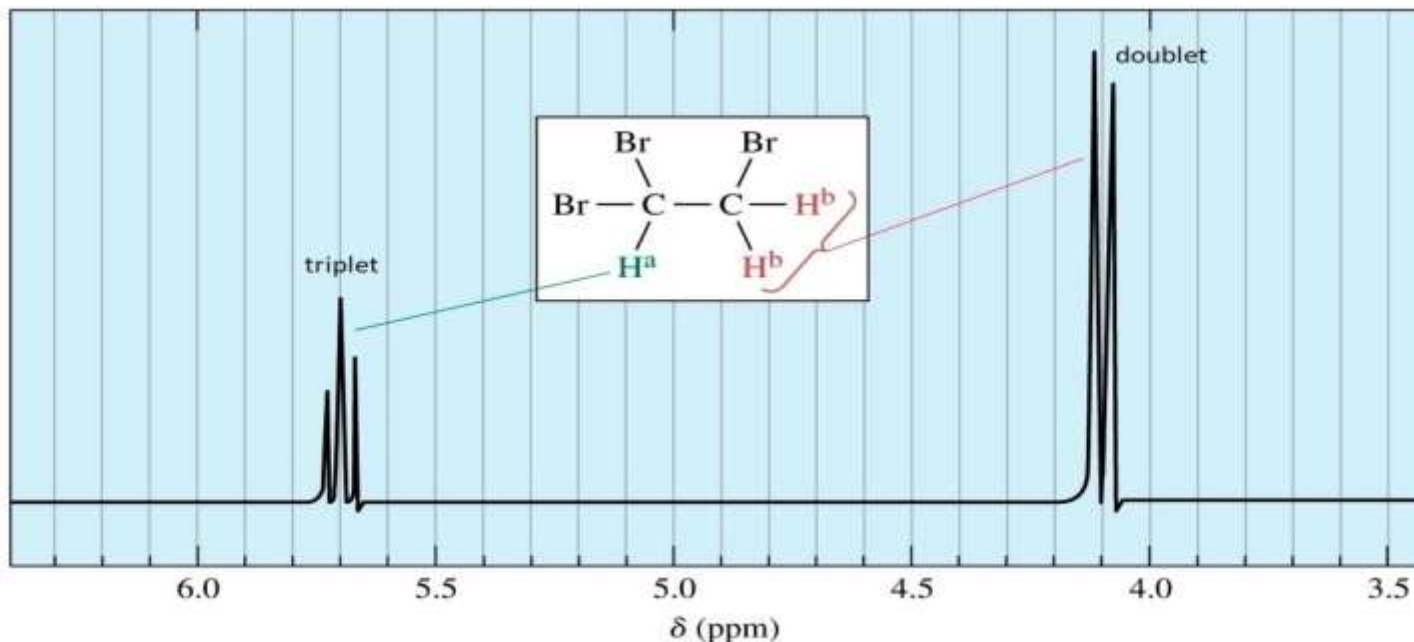
The signal for methine proton (-CH$_a$) splits into three signals at 5.7 δ ppm – triplet

n + 1 rule, 2 (H$_b$) + 1 = 3

The signal for methylene protons (-CH$_{2b}$) splits into two signals at 4.1 δ ppm – doublet
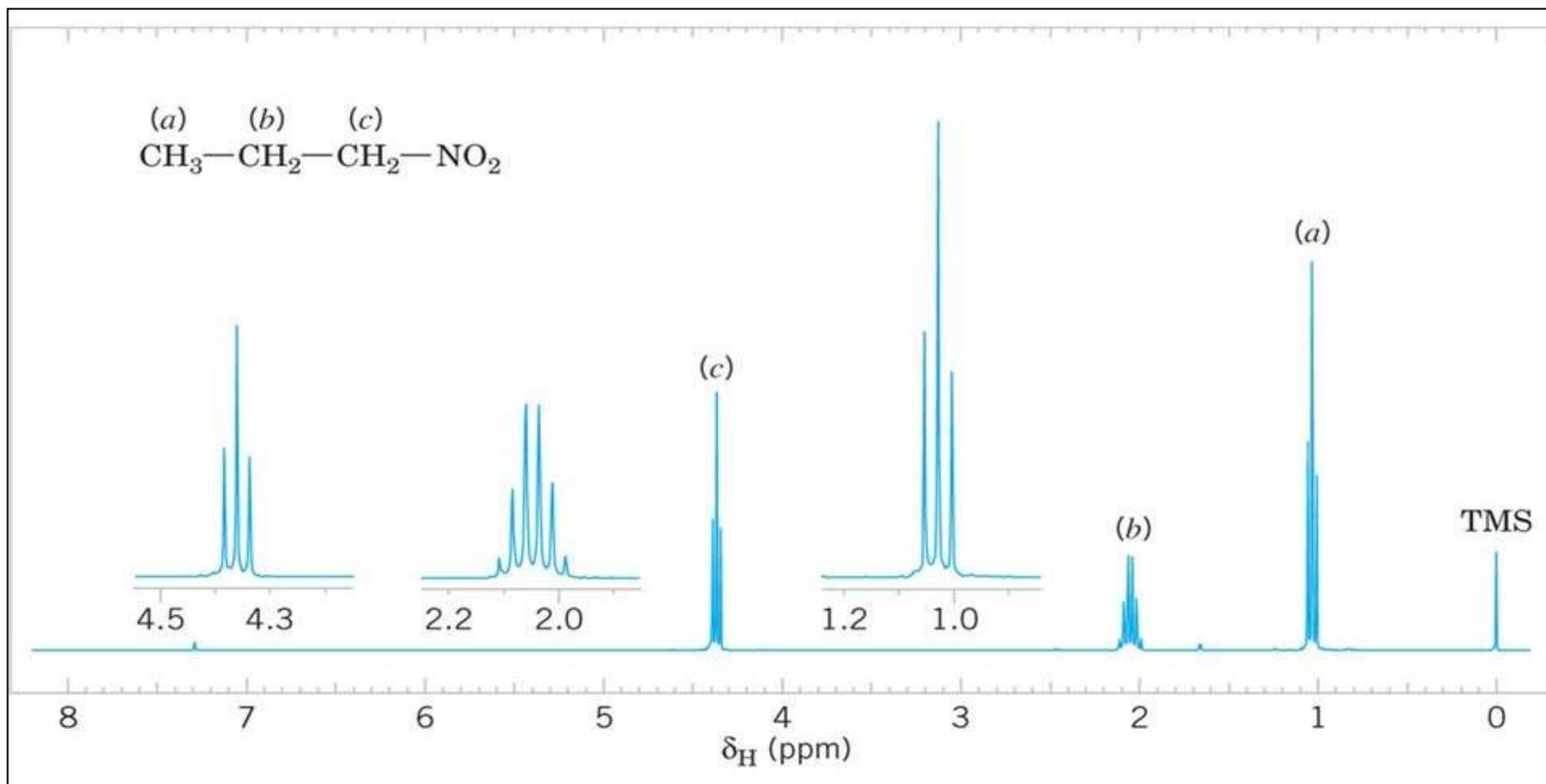
n + 1 rule, 1 (H$_a$) + 1 = 2

NMR spectrum of ethyl bromide (CH_3CH_2Br)

ethyl bromide

$$\overset{a}{CH_3}\overset{b}{CH_2}\text{-Br}$$

a   triplet 3H
b   quartet 2H

HSP-00-768

ppm
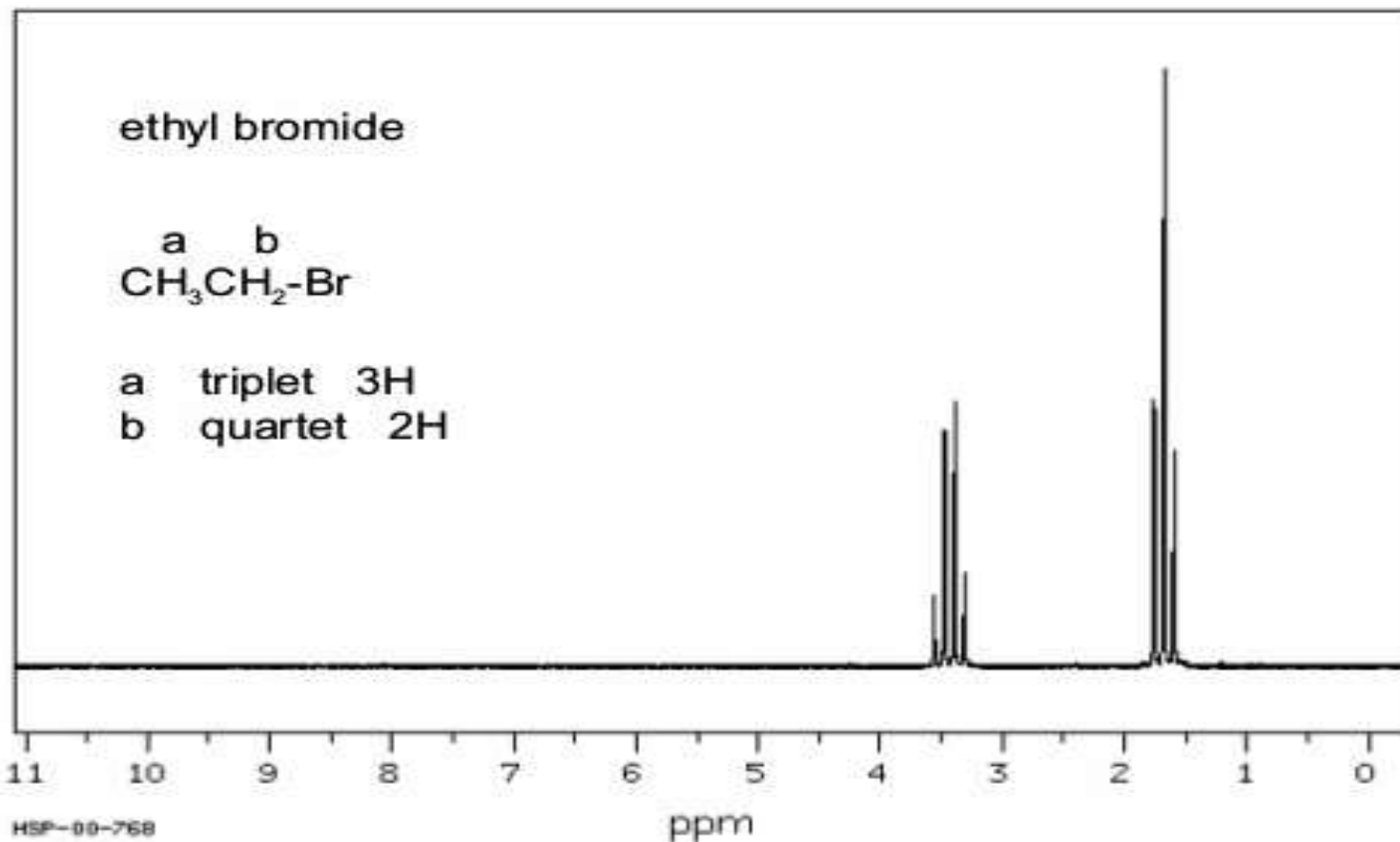
The signal for methyl protons (-CH_{3a}) splits into three signals at 1.6 δ ppm – triplet

n + 1 rule, 2 (H_b) + 1 = 3

The signal for methylene protons (-CH_{2b}) splits into four signals at 3.4 δ ppm – quartet

n + 1 rule, 3 (H_a) + 1 = 4

# NMR spectrum of 1-nitropropane ($CH_3CH_2CH_2NO_2$)

The signal for methyl protons (-CH_{3a}) splits into three signals at 1.0 δ ppm – triplet
n + 1 rule, 2 (H_b) + 1 = 3

The signal for methylene protons (-CH_{2b}) splits into six signals at 2.1 δ ppm – sextet (multiplet)
n + 1 rule, 5 (3H_a & 2H_c) + 1 = 6

The signal for methylene protons (-CH_{2c}) splits into three signals at 4.4 δ ppm – triplet
n + 1 rule, 2 (2H_b) + 1 = 3

NMR spectrum of 2-chloropropane $(CH_3)_2CHCl$
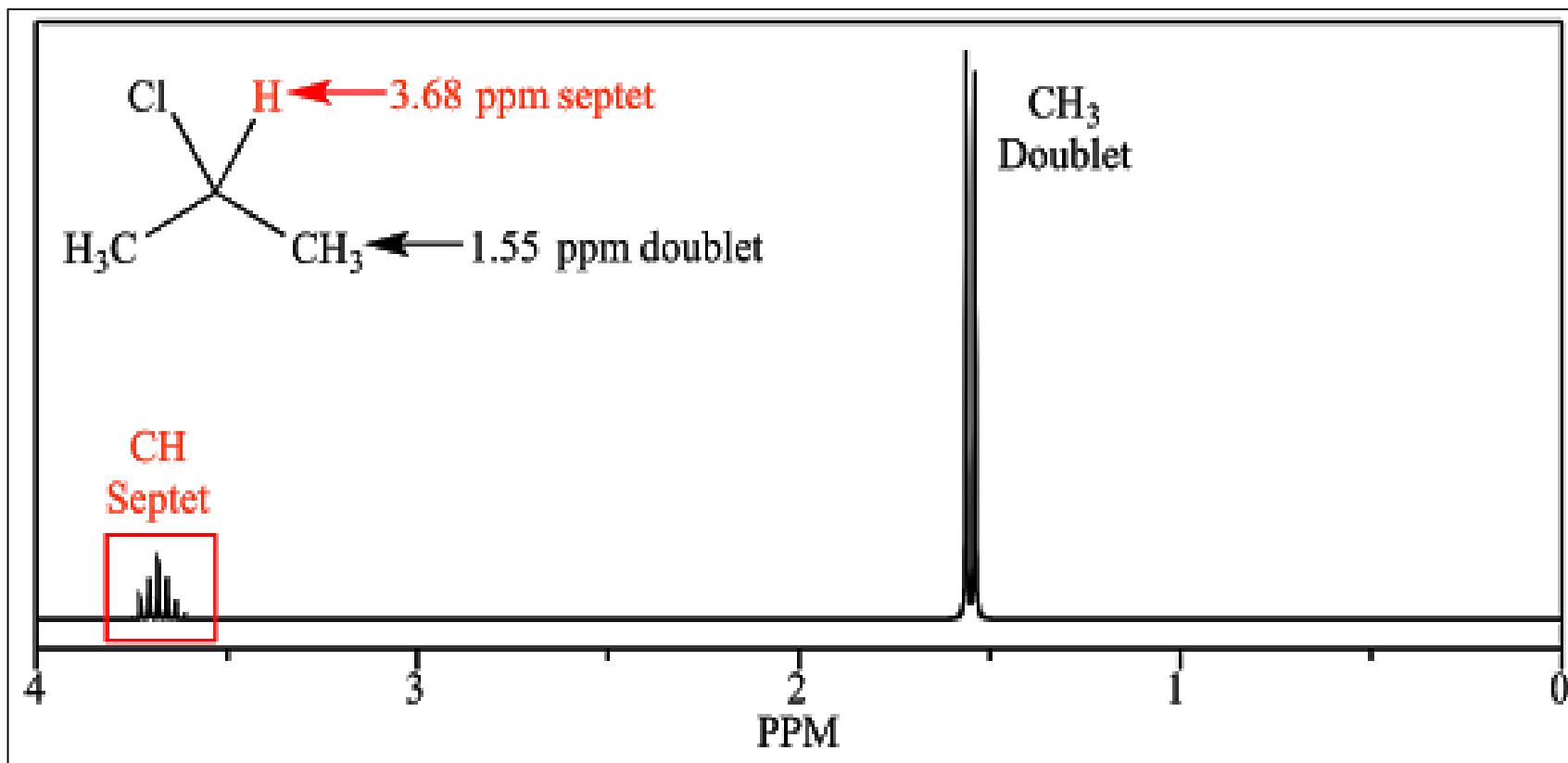
The signal for two sets of methyl protons (6H) splits into two signals at 1.5 δ ppm – doublet
n + 1 rule, 2 (CH)+ 1 = 3

The signal for methine protons (1H) splits into seven signals at 3.7 δ ppm – septet (multiplet)
n + 1 rule, 6 ($2CH_3$) + 1 = 7

Examples of splitting patterns in some compounds

Spin multiplicity


No. of protons on the adjacent carbon(s) 'n'	Splitting (no. of absorption peaks) '(n + 1) rule'	Name (spin multiplicity)
0	1	Singlet (s)
1	2	Doublet (d)
2	3	Triplet (t)
3	4	Quartet (q)
4	5	Quintet or multiplet (m)
5	6	Sextet or multiplet (m)
6	7	Septet or multiplet (m)

Reference: Pavia, Lampman, Kriz and Vyvyan

Origin of spin-spin coupling

- Spin-spin coupling arises because hydrogens on adjacent carbon atoms can "sense" one another

$$
\begin{array}{ccc}
\text{H}_\text{A} & & \text{H}_\text{X} \\
| & & | \\
-\text{C} & - & \text{C}- \\
| & & |
\end{array}
$$
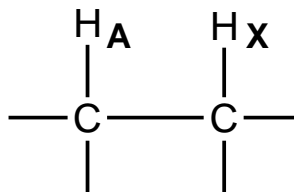
- The resonance position for H_A proton depends on its total magnetic environment;

(i) part of its magnetic environment is the nearby proton H_X, which is itself magnetic, and

(ii) the proton H_X can have its nuclear magnetic field **aligned with** proton H_A or **opposed to** proton H_A

- Thus, the net magnetic field experienced by proton H_A can either increase when H_X magnetic field is aligned or decrease when H_X magnetic field is opposed

- The two spin orientations of H_X create two different magnetic fields around proton H_A

- In roughly half of the molecules the spin orientation of H_X creates a shielding field (when H_X magnetic field is opposite to B_0) around proton H_A, and

- In the other half a deshielding field (when H_X magnetic field is aligned with B_0)

- Therefore, proton H_A comes to resonance, not once, but twice, and proton H_A gives rise to a doublet

- Similarly, proton H_A also generates its own magnetic field having two spin orientations with respect to H_X

- Either aligned or opposed to applied magnetic field B_0

- Hence, H_A creates two magnetic fields around H_X

- Therefore, proton H_X comes to resonance twice and gives rise to a doublet

Schematic representation of spin-spin coupling of protons H$_A$ and H$_X$

H_X magnetic field is **alligned with B$_0$**
H_A experiences increased magnetic field (deshielding effect)

H_X magnetic field is **opposed to B$_0$**
H_A experiences decreased magnetic field (shielding effect)

H$_X$ **H$_A$**   **H$_X$**   **H$_A$**

direction of applied magnetic field **B$_0$**

H_A magnetic field is **alligned with B$_0$**
H_X experiences increased magnetic field (deshielding effect)

H_A magnetic field is **opposed to B$_0$**
H_X experiences decreased magnetic field (shielding effect)

H$_A$ **H$_X$**   **H$_A$**   **H$_X$**

direction of applied magnetic field **B$_0$**

H$_X$
splits as doublet

H$_A$
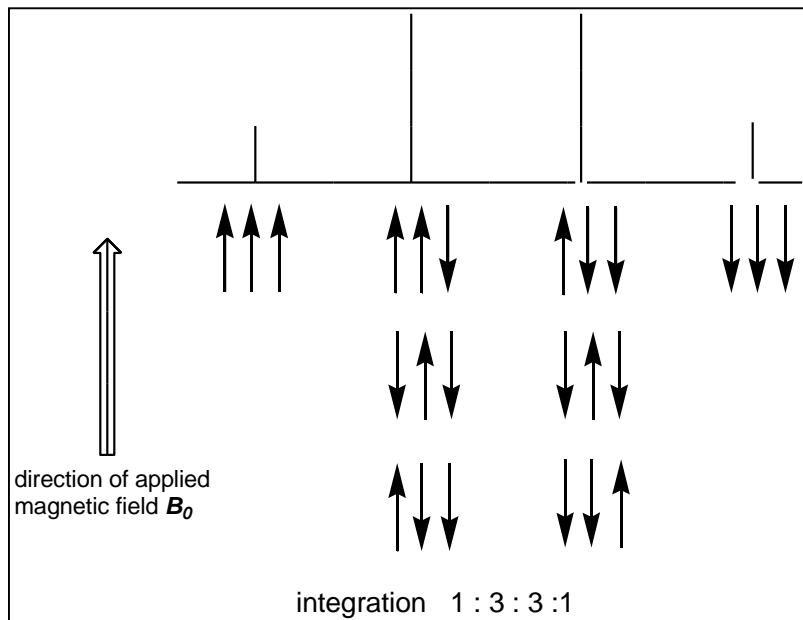splits as doublet

integration   1 : 1

# Spin-spin coupling in ethyl group (CH$_3$-CH$_2$-)

Ethylbromide shows two absorption peaks; a quartet at 3.52 ppm for methylene protons, and a triplet at 1.75 ppm for methyl protons
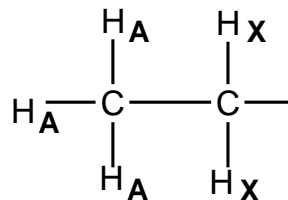
Possible spin orientations of methyl protons (H$_A$) with respect to methylene protons (H$_X$)

direction of applied magnetic field B_0

integration   1 : 3 : 3 : 1

Possible spin orientations of methylene protons (H$_X$) with respect to methyl protons (H$_A$)

direction of applied magnetic field B_0
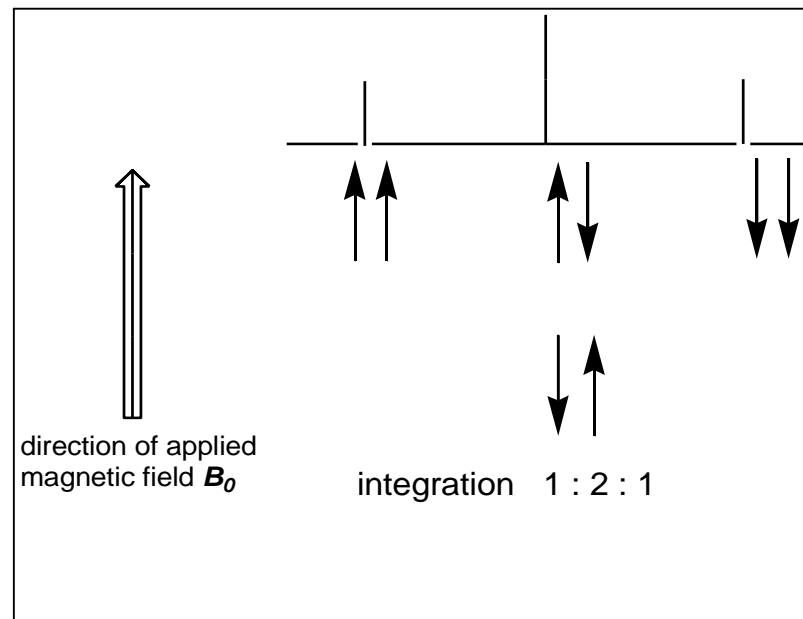
integration   1 : 2 : 1

One can easily identify the intensity ratios (integration) of the absorption peaks from

Pascal's triangle

Singlet					1			
Doublet				1		1		
Triplet				1	2	1		
Quartet			1	3		3	1	
Quintet			1	4	6	4	1	
Sextet		1	5	10	10	5	1	
Septet	1	6	15	20	15	6	1	

Interpretation of NMR spectra of simple organic molecules

NMR instrument (NMR spectrometer)

1) Ethylbromide: CH_3-CH_2-Br

CH₃CH₂Br

Ethyl bromide has two types of hydrogen.
The downfield peak at about 3.5 ppm is the
CH₂ deshielded by the Br and appears as
quartet due to the adjacent methyl group (n=3)
The upfield peak at about 1.7 ppm is the CH₃
and appears as a triplet due the adjacent
methylene (n=2)

Integral   2   3

11   10   9   8   7   6   5   4   3   2   1   0
                         ppm
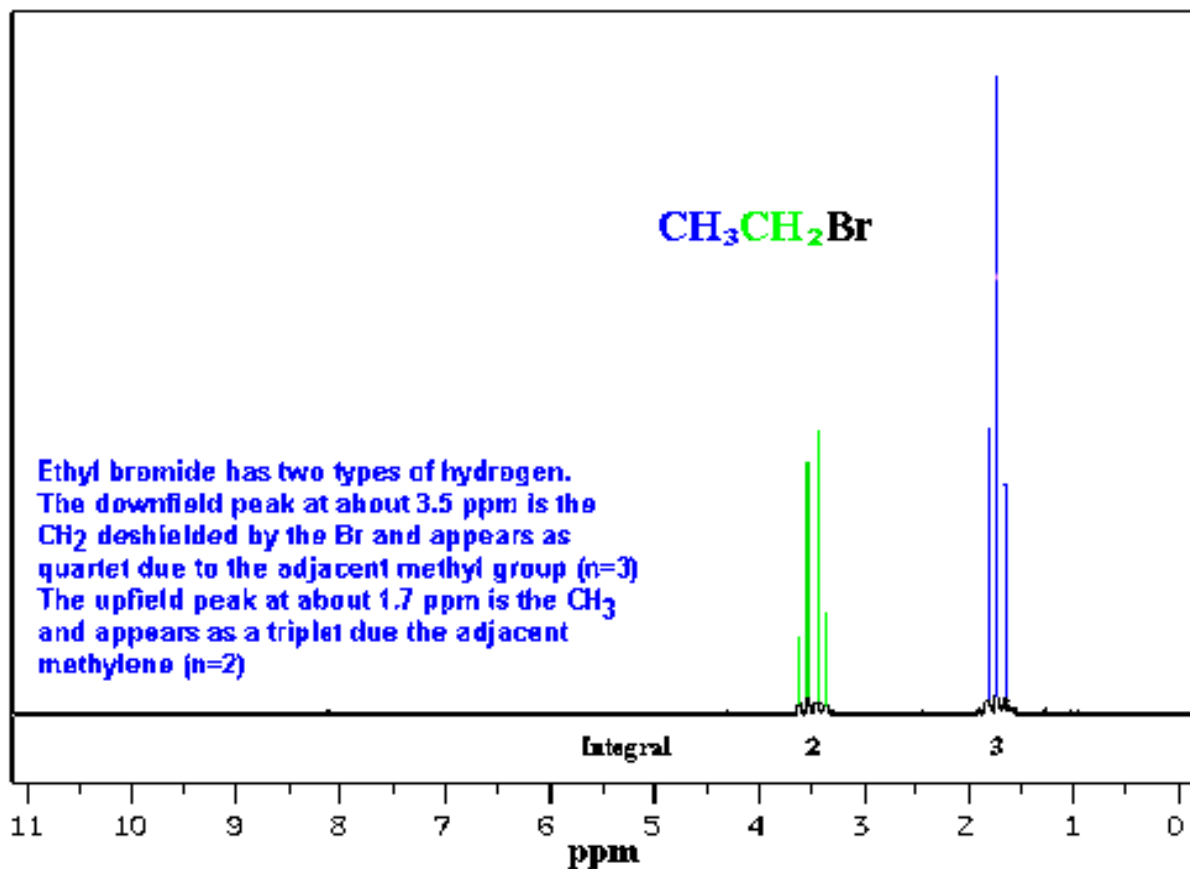
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
CH_3	3	triplet	1.75
CH_2	2	quartet	3.55

2) *n*-Propylbromide: CH_3-CH_2-CH_2-Br

1-Bromopropane
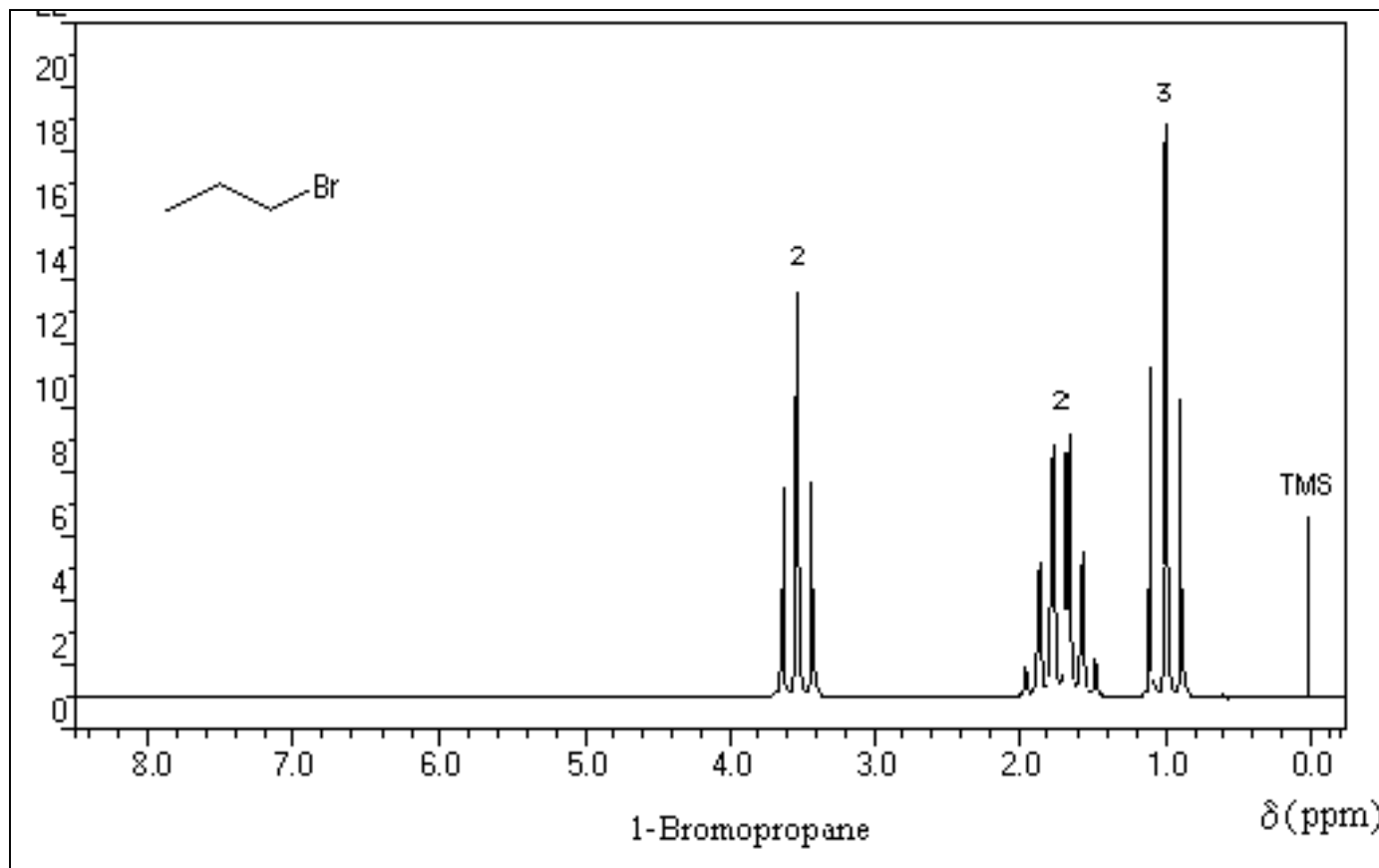
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
CH_3	3	triplet	1.00
CH_2	2	sextet	1.85
CH_2	2	triplet	3.45

3) *iso*-Propyl bromide (2-propyl bromide):
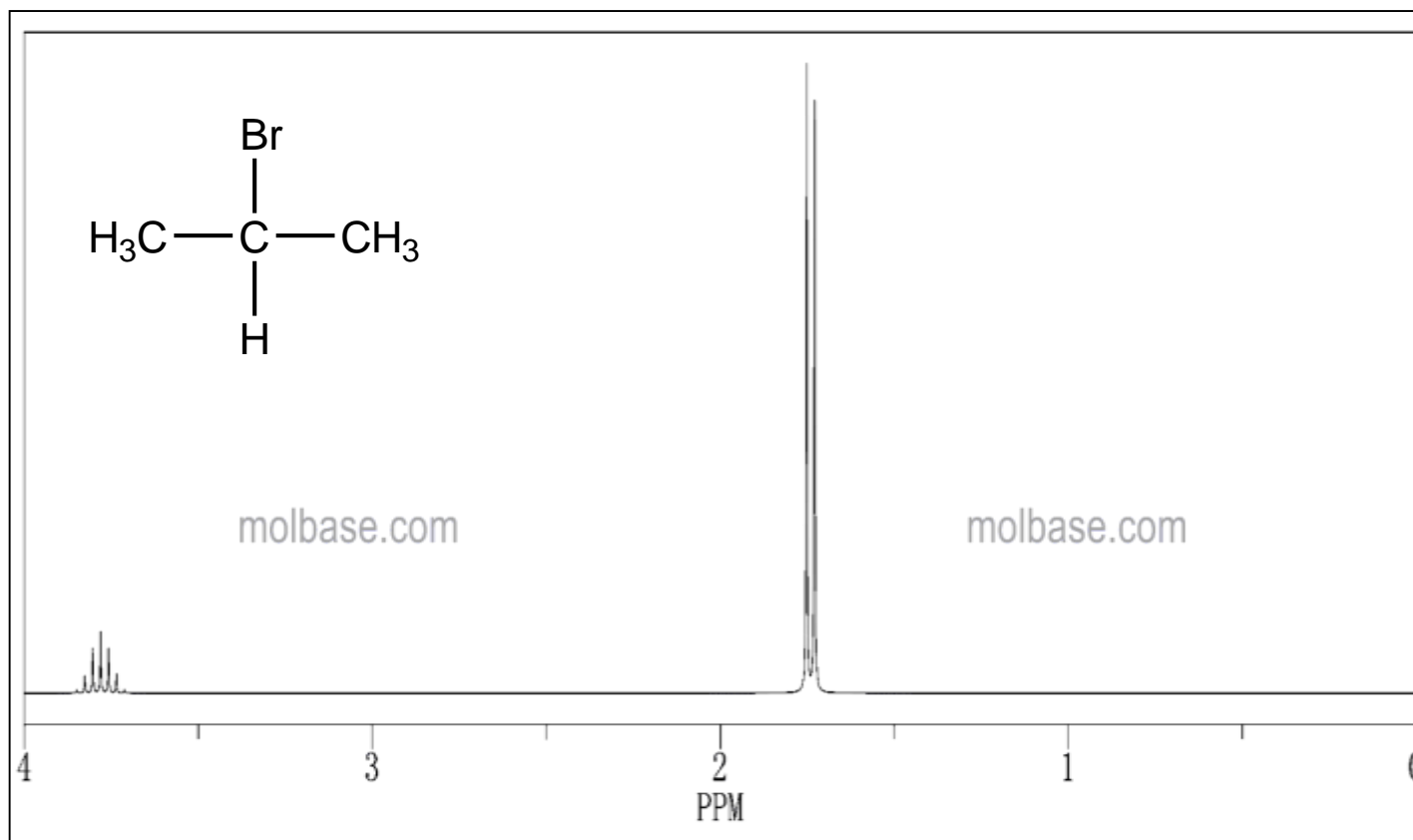
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
CH_3	6	doublet	1.72
CH	1	septet	3.83

4) Ethanol CH_3-CH_2-OH:
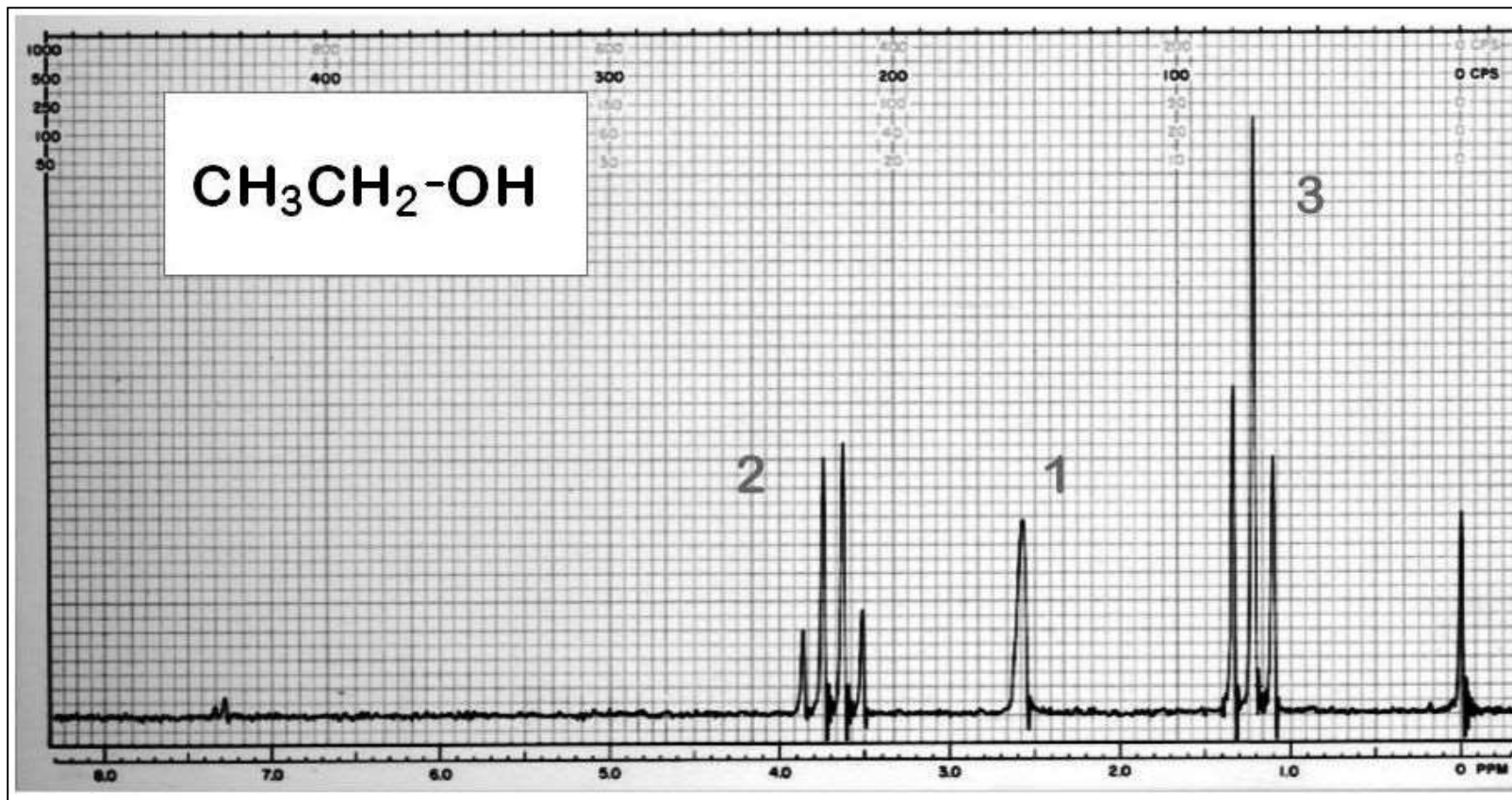
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
CH_3	3	triplet	1.24
OH	1	singlet	2.60
CH_2	2	quartet	3.75

5) Acetaldehyde:
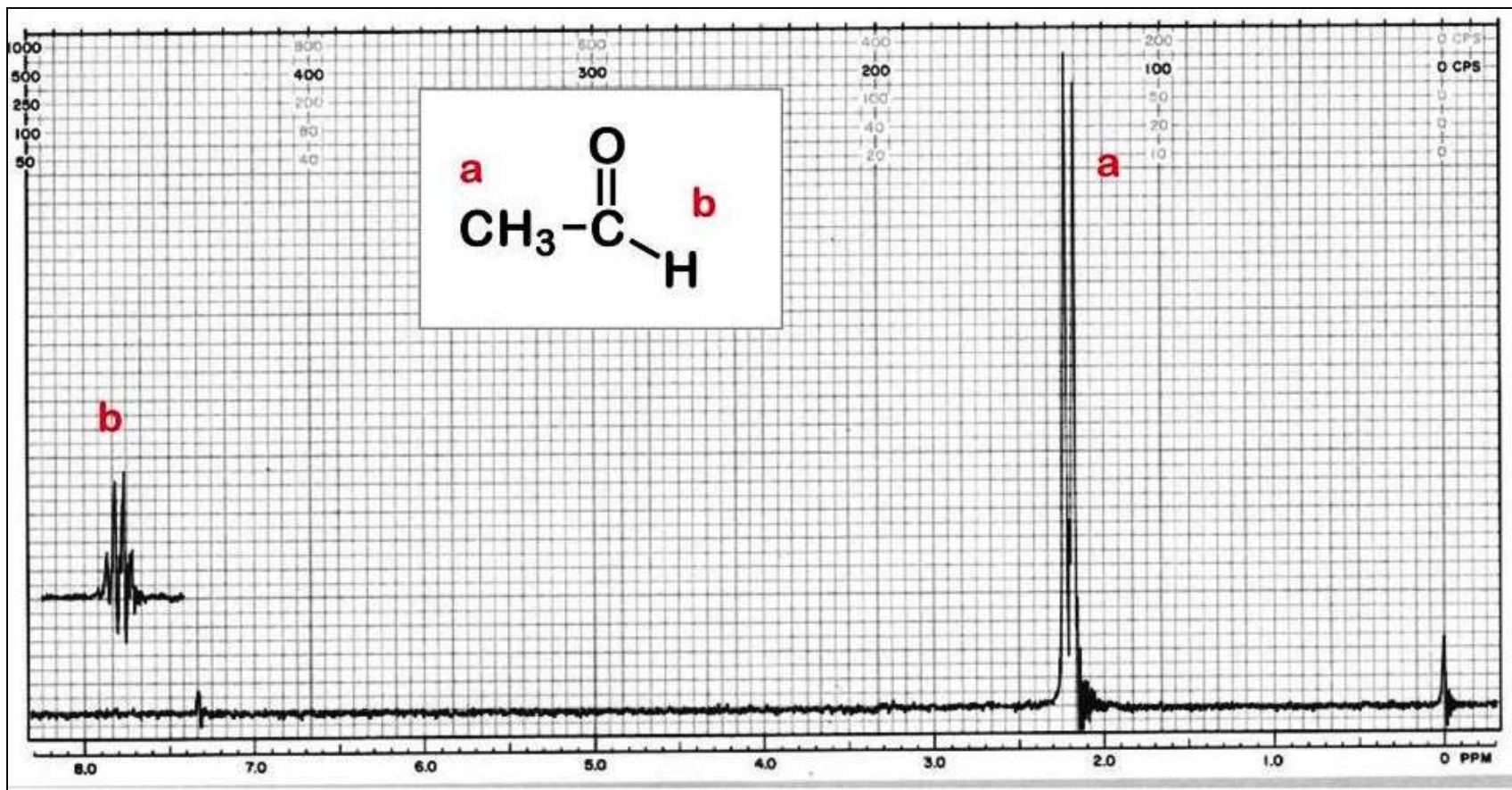
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
CH$_3$	3	doublet	2.13
CH	1	quartet	7.44

6) Benzene:
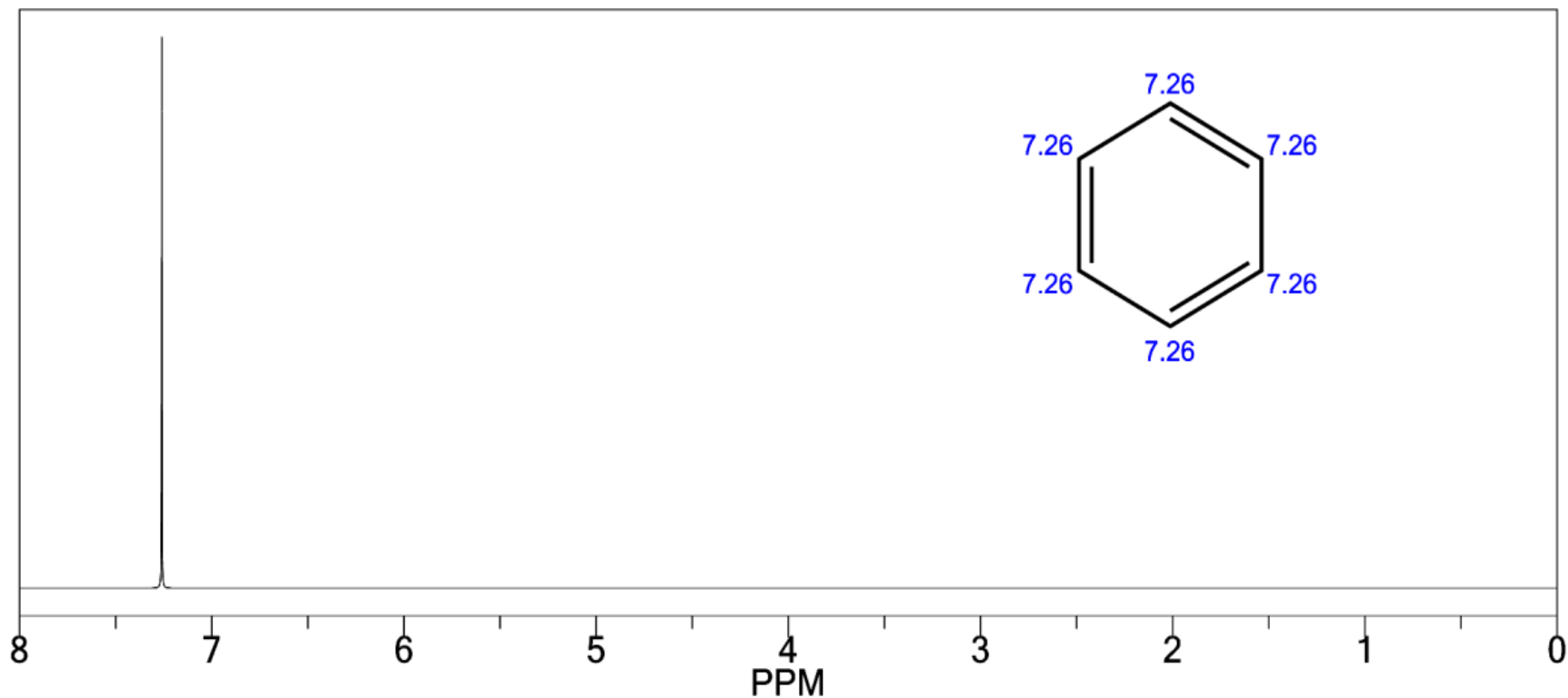
Proton	No. of protons	Spin multiplicity	Chemical shift (ppm)
Ar-H	6	singlet	7.26