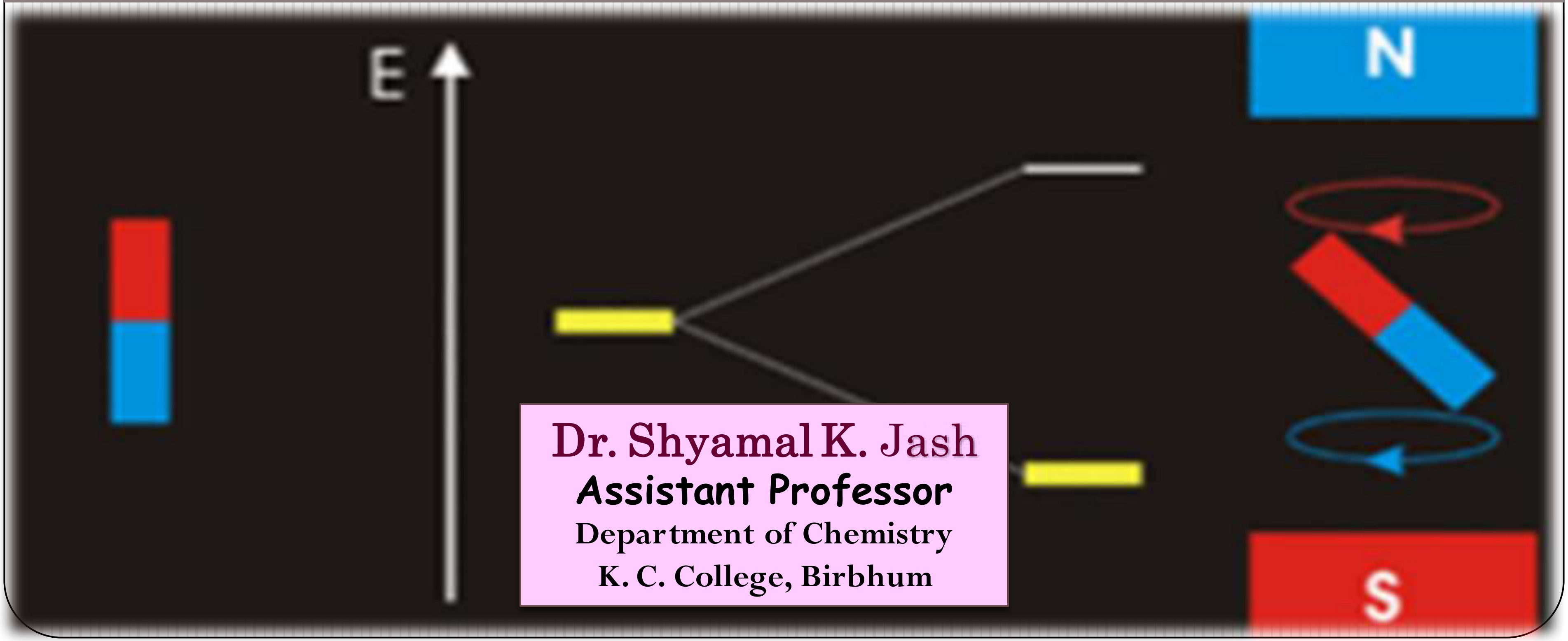
B.Sc SEM-IV Chemistry (Honours)
PAPER-CC-10

Nuclear Magnetic Resonance (NMR) Spectroscopy

A diagnostic tool for Structure determination



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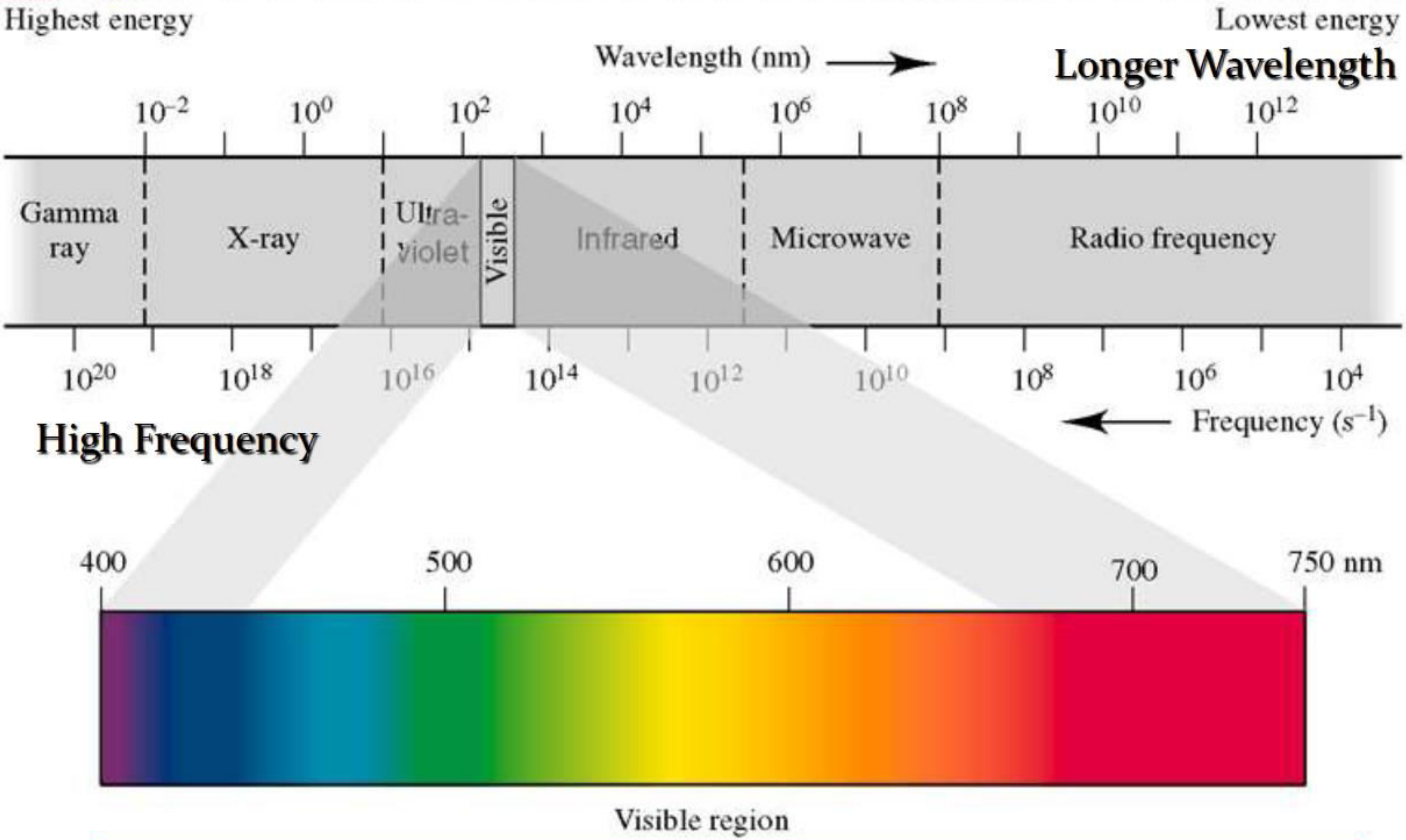
Introduction

NMR Spectroscopy

- Nuclear Magnetic Resonance is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule.



The Electromagnetic Spectrum

The frequency of radio waves lies between 10^7 and 10^8cps

The energy of radio frequency (rf) radiation can be calculated by using the equation :

$$E = h\,v$$

h = Planck's constant = 6.6×10^{-27} erg sec

v = frequency = $10^7 - 10^8$ cps(cycles per sec).

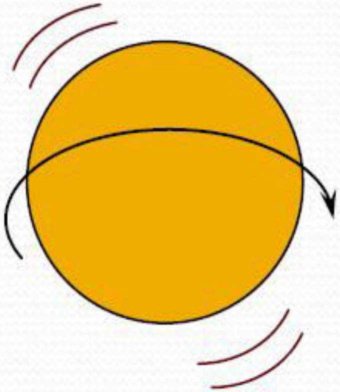
$E = 6.6 \times 10^{-27} \times 10^7$ (or 10^8 ergs)

$= 6.6 \times 10^{-20}$ (or 6.6×10^{-19} ergs)

Energy of rf radiation is very small to vibrate, rotate , or excite an atom or molecule. But this energy is sufficient to affect the nuclear spin of the atoms of a molecule.

NUCLEAR SPIN

The nuclei of some atoms have a property called "SPIN".



These nuclei behave as if they were spinning.

This is like the spin property of an electron, which can have two spins: +1/2 and -1/2 .

Each spin-active nucleus has a number of spins defined by its spin quantum number, **I**.

The number of Spin states = 2I + 1

NMR Active & Inactive Nucleus

- If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin. ${}_{12}C$, ${}_{16}O$,${}_{32}S$ etc.
- If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2) ${}_{1}H$,${}_{19}F$, ${}_{31}P$
- If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3) ${}_{2}H$, ${}_{14}N$

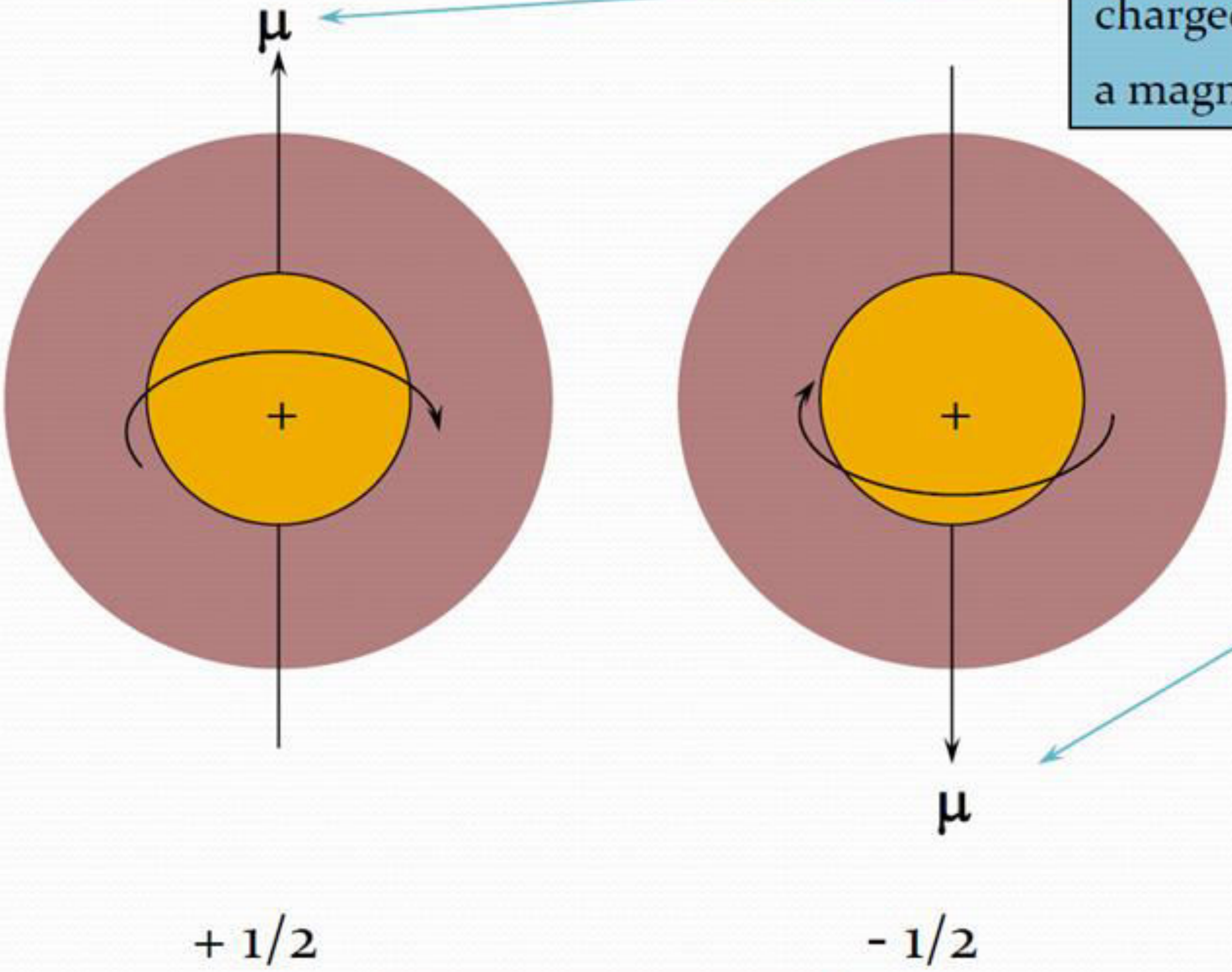
Element	^{1}H	^{2}H	^{12}C	^{13}C	^{14}N	^{15}N	^{16}O	^{19}F	^{31}P	^{32}S
Nuclear spin quantum number (*I*)	**1/2**	**1**	**0**	**1/2**	**1**	**1/2**	**0**	**1/2**	**1/2**	**0**
Number of spin states	**2**	**3**	**1**	**2**	**3**	**2**	**1**	**2**	**2**	**1**

Fundamental Principles of NMR

Principle

- NMR spectroscopy is the interaction of magnetic field with spin of nuclei and then absorption of radio frequency. For example, the nucleus of proton $_1H^+$ has two spin rotations : clockwise rotation with a spin quantum number I = +½ and | counterclockwise rotation with a spin quantum number I = - ½
- The number of spin sates is 2I+1 which is 2x (1/2) +1 = 2 state

NUCLEAR SPIN STATES - HYDROGEN NUCLEUS



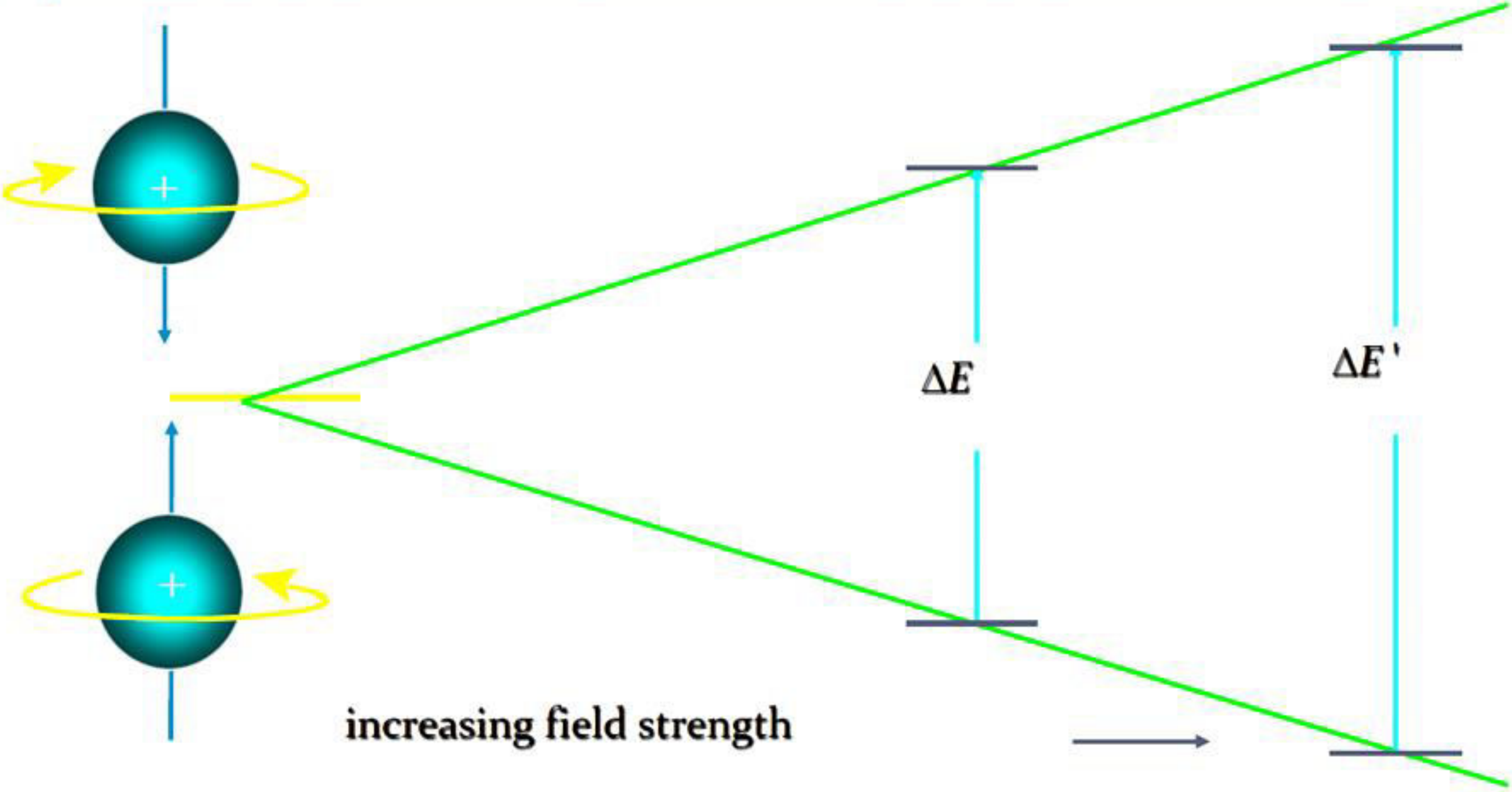
The spin of the positively charged nucleus generates a magnetic moment vector, **μ**.

The two states are equivalent in energy in the absence of a magnetic or an electric field.

TWO SPIN STATES

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

Energy Differences Between Nuclear Spin States



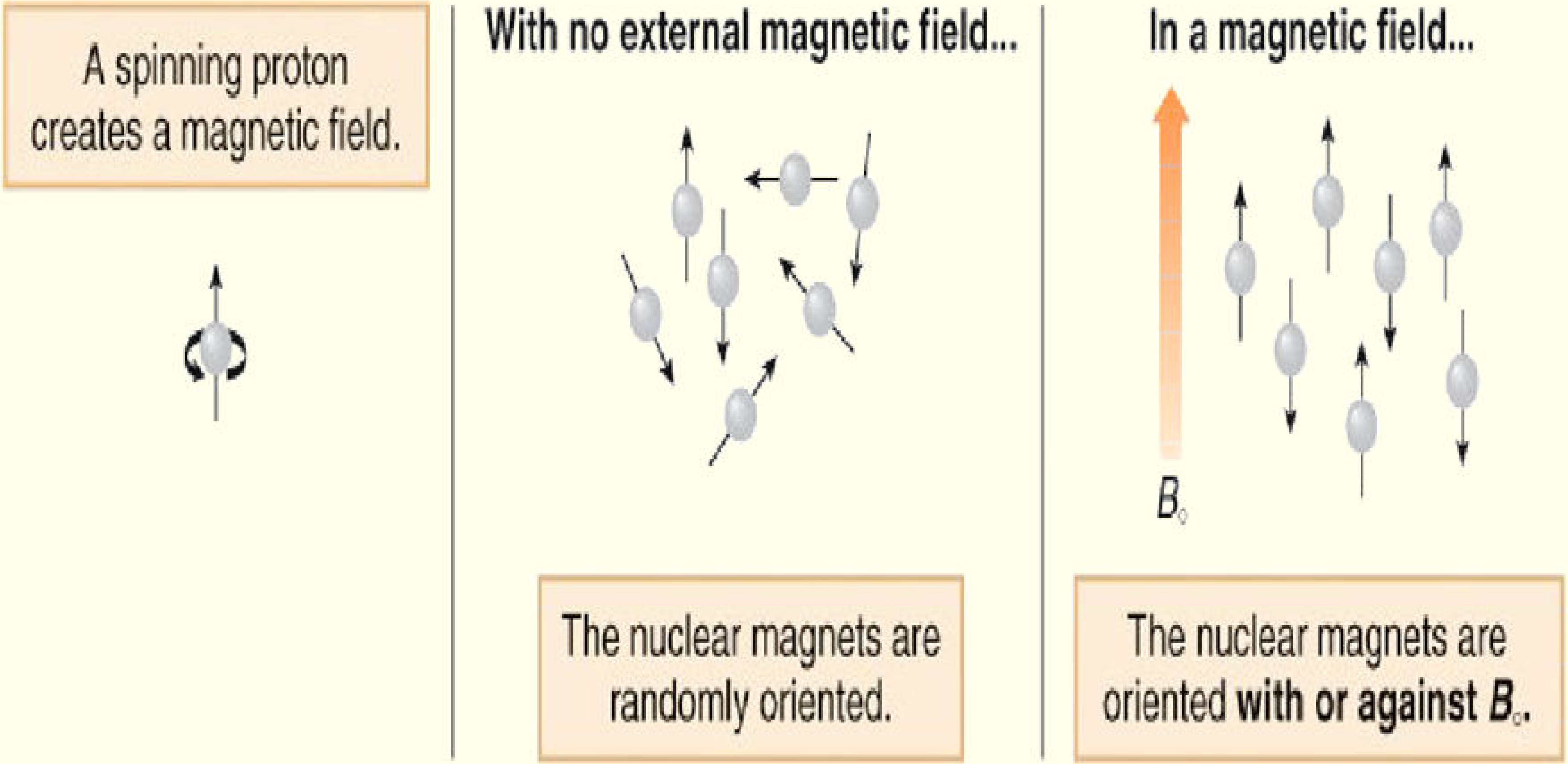
no difference in absence of magnetic field

proportional to strength of external magnetic field

Some important relationships in NMR

	Units
The frequency of absorbed electromagnetic radiation is proportional to	Hz
the energy difference between two nuclear spin states which is proportional to	kJ/mol (kcal/mol)
the applied magnetic field	tesla (T)

Effect of Magnetic field…



A spinning proton creates a magnetic field.

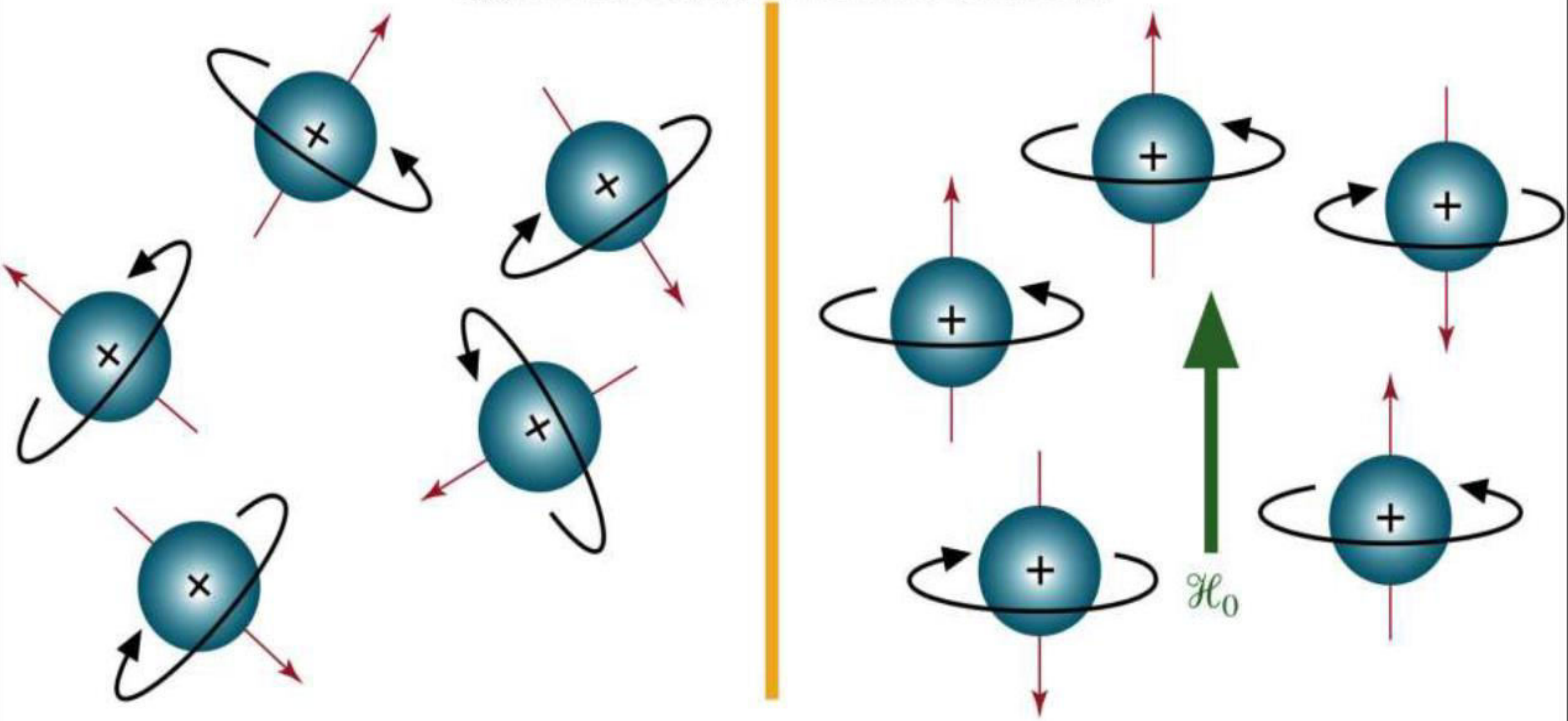
With no external magnetic field...

The nuclear magnets are randomly oriented.

In a magnetic field...

The nuclear magnets are oriented **with or against B_o.**

Nuclear Spin



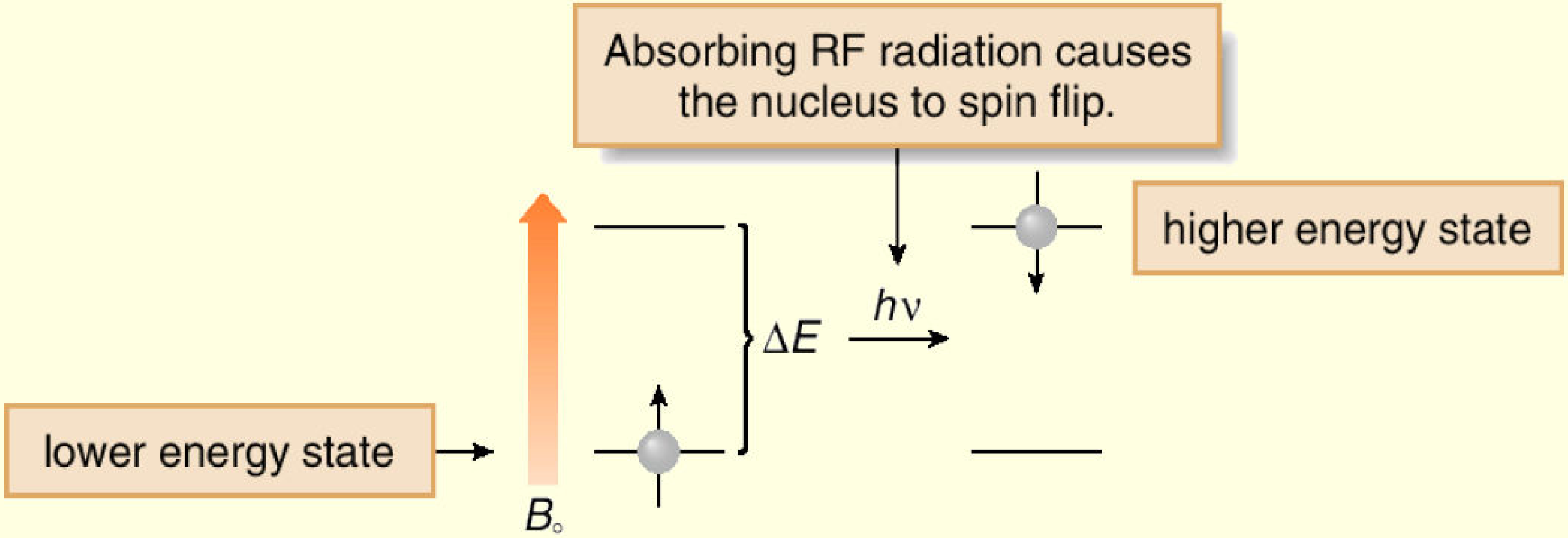
(*a*) No external magnetic field

(*b*) Apply external magnetic field $\mathcal{H}_0$

Effect of Magnetic field(Contd..)

A nucleus is in resonance when it absorbs RF radiation and "spin flips" to a higher energy state.

- Thus, two variables characterize NMR: an applied magnetic field B_0, the strength of which is measured in tesla (T), and the frequency n of radiation used for resonance, measured in hertz (Hz), or megahertz (MHz).



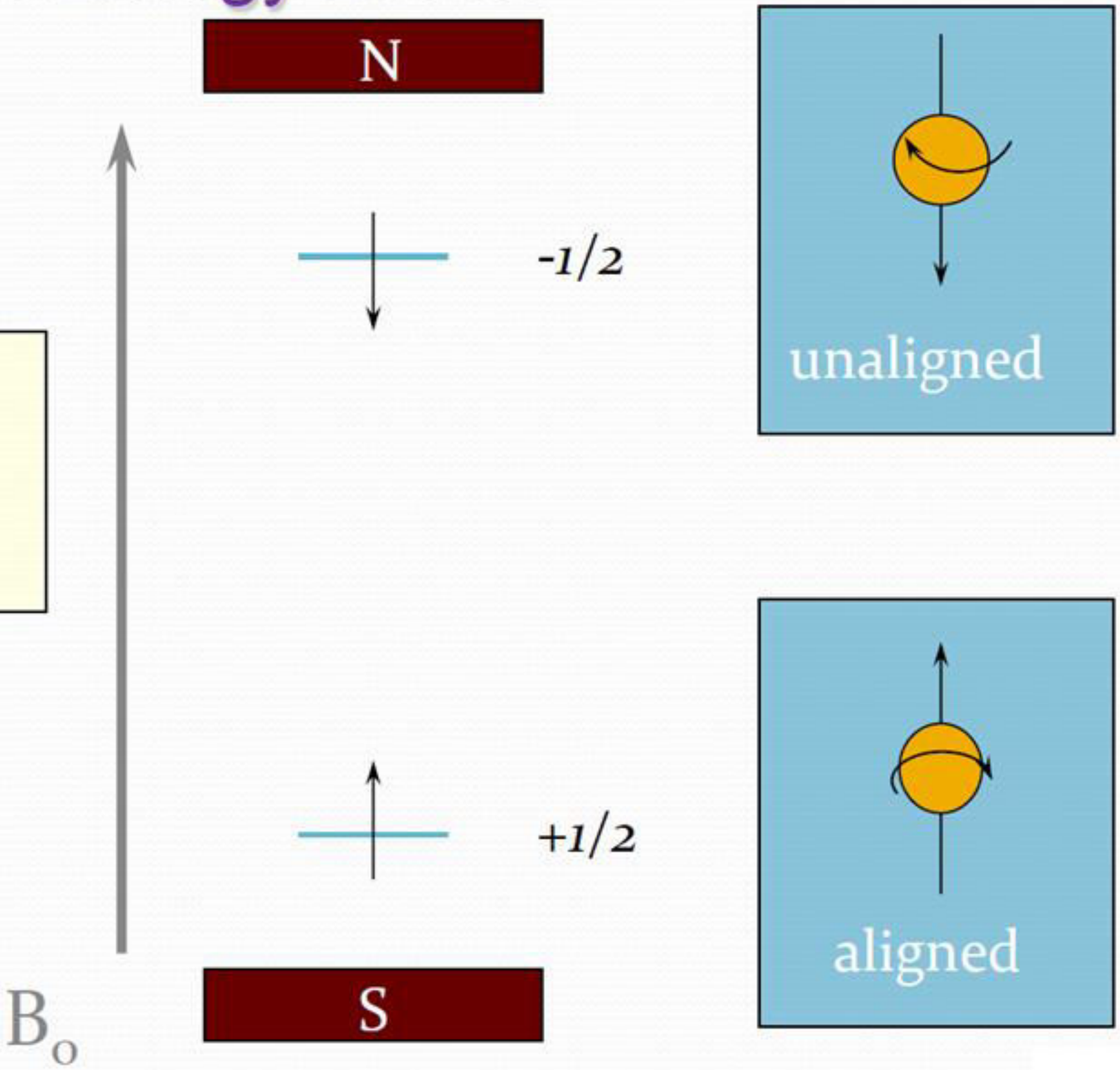
Absorbing RF radiation causes the nucleus to spin flip.

higher energy state

lower energy state

Nuclear Spin Energy Levels

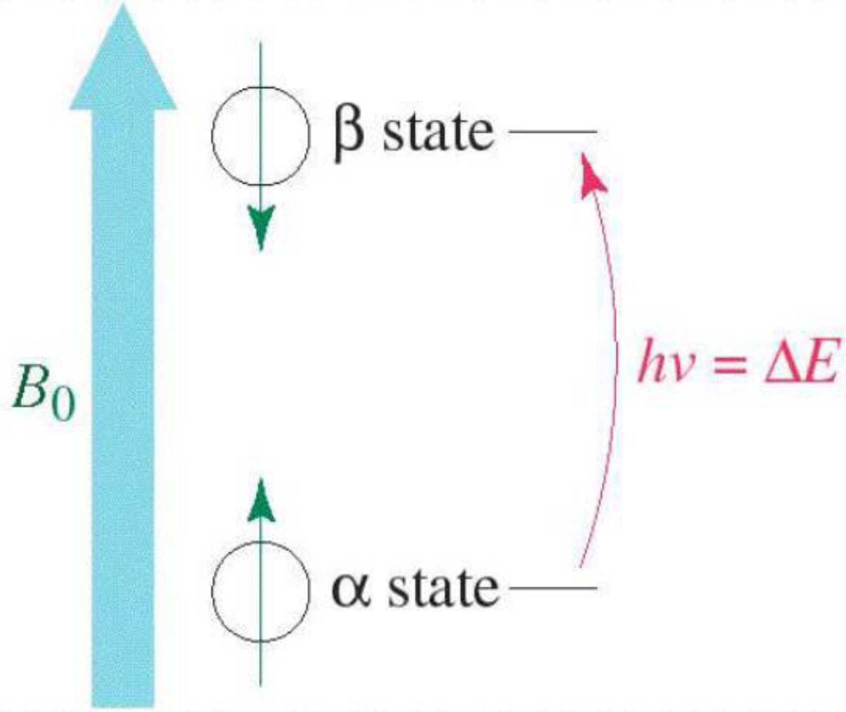
In a strong magnetic field (B_o) the two spin states differ in energy.

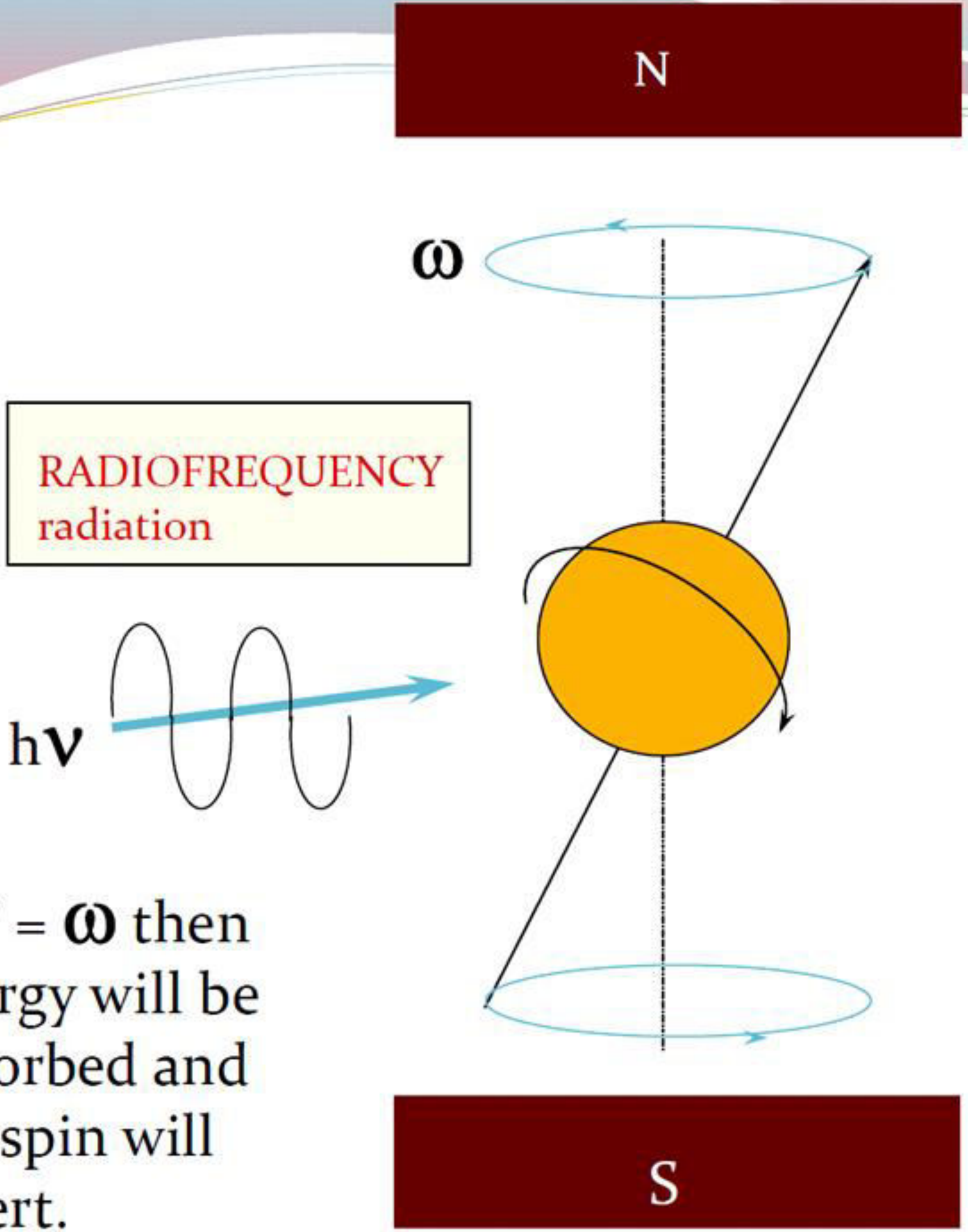


Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.





Nuclei precess at frequency **ω** when placed in a strong magnetic field.

If **ν** = **ω** then energy will be absorbed and the spin will invert.

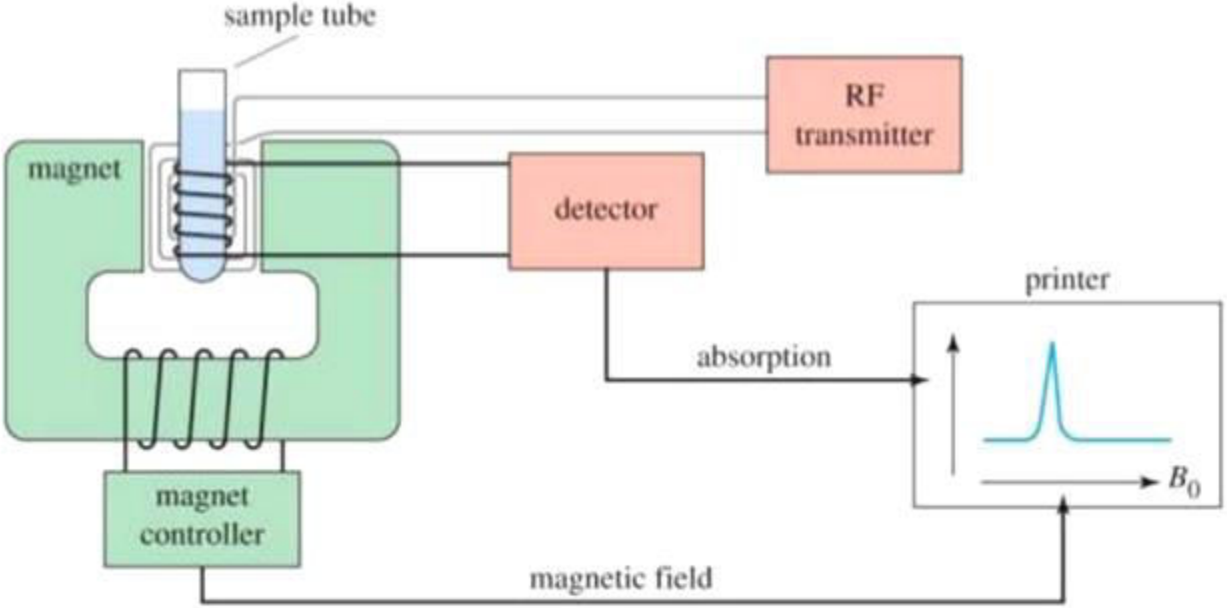
NUCLEAR MAGNETIC RESONANCE

NMR

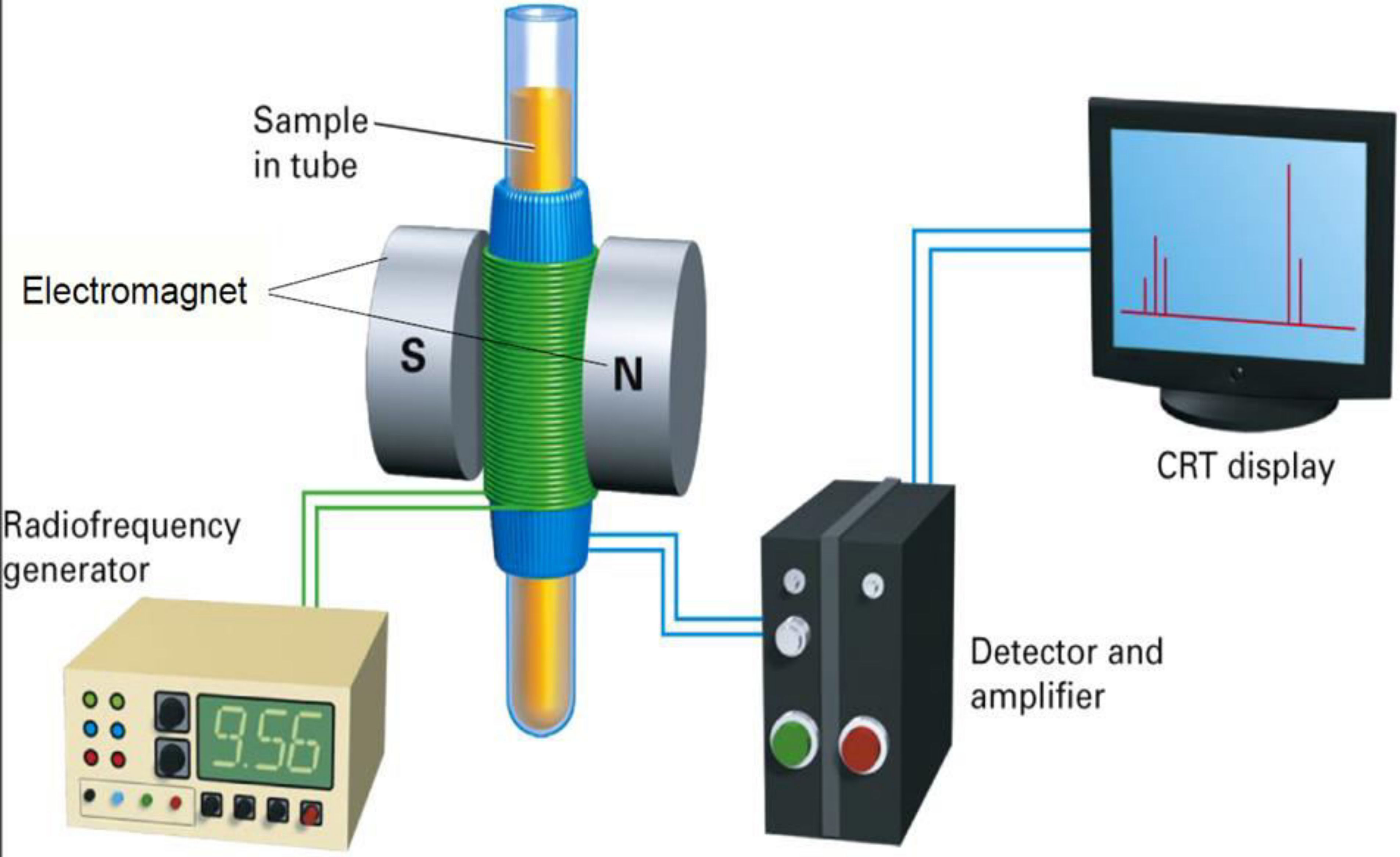
About Instrument & Their Working Process

NMR INSTRUMENTATION

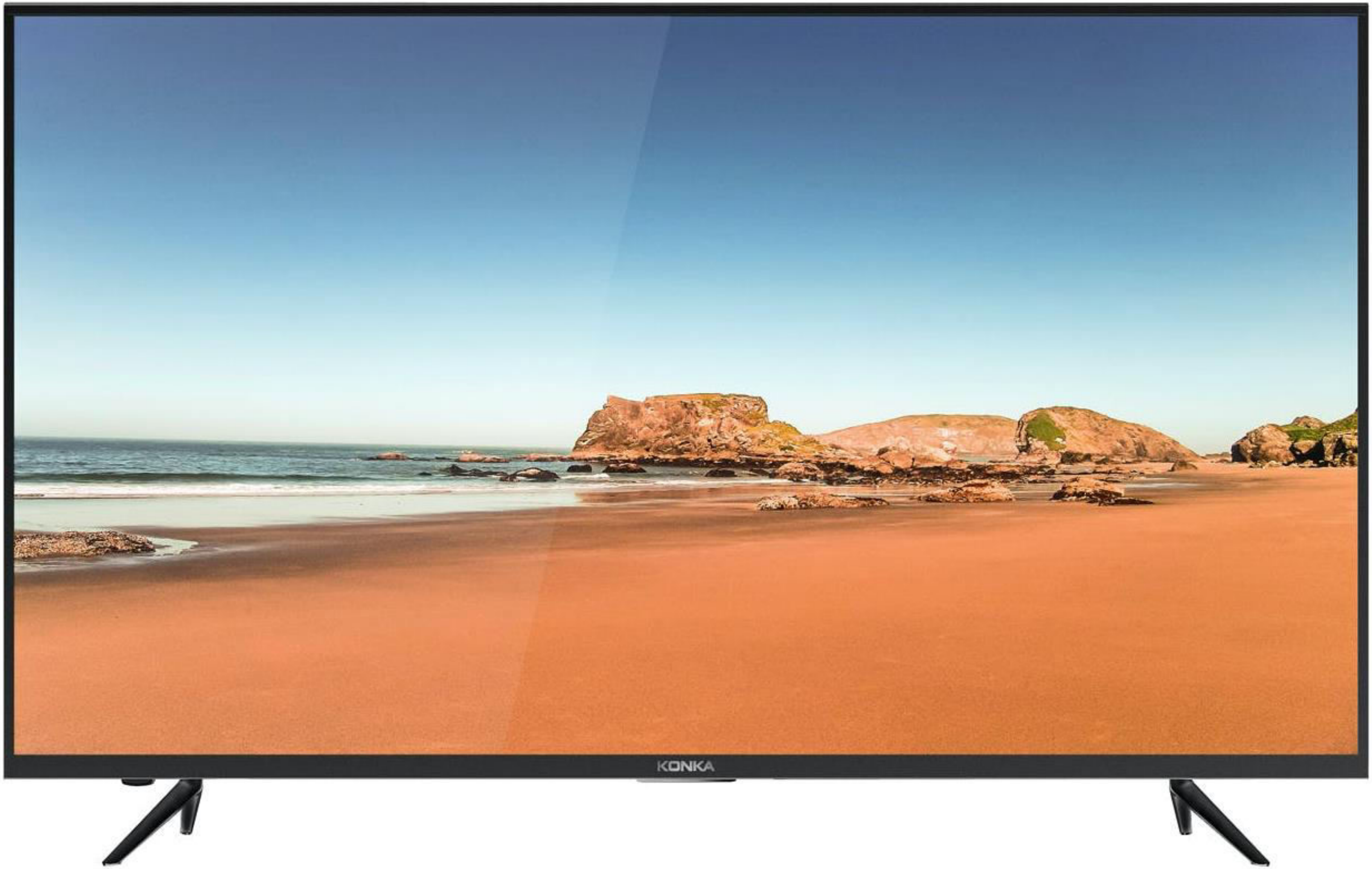
1. Sample Holder
2. Permanent Magnet
3. Probe
4. Sweep Generator
5. Radio Frequency Transmitter
6. Radio Frequency Receiver
7. Read Out Systems



Schematic diagram of NMR set-up



Instrumentation & Working

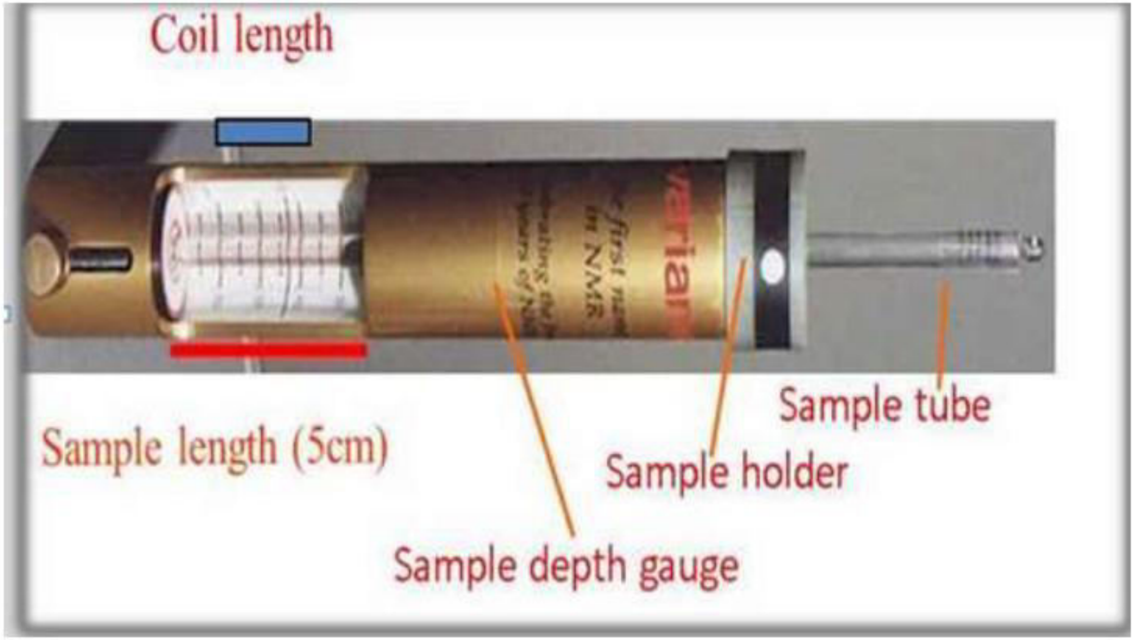


1.Sample Holder:-

Sample should be held in a holder which should be chemically inert, durable and transparent to radiation.

Glass tube with 8.5cm long,0.3 cm in diameter. The sample holder in NMR is normally tube-shaped and is therefore called the sample tube.

Glass or Pyrex tubes are commonly used.



2. Permanent Magnet:-

The important feature of the magnet it should gives homogeneous magnetic field i.e., the strength & direction of magnetic field should not change from point to point. The strength of the field should be very high i.e. atleast 20000 gauss(G) electro magnets are more stable than permanent magnets.

Range from 60 MHz (1.4 T) to 700 MHz (16.4 T) and higher.

1HNMR Operates at **60-100 MHz**

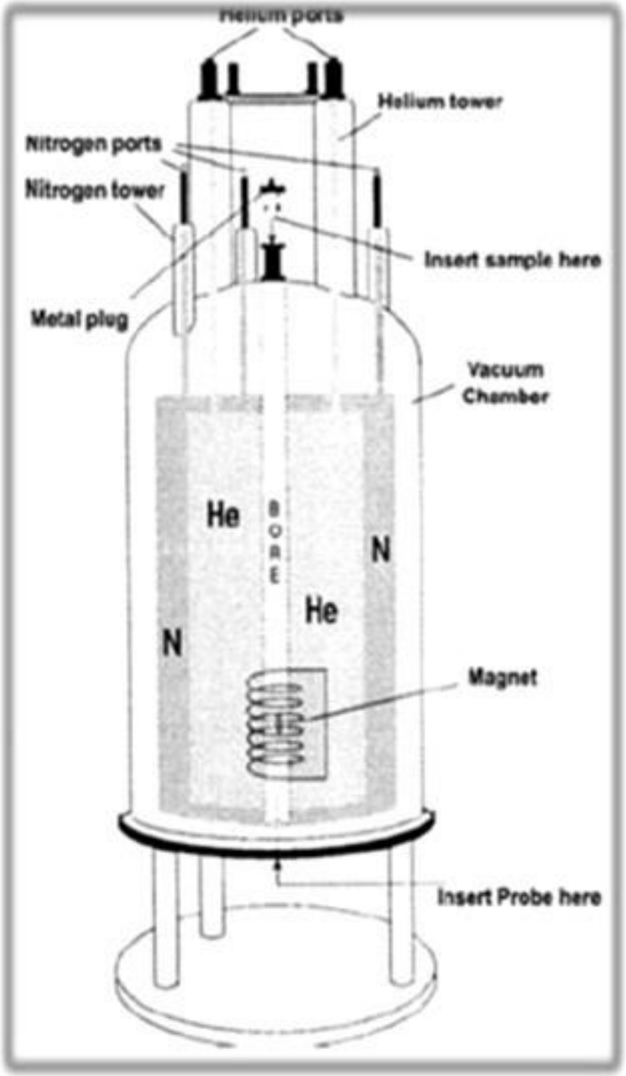
13CNMR Operates at **200-600MHz**

There are two parts of magnet-

a) Superconducting magnet
b) Shim Coils

a)Superconducting magnet-

- It is made up of superconducting Nb/Sn or Sb/Ti wire.
- The magnet is submerged liquid helium, for providing the sufficient cooling.
- The magnet and the liquid helium reservoir are encased in a liquid nitrogen reservoir to decrease the evaporative loss of more expensive liquid helium.
- The sample probe is put in the bore.



b)Shim Coils-

- Shim coils are used for making magnetic field homogeneous, provided by the magnets.
- Through these coils current is adjusted until the magnetic field has the required homogeneity.

3.Probe:-

- In which the sample holder is placed.
- Contains an Air turbine to spin the sample holder, while the spectrum is collect.
- Used to Excite and Detect the magnetization in radio-frequency of sample.
- The most essential component is the RF transmitting and receiving coil.
- For maximum sensitivity, a fixed frequency probe is needed (mean: a separate probe is required for each nucleus like1H, 13C, 19F).

4.Sweep Generator:-

To produce a amount of magnetic field pass through the sample. For a nucleus to resonate, the precession frequency should become equal to the frequency of the applied RF radiation.

This can be achieved by,

I. Frequency Sweep method:

This method is used to resonate the nucleus.
The frequency of the RF radiation is changed so that it become equal to resonance frequency or precession frequency.

II. Field sweep method:

In this method to resonate the nucleus the frequency of the RF radiation is kept constant and the precession frequency is changed by changing the applied magnetic field.

5.Radio Frequency Transmitter:-

The RF radiation is generated by RF crystal oscillator.

The output of the oscillator is amplified, mixed, and filtered to produce monochromatic RF radiation and delivered to the sample.

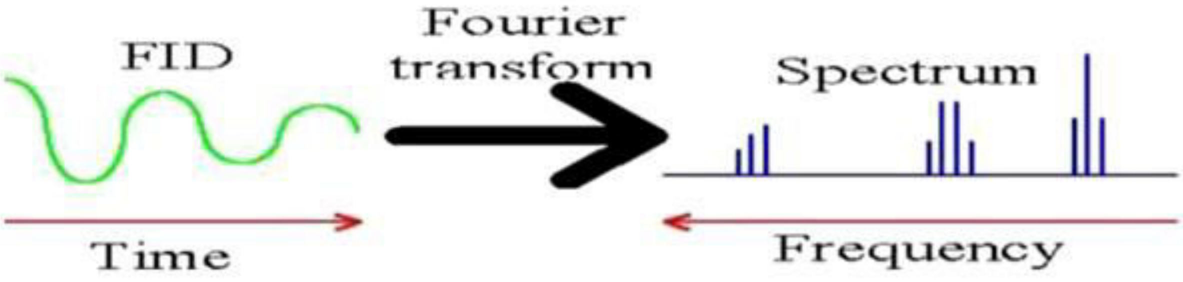
A radio transmitter coil that produces short powerful pulse of radio waves.

6.Radio Frequency Receiver:-

A radio receiver coil that detects radio frequencies emitted as nuclei relax to lower energy level.

The NMR signal emanating from the probe is detected by a digitizer receiver at regular time intervals.

These signals in the time domain must be converted to a frequency domain spectrum by application of a "Fourier transformation" or other mathematical transformation



7.Readout System:-

A computer that analyses and record the data.

SOLVENTS USED IN NMR

- Frequently the sample cannot be obtained in the pure state (or) it may be in the solid (or) gas phase.
- Most NMR spectra are recorded for compounds dissolved in a solvent. Therefore, signals will be observed for the solvent and this must be accounted for in solving spectral problems.
- It may be necessary to dissolve it or extract it for some other medium in this case a solvent must be used. Several requirements must retain by a good solvent, including then it

  i) It can be **Chemically inert** towards the sample,

  ii) It should not interfer with **NMR absorption spectrum,**

  iii) The using solvents should not contain **HYDROGEN** in the molecule.
- A substance free of proton should be used as a solvent, i.e., which does not give absorption of its own in NMR spectrum.
- Moreover, the solvent should be capable of dissolving at least 10% of the substance under investigation.
- The best solvents for proton NMR contain **No protons.**

- To avoid spectra dominated by the solvent signal, most ^{1}**H NMR** spectra are recorded in a **deuterated solvent**{deuterium nucleus does not respond, in the same region as the hydrogen nucleus}. However, deuteration is not "100%", so signals for the residual **protons** are observed. In **chloroform** solvent (**$CDCl_3$**), this corresponds to **$CHCl_3$**, so a singlet signal is observed at 7.26 ppm.
- The following solvents are normally used in which hydrogen replaced by deuterium.

CCL_4 - Carbon Tetrachloride

CS_2 - Carbon disulfide

$CDCL_3$ - Deuteriochloroform

$CDCl_3$ is a common solvent used for NMR analysis. It is used because most compounds will dissolve in it, it is volatile and therefore easy to get rid of, and it is **Non-reactive** and will not exchange its deuterium with protons in the molecule being studied.

C_6D_6 - Hexa deuteriobenzene

D_2O - Deuterium oxide

$(CCL_3)_2CO$ - Hexa chloroacetone

Interpreting Proton NMR Spectra

 Chemical shift **Number of Signals** **Integrals** **Spin-Spin Coupling: Splitting of Signals** **Coupling Constant**

TYPES OF INFORMATION FROM THE NMR SPECTRUM

1. Each different type of hydrogen gives a peak or group of peaks (multiplet).

2. The chemical shift ($^{\delta}$, **in ppm**) gives a clue as to the type of hydrogen generating the peak (alkane, alkene, benzene, aldehyde, etc.)

3. The integral gives the relative numbers of each type of hydrogen.

4. Spin-spin splitting gives the number of hydrogens on adjacent carbons.

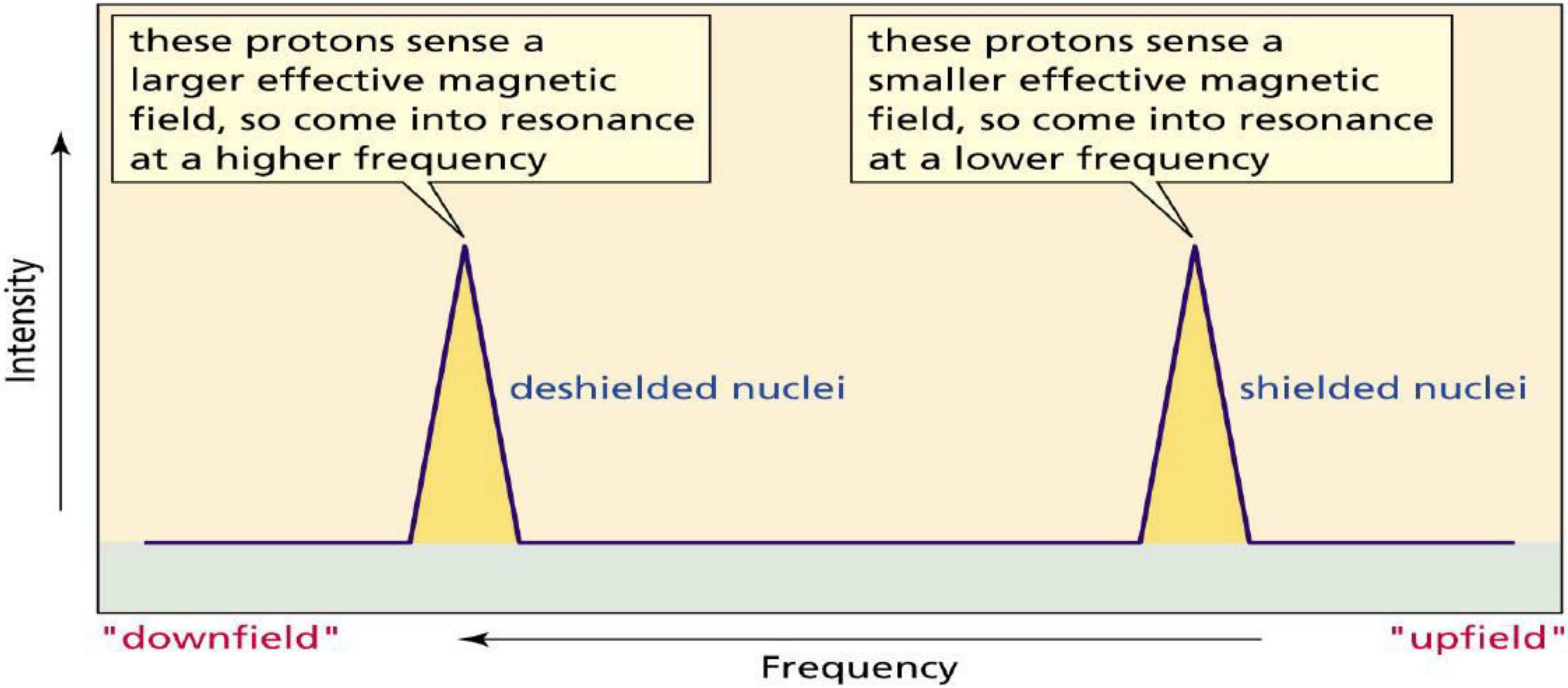
5. The coupling constant J also gives information about the arrangement of the atoms involved.

Chemical shift

- The relative energy of resonance of a particular nucleus resulting from its local environment is called chemical shift.
- NMR spectra show applied field strength increasing from left to right.
- Left part is downfield, the right is upfield.
- Nuclei that absorb on upfield side are strongly shielded where nuclei that absorb on downfield side is weakly shielded.
- Chart calibrated versus a reference point, set as 0, tetramethylsilane [TMS].

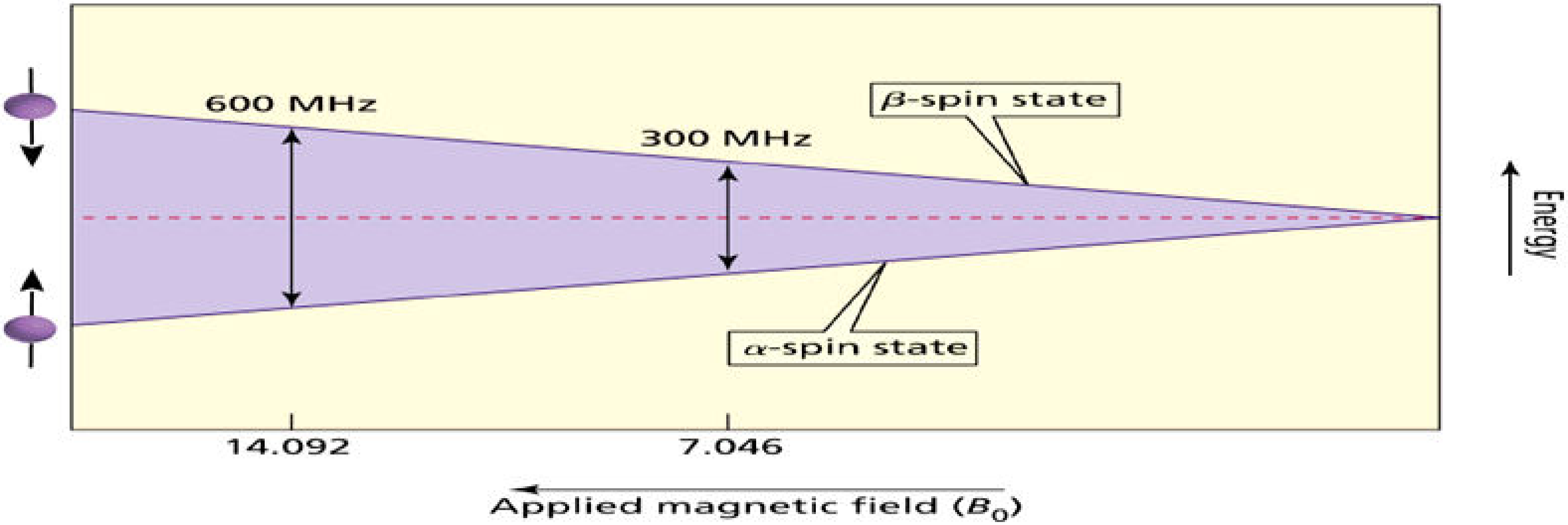
Chemical shift(Contd…)

- The electrons surrounding a nucleus affect the effective magnetic field sensed by the nucleus.



Chemical shift(Contd…)

- Shielded nuclei do not ‘sense’ as large a magnetic field as deshielded nuclei do. As a result, the energy difference between the α- and β-spin states is much lower in energy for shielded nuclei and resonate at a lower frequency.

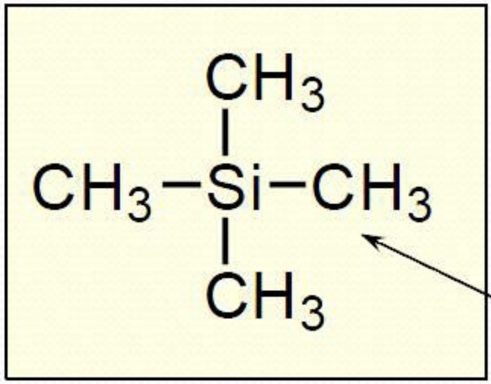


- Deshielded nuclei have a much higher energy difference between the α- and β-spin states and these resonate at a much higher frequency.

Measurement of Chemical Shift

- Numeric value of chemical shift: difference between strength of magnetic field at which the observed nucleus resonates and field strength for resonance of a reference.
  - Difference is very small but can be accurately measured
  - Taken as a ratio to the total field and multiplied by 10^6 so the shift is in parts per million (ppm)
- Absorptions normally occur downfield of TMS, to the left on the chart.

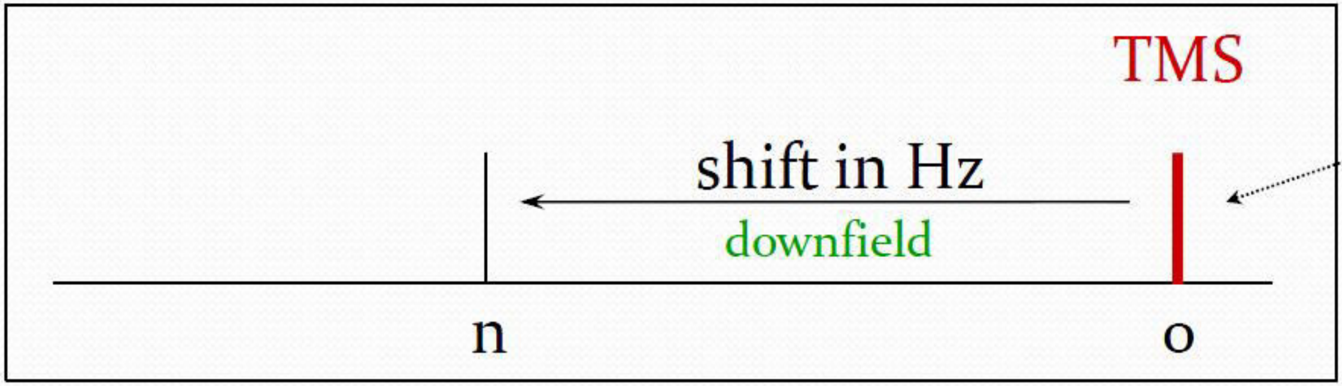
Rather than measure the exact resonance position of a peak, we measure how far downfield it is shifted from TMS.



$$\mathrm{CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{Si}}-CH_3}$$

reference compound
tetramethylsilane
"TMS"

Highly shielded protons appear way upfield.



Chemists originally thought no other compound would come at a higher field than TMS.

- TMS (Tetra methyl silane) is most commonly used as IS in NMR spectroscopy. Due to following reasons;
  - It is chemically inert and miscible with a large range of solvents.
  - Its twelve protons are all magnetically equivalent.
  - Its protons are highly shielded and gives a strong peak even small quantity.
  - It is less electronegative than carbon.
  - It is highly volatile and can be easily removed to get back sample.

the "chemical shift" in the following way:

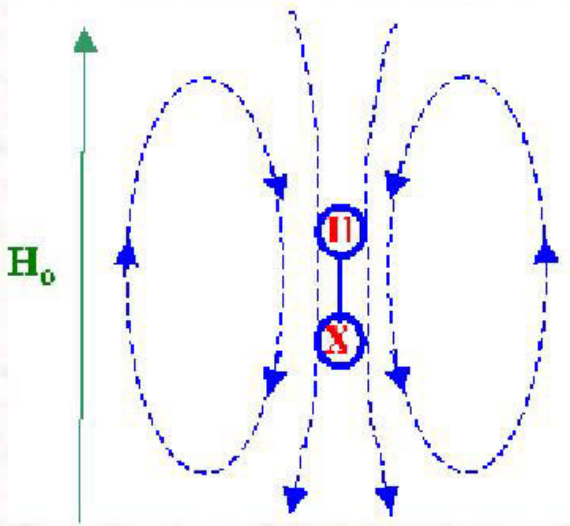
parts per million

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

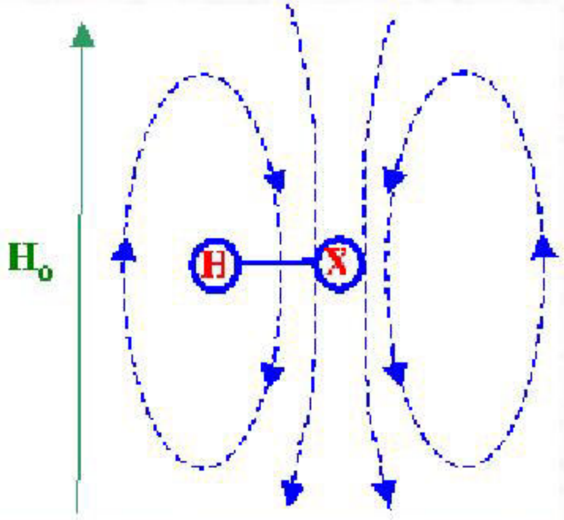
This division gives a number independent of the instrument used.

- If the induced magnetic field opposes the applied field, then the nuclei in a molecule exert an external force, which shields the nucleus from the influence of the applied field and the proton is said to be ***shielded.***

- If the induced field reinforces the applied field the proton feels a higher field strength and thus such a proton is said to be ***deshielded.***



Shielding effect



Deshielding effect

Shielded & Deshielded Effect

Factors Influencing Chemical Shift

A. Intra-molecular factors

1. Inductive effect.
2. Vander Waal's deshielding.
3. Anisotropic effects

B. Intermolecular factors

1. Hydrogen bonding.
2. Temperature.
3. Solvents.

ELECTRONEGATIVITY – CHEMICAL SHIFT

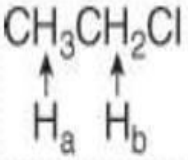
Dependence of the Chemical Shift of CH_3X on the Element X

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

most deshielded

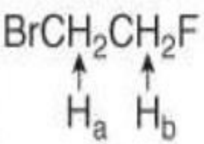
TMS

deshielding increases with the Electronegativity of atom X



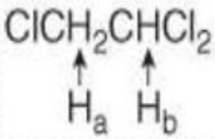
$\underset{H_a}{\underset{\uparrow}{CH_3}}\underset{H_b}{\underset{\uparrow}{CH_2}}Cl$

- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.



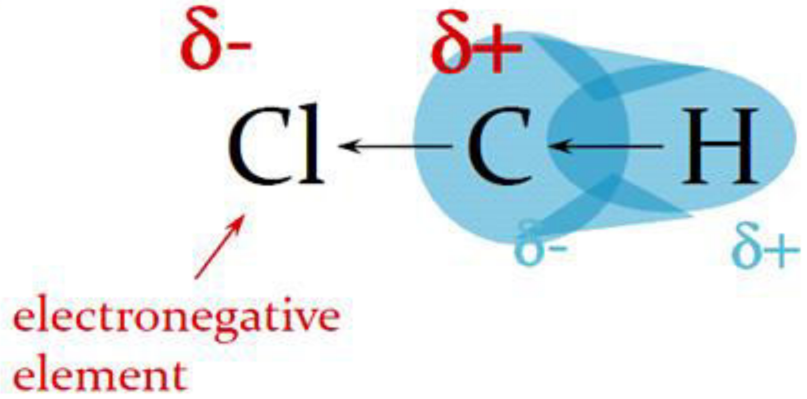
$Br\underset{H_a}{\underset{\uparrow}{CH_2}}\underset{H_b}{\underset{\uparrow}{CH_2}}F$

- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb further **downfield.**



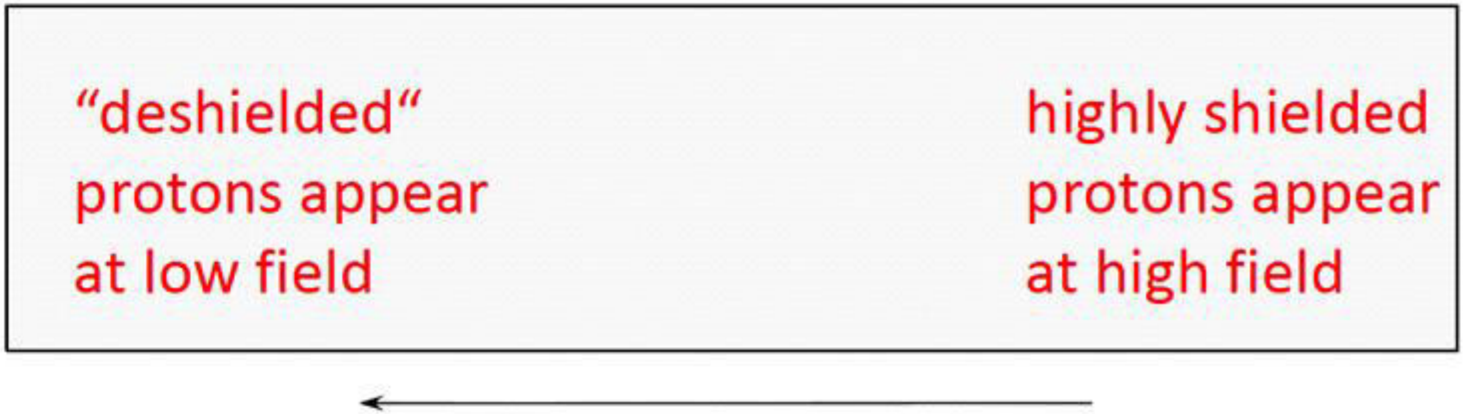
$Cl\underset{H_a}{\underset{\uparrow}{CH_2}}\underset{H_b}{\underset{\uparrow}{CH}}Cl_2$

- The larger number of electronegative Cl atoms (two versus one) **deshield** H_b more than H_a, so it absorbs **downfield** from H_a.



Chlorine “deshields” the proton, that is, it takes valence electron density away from carbon, which in turn takes more density from hydrogen deshielding the proton.

NMR CHART



“deshielded“ protons appear at low field

highly shielded protons appear at high field

deshielding moves proton resonance to lower field

DESHIELDING BY AN ELECTRONEGATIVE ELEMENT

Substitution Effects on Chemical Shift

most deshielded

$CHCl_3$ CH_2Cl_2 CH_3Cl

7.27 5.30 3.05 ppm

The effect increases with greater numbers of electronegative atoms.

most deshielded

$-CH_2-Br$ $-CH_2-CH_2Br$ $-CH_2-CH_2CH_2Br$

3.30 1.69 1.25 ppm

The effect decreases with increasing distance.

2. Vander Waal's deshielding

- The presence of bulky groups in a molecule can cause deshielding due to the week Vander Waal's force and give slightly higher value of **δ** than expected.

3. Anisotropic effect (space effect)

- Anisotropic effect arises due to the orientation of nuclei with respect to the applied magnetic field.

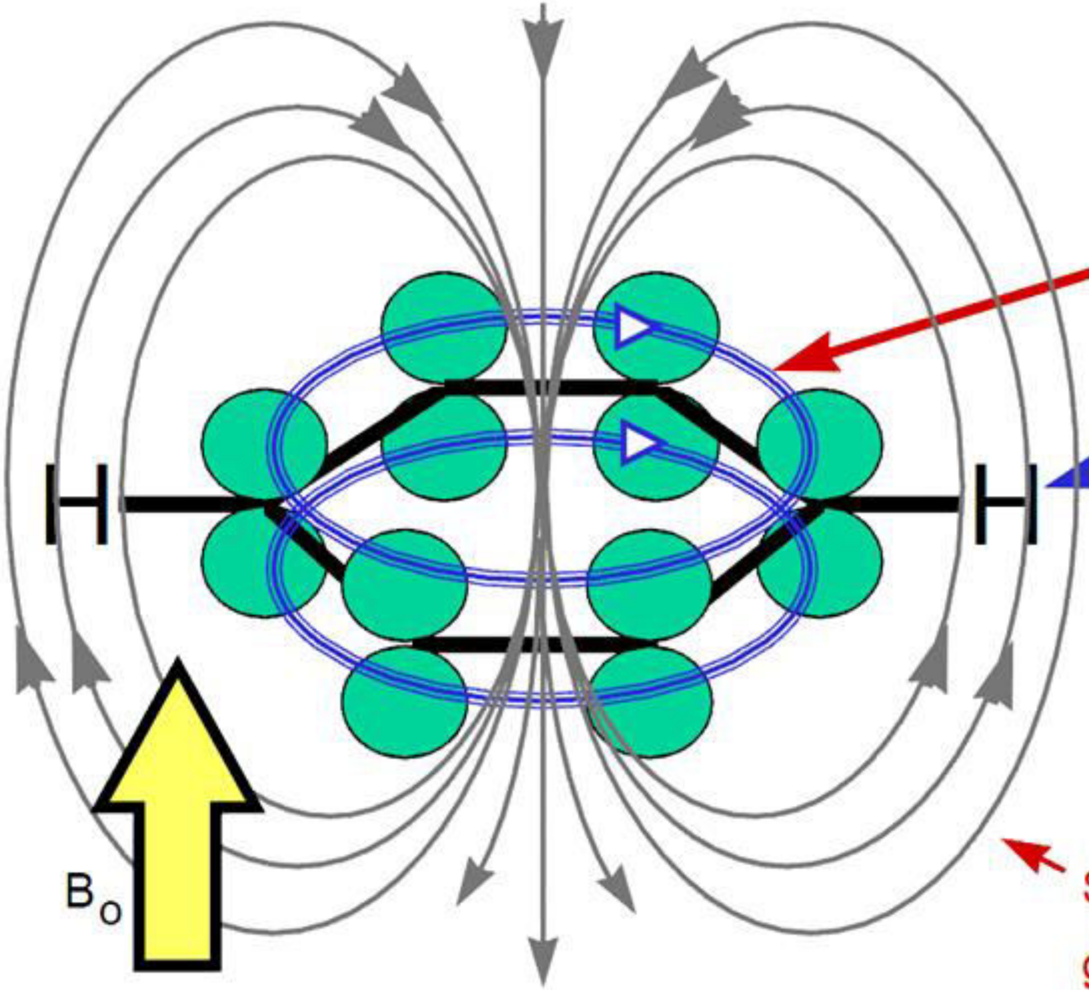
- Chemical bonds can set up magnetic field, the effect of this field on the chemical shift is depend upon the spacial arrangements.

- π – bonds effects the chemical shift and cause downfield shift with higher **δ** value.

- E.g. CH_3H — $\delta_H = 0.23$ $\delta_C = 2.3$

  $CH_2{=}{=}CH_2$ — $\delta_H = 5.25$ $\delta_C = 123.3$

Ring Current in Benzene



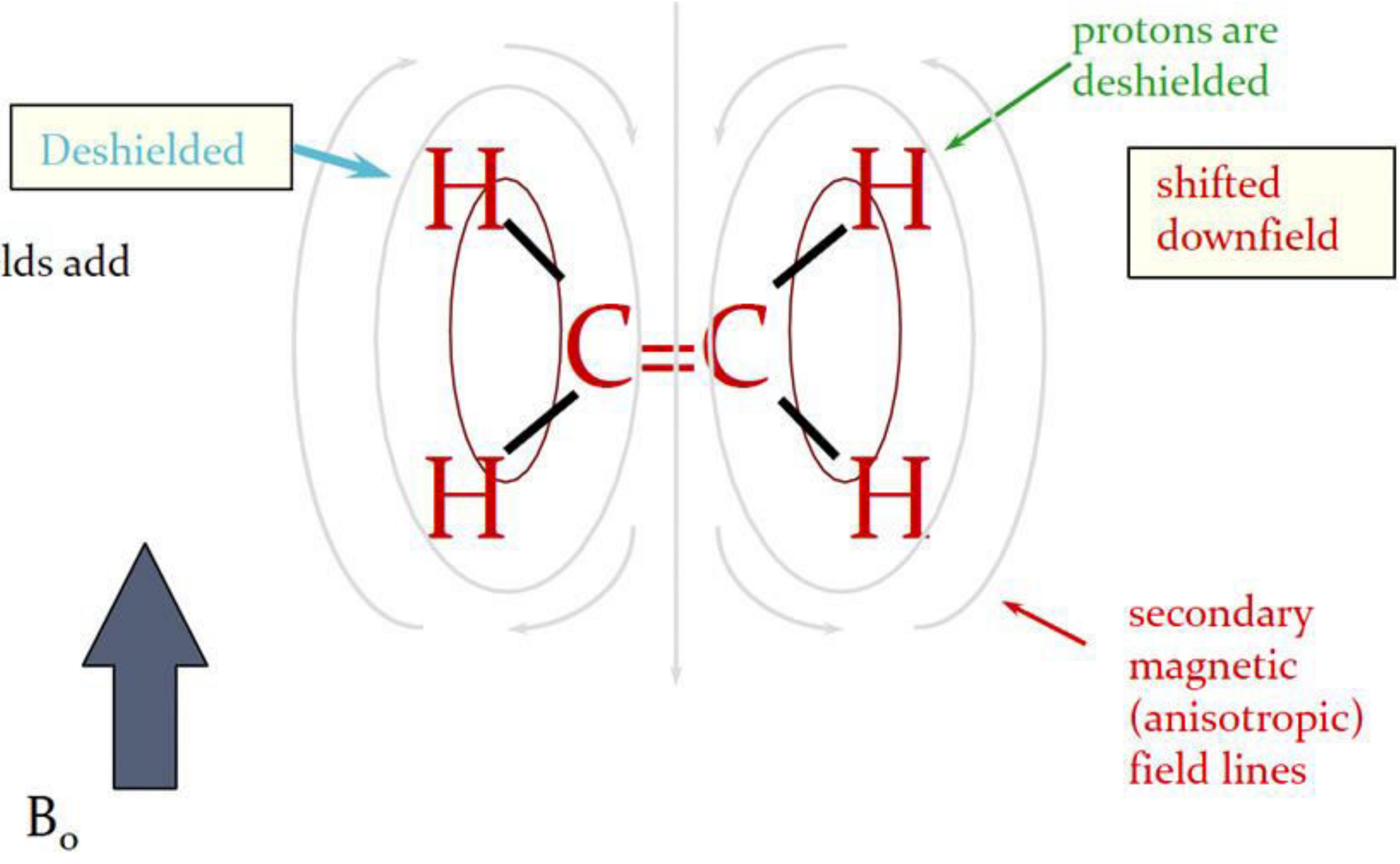
Circulating π electrons

Deshielded

fields add together

Secondary magnetic field generated by circulating π electrons deshields aromatic protons

ANISOTROPIC FIELD IN AN ALKENE



Deshielded

fields add

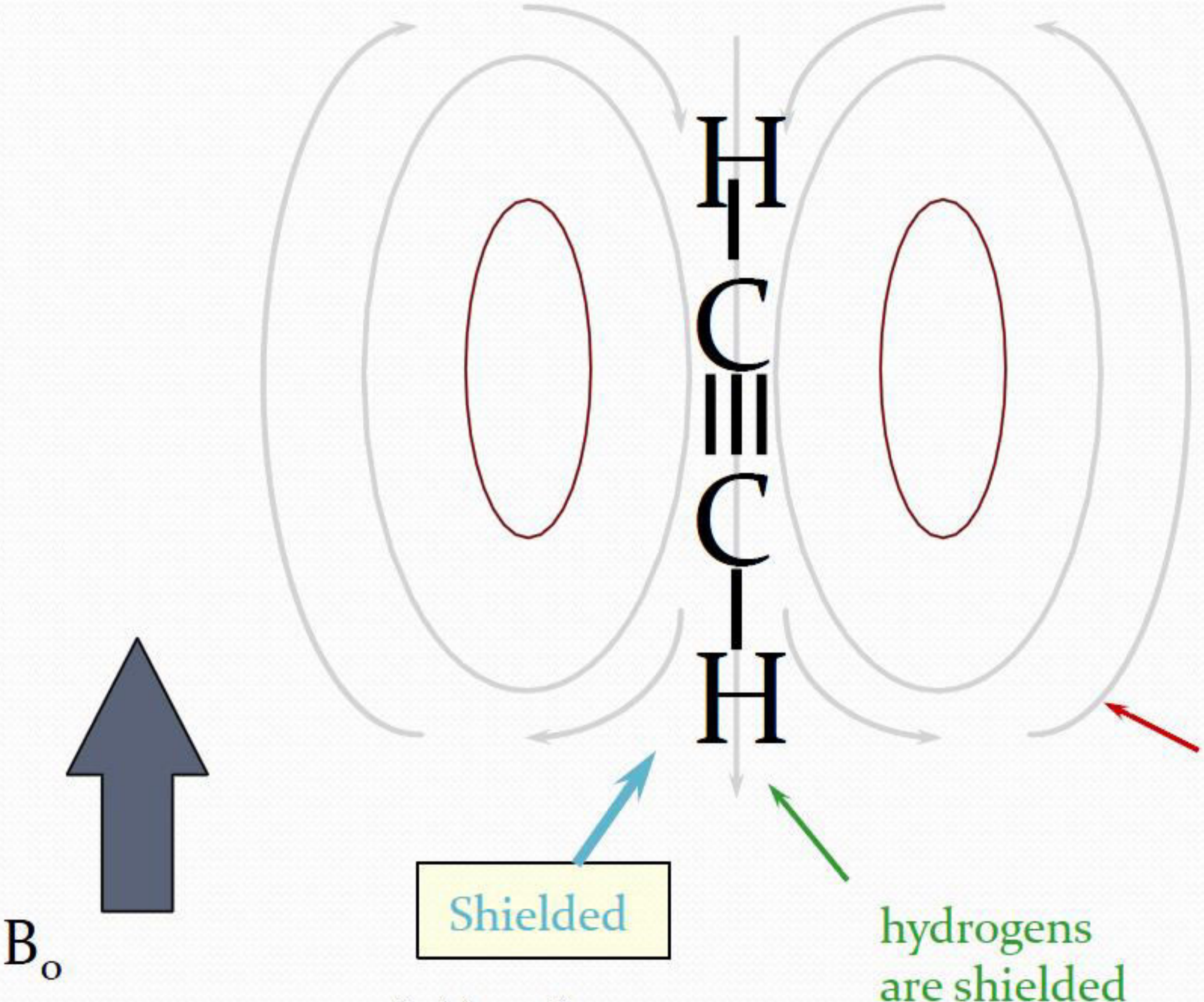
protons are deshielded

shifted downfield

secondary magnetic (anisotropic) field lines

B_o

ANISOTROPIC FIELD FOR AN ALKYNE



Shielded

fields subtract

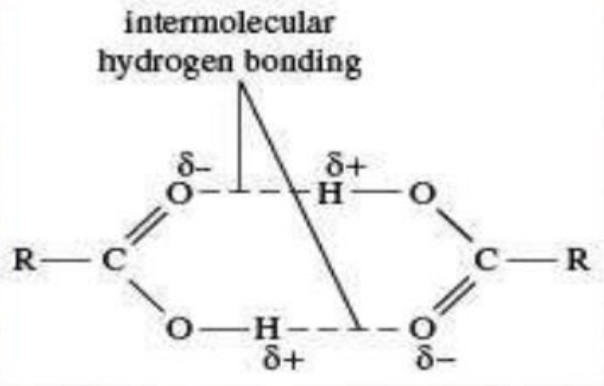
hydrogens are shielded

secondary magnetic (anisotropic) field

❑ Intermolecular factors

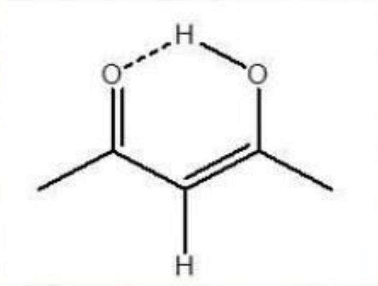
1. Hydrogen bonding

- Intra-molecular hydrogen bonding does not show any change in absorption due to change in concentration.
- While hydrogen atom involved in the intermolecular H-bonding shares its electrons with two electronegative elements and as a result it itself deshielded and get higher **δ** value.
- E.g. Carboxylic acid dimer and β-diketones.



δ = 9-15

Downfield shift



δ = 15.4

No change

2. Temperature

- The resonance position of most signals is little affected by temperature.

- — OH, —NH—, and —SH protons show upfield shift at higher temperature

3. Solvents

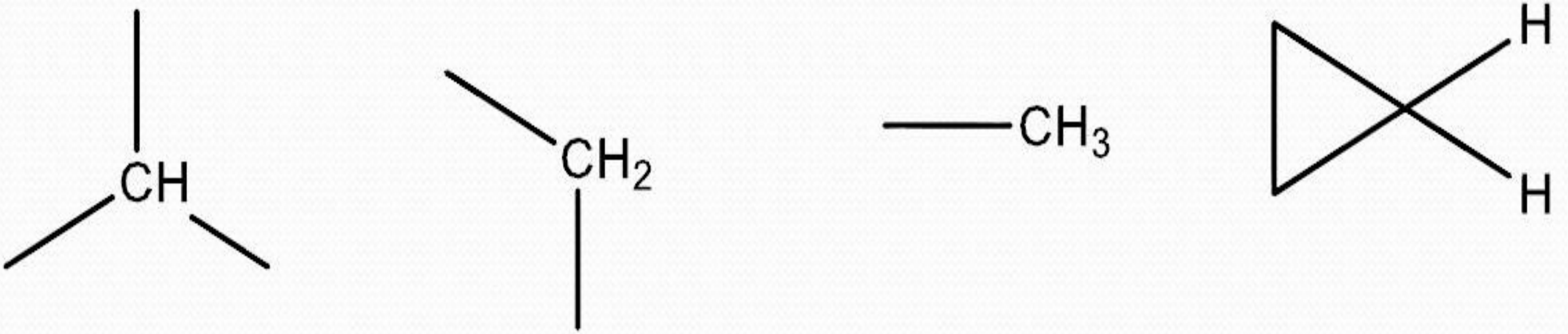
- The solvents used in NMR spectroscopy should be chemically inert, magnetically isotropic, devoid of hydrogen atom and should dissolve the sample to a reasonable extent.

- E.g. CCl_4, CS_2, $CDCl_3$ etc.

- Hybridization

sp^3 Hydrogens (no electro negative elements and Π bonded groups)

3^0 > 2^0 > 1^0 > cyclopropane



- sp^2 Hydrogens:

  In an sp^2 C-H bond, the carbon atom has more s character (33% s), which effectively renders it *more electronegative* than an sp^3 carbon (25% s).

- If the sp^2 carbon atom holds its electrons more tightly, this results in less shielding for the H nucleus than in an sp^3 bond.
- Another effect anisotropy.

- sp Hydrogens:

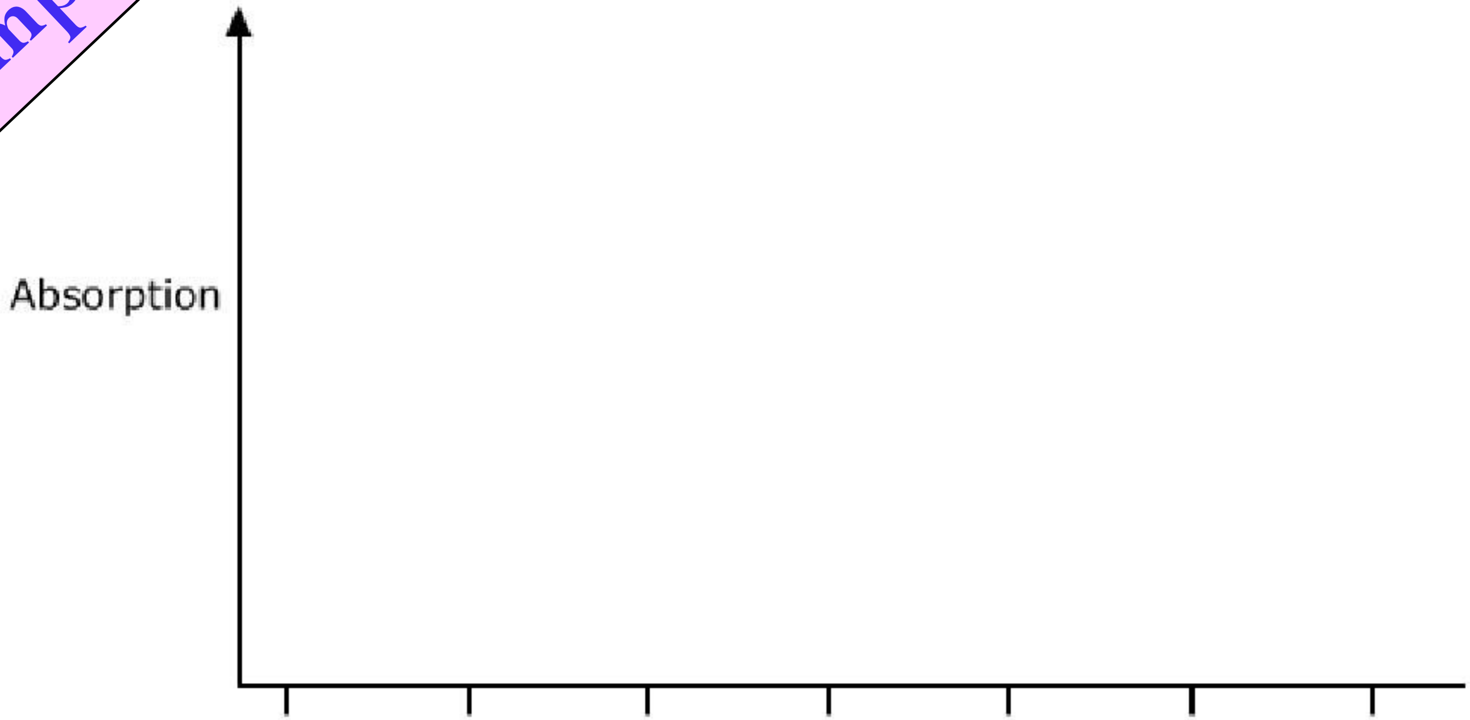
  On the basis of hybridization, acetylenic proton to have a chemical shift greater than that of vinyl proton.

  But chemical shift of acetylenic proton is less than that of vinyl proton.

- Finally $sp^2 > sp > sp^3$.

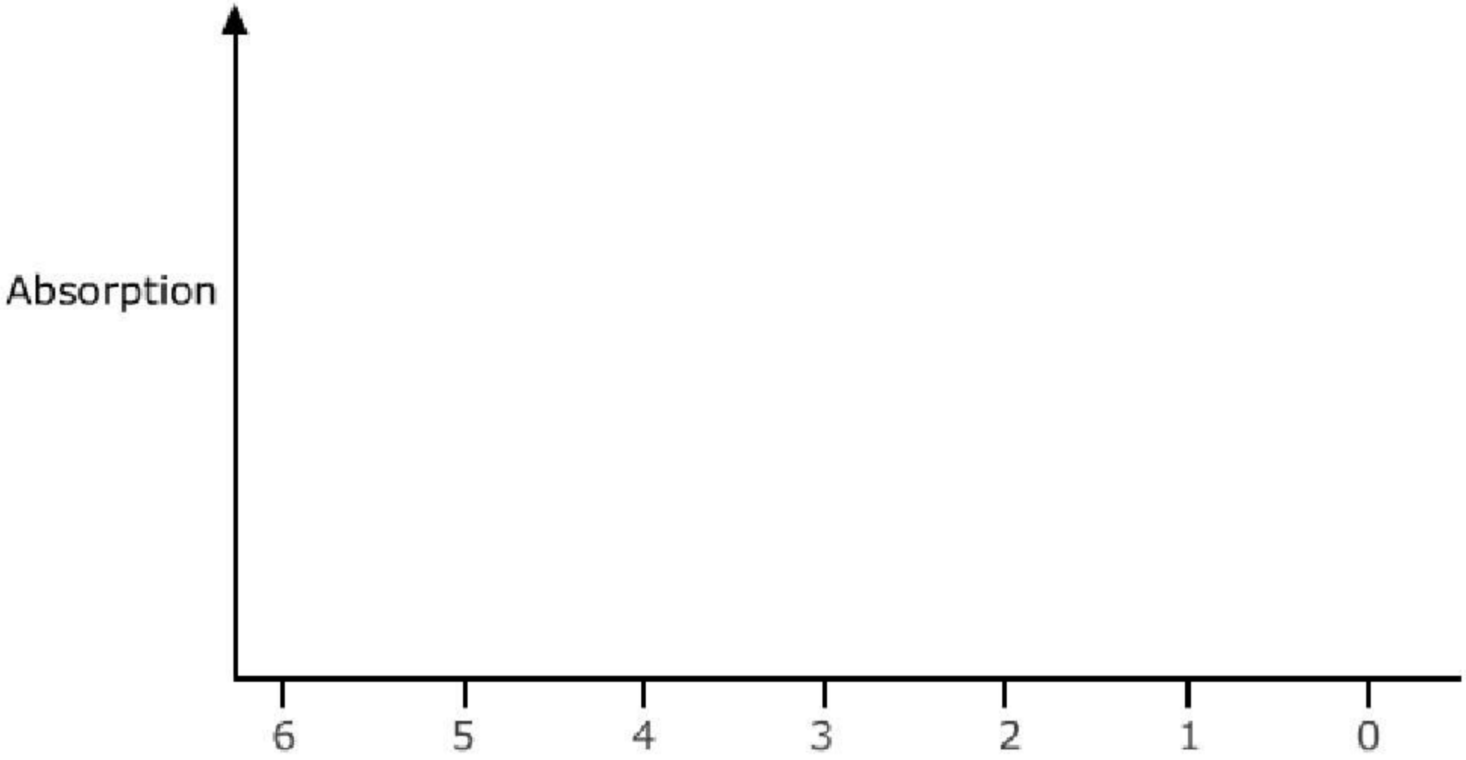
Proton n.m.r. spectroscopy

Example



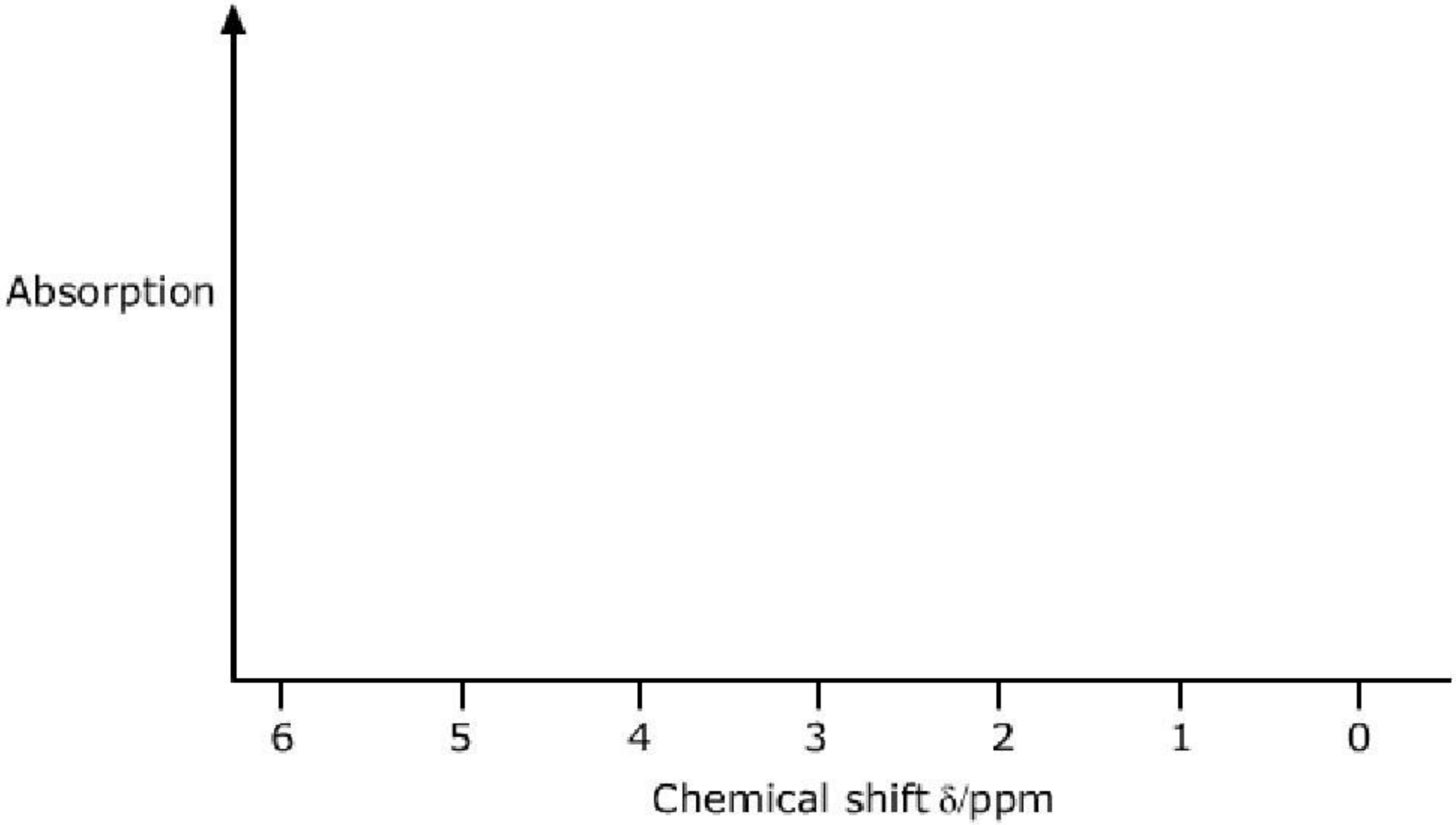
Let's look at an **n.m.r. spectrum** for ethanol, CH_3CH_2OH.

Proton n.m.r. spectroscopy



Notice that zero is on the right on the horizontal axis.

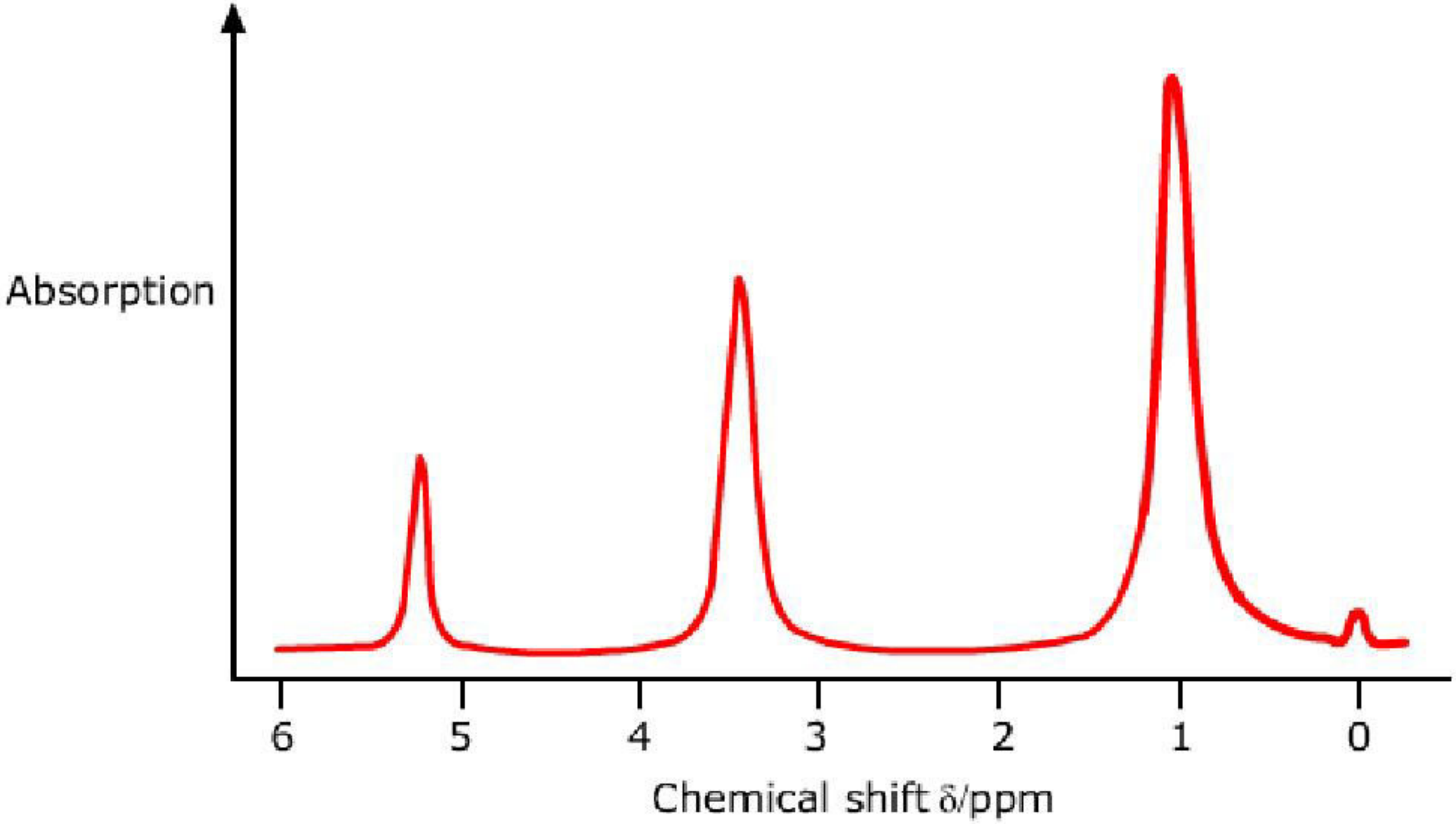
Proton n.m.r. spectroscopy



The horizontal axis represents the **chemical shift**. This is given the symbol δ (delta) and it is measured in parts per million (**ppm**).

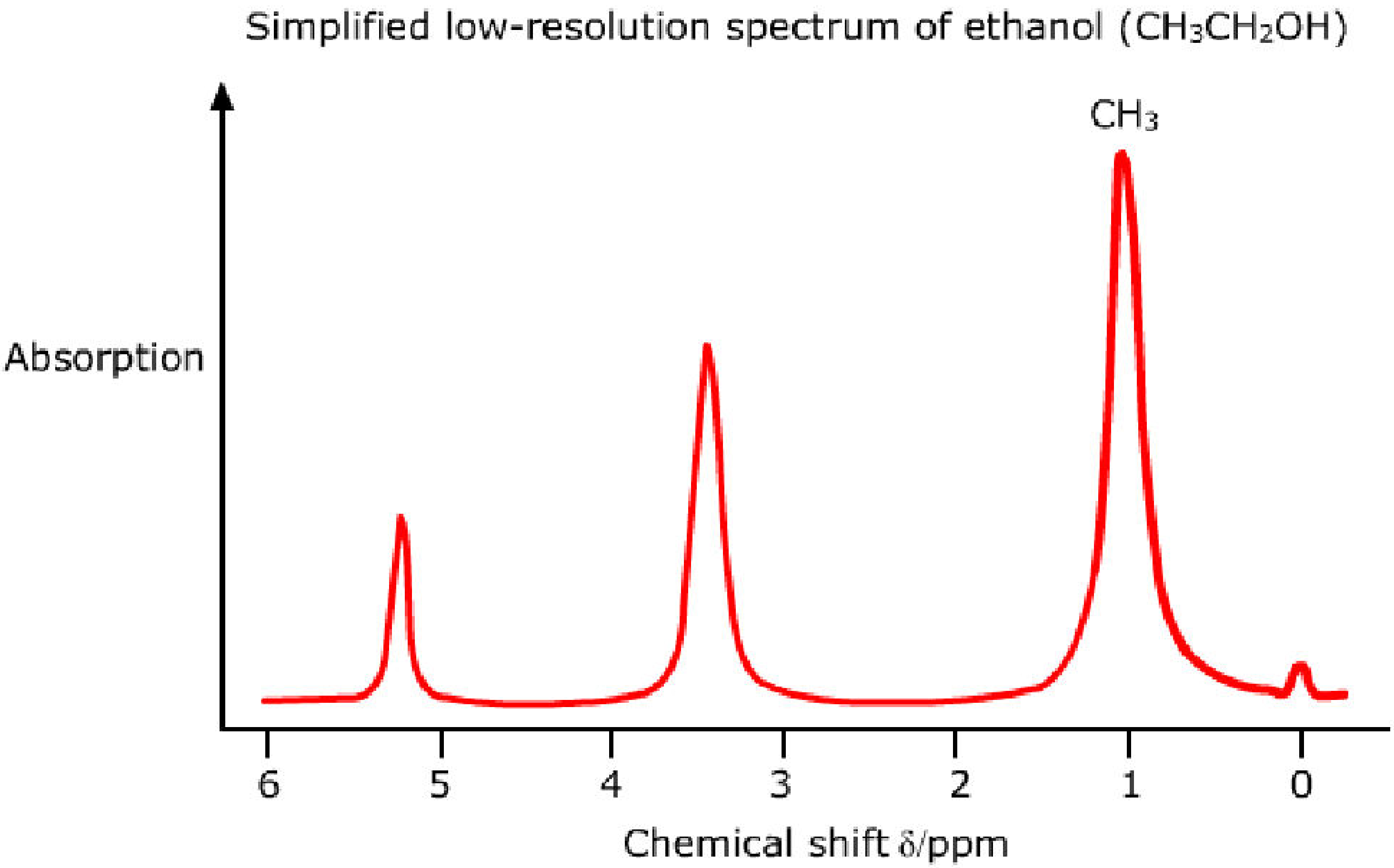
Proton n.m.r. spectroscopy

Simplified low-resolution spectrum of ethanol (CH_3CH_2OH)



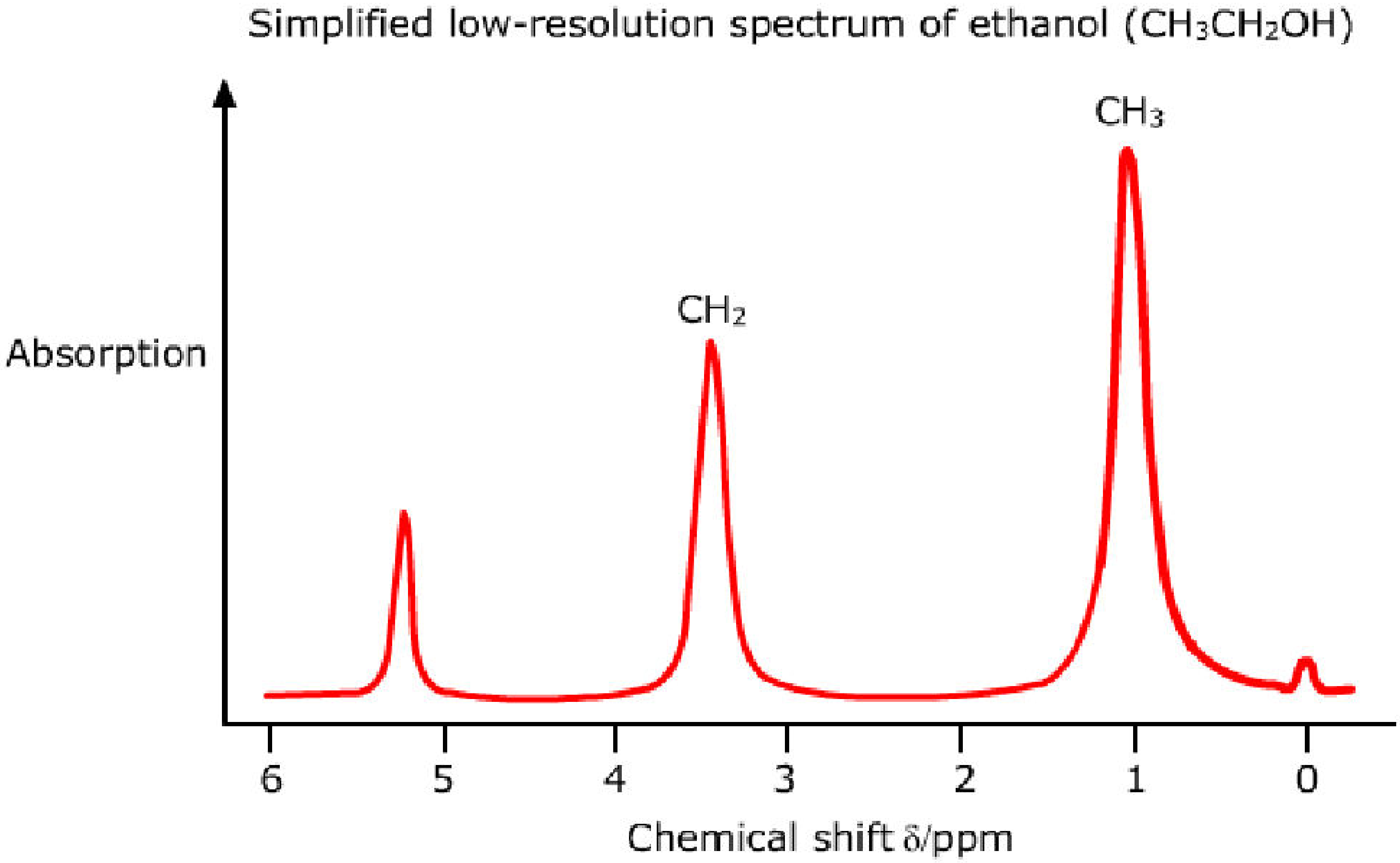
This is a simplified low-resolution spectrum for ethanol.

Proton n.m.r. spectroscopy



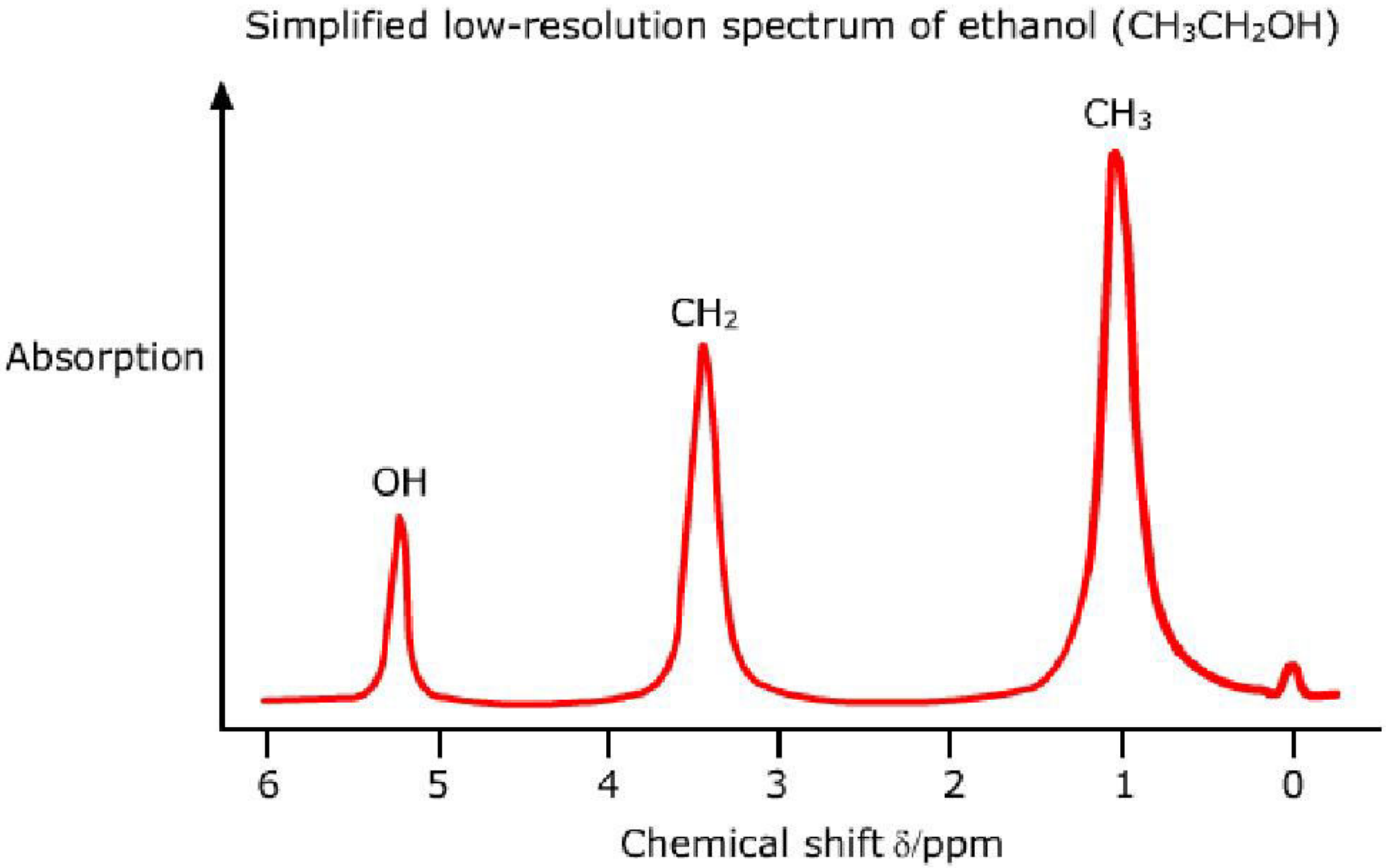
The three hydrogen atoms in the CH_3 group produce this peak.

Proton n.m.r. spectroscopy



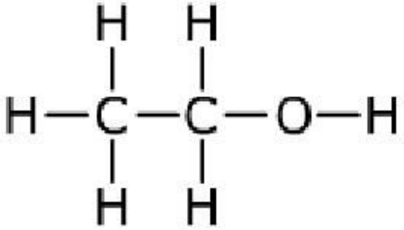
The two hydrogen atoms in the CH_2 group produce this peak.

Proton n.m.r. spectroscopy



The hydrogen atom in the OH group produces this peak.

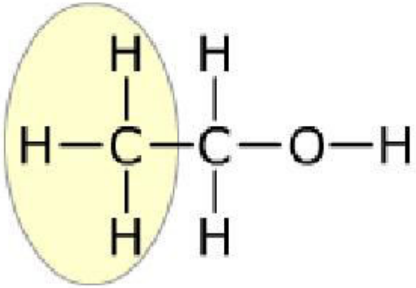
Proton n.m.r. spectroscopy



ethanol

This is the displayed formula for ethanol. How many different chemical environments does it have?

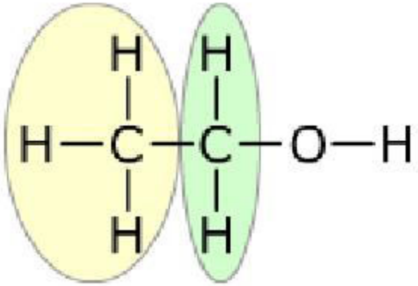
Proton n.m.r. spectroscopy



ethanol

There are three equivalent hydrogen atoms in this chemical environment.

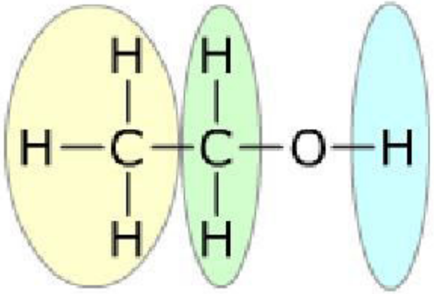
Proton n.m.r. spectroscopy



ethanol

There are two equivalent hydrogen atoms in this chemical environment.

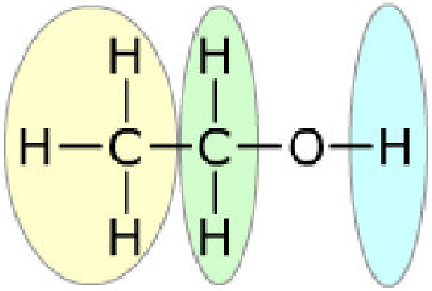
Proton n.m.r. spectroscopy



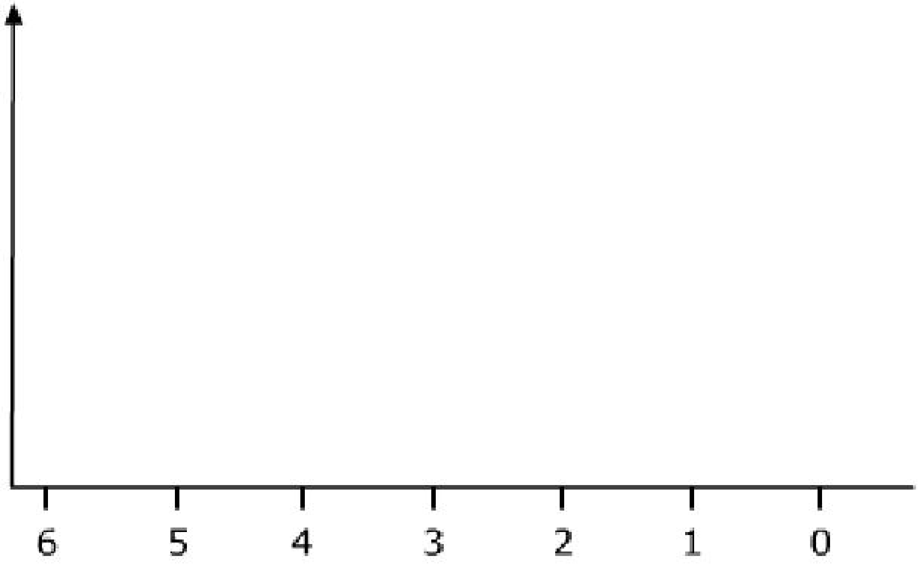
ethanol

There is just one hydrogen atom in this chemical environment.

Proton n.m.r. spectroscopy

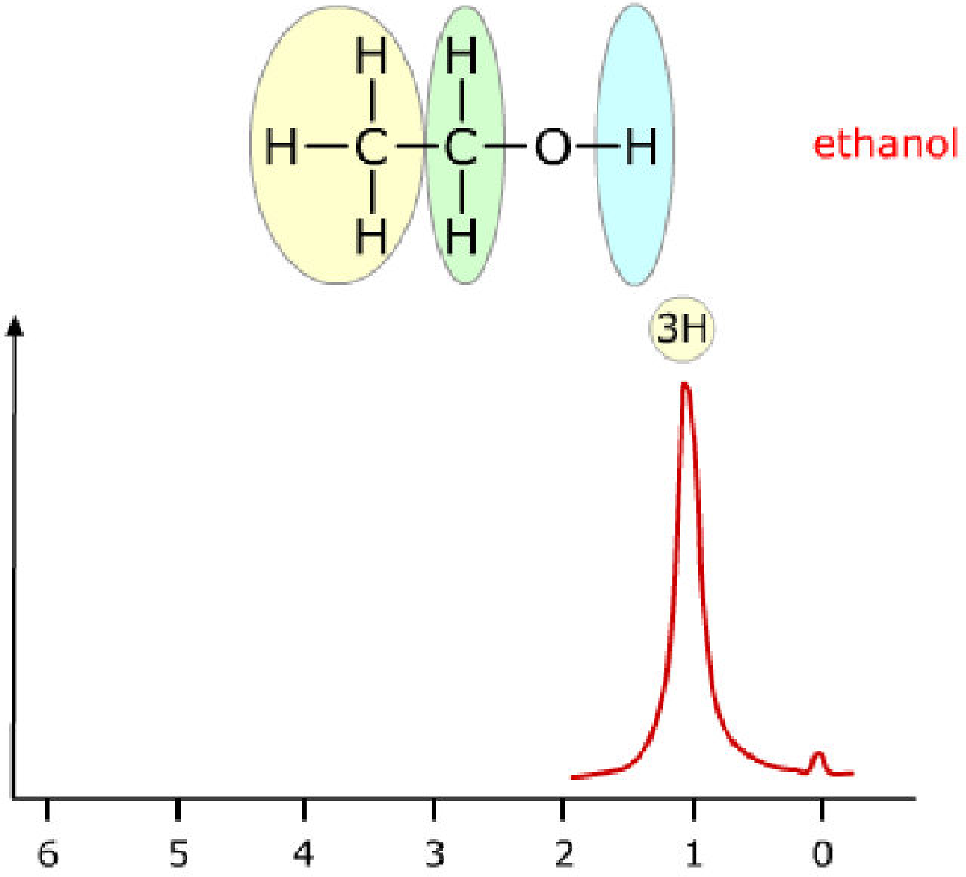


ethanol



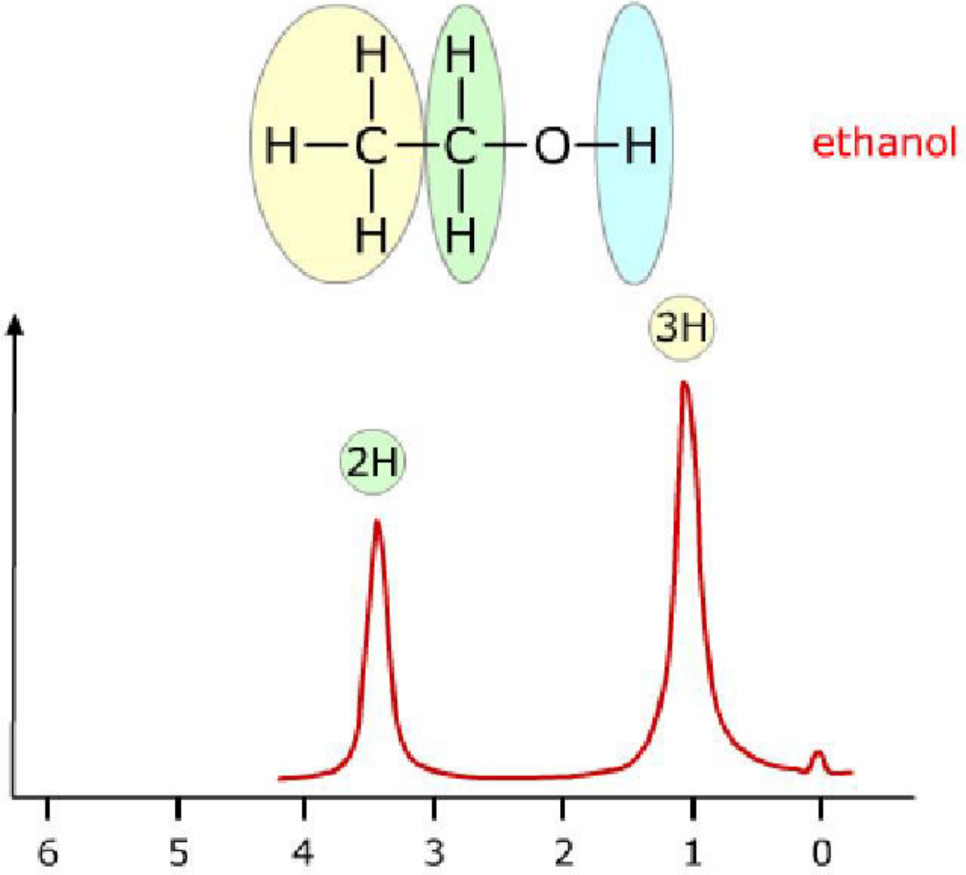
What peaks would we expect in a low-resolution n.m.r. spectrum of ethanol?

Proton n.m.r. spectroscopy



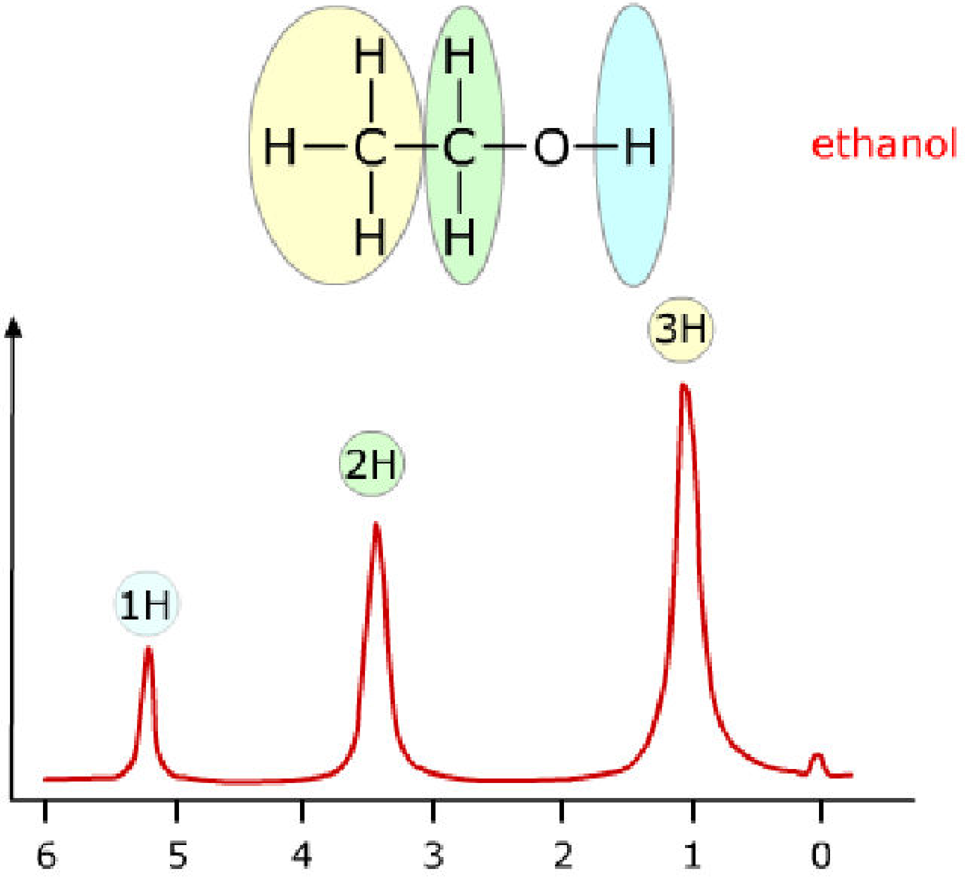
The CH$_3$ group contains three hydrogen atoms, which form a large peak

Proton n.m.r. spectroscopy



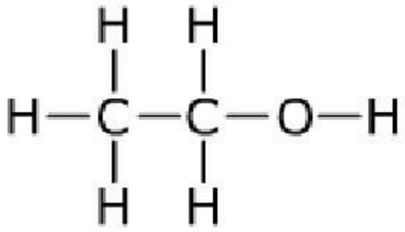
The CH_2 group contains two hydrogen atoms, which form a smaller peak.

Proton n.m.r. spectroscopy

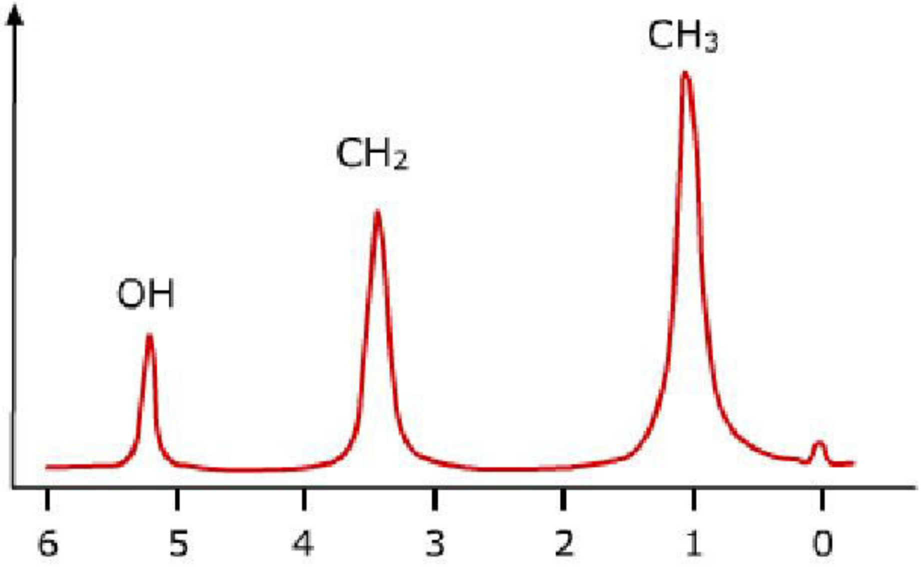


The OH group contains one hydrogen atom, which forms a small peak.

Proton n.m.r. spectroscopy

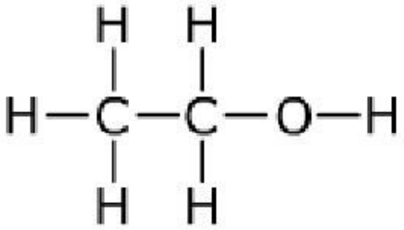


$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H}$$

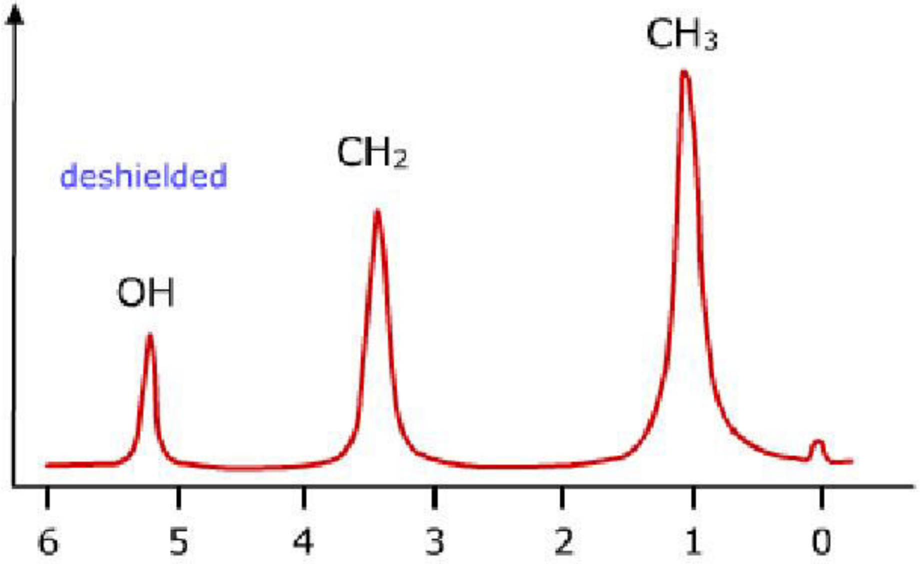


The position of each peak on the n.m.r. spectrum gives us information about the corresponding chemical environment.

Proton n.m.r. spectroscopy

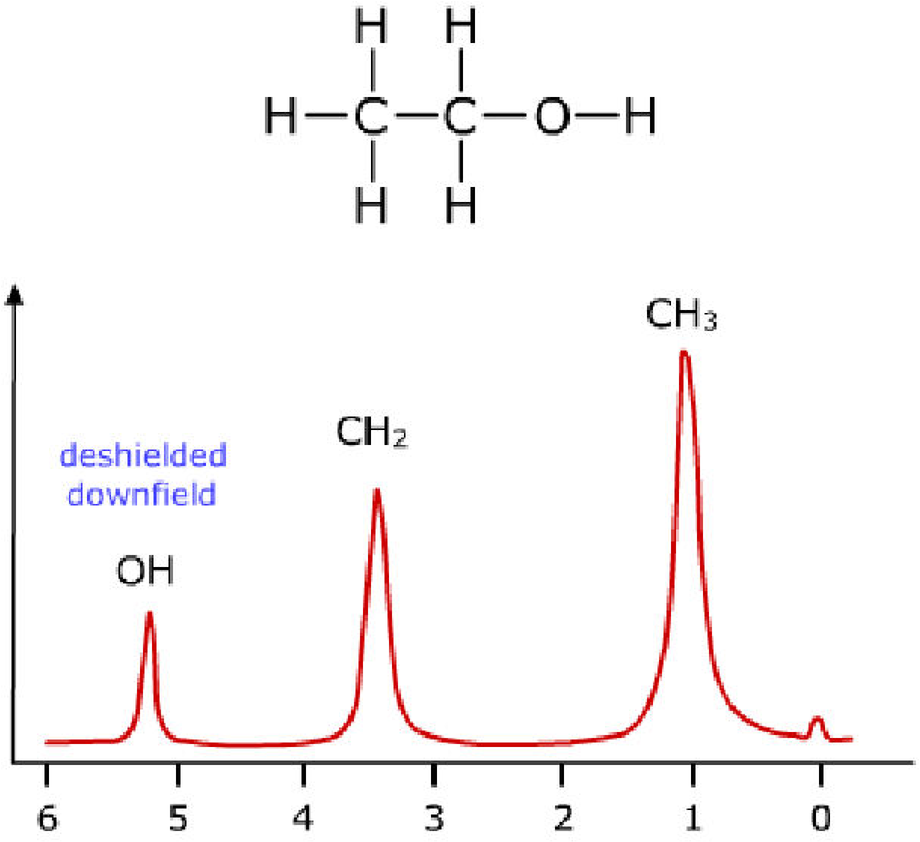


$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H}$$



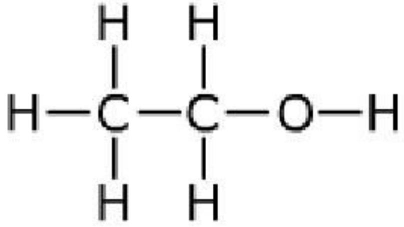
The hydrogen atom in the OH group is attached to an oxygen atom, which is very electronegative. A hydrogen atom like this is **deshielded**.

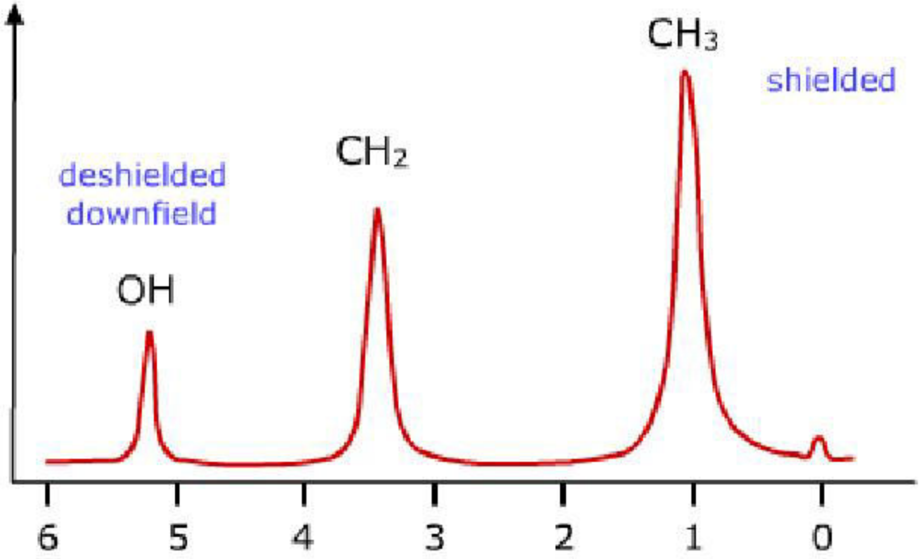
Proton n.m.r. spectroscopy



The peak it produces is shifted **downfield** in the spectrum.

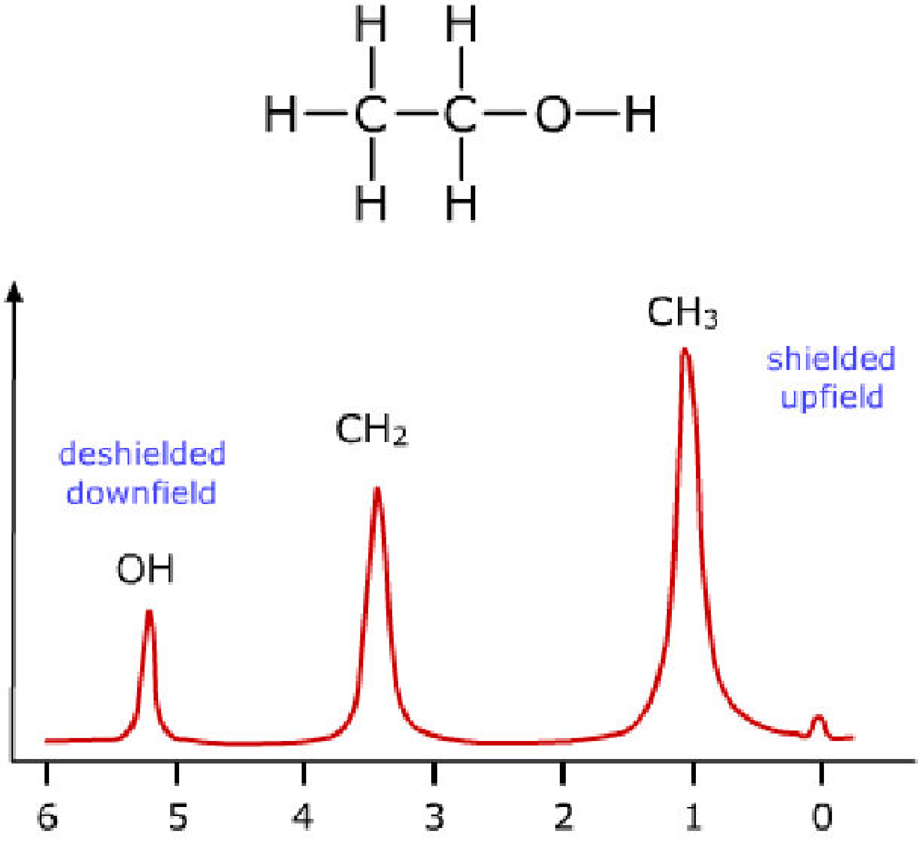
Proton n.m.r. spectroscopy





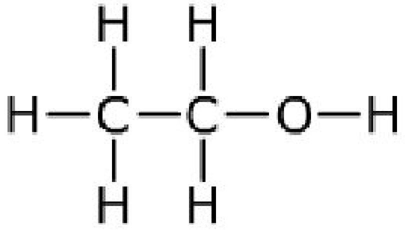
The hydrogen atoms in the CH_3 group are far from the oxygen atom. They are **shielded**.

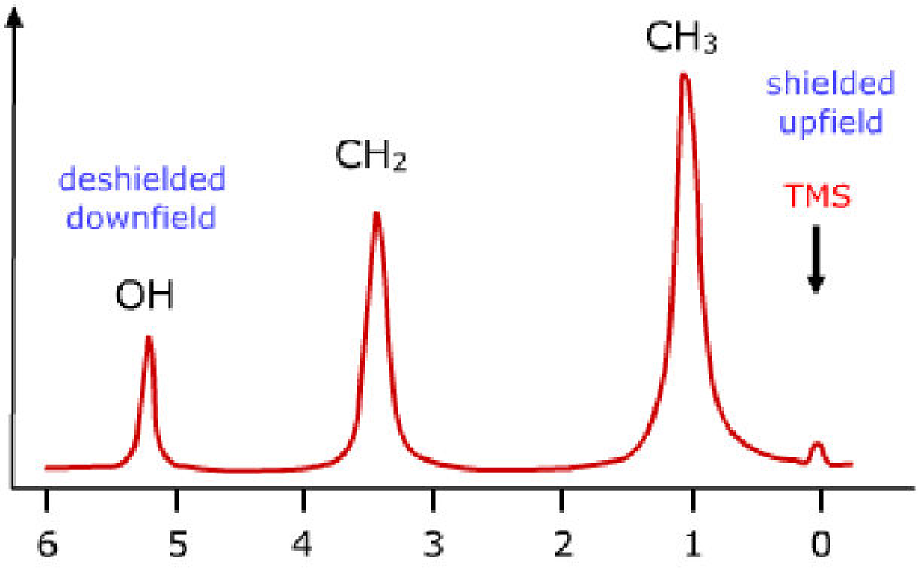
Proton n.m.r. spectroscopy



The peak they produce is **upfield** in the spectrum, close to 0 ppm.

Proton n.m.r. spectroscopy

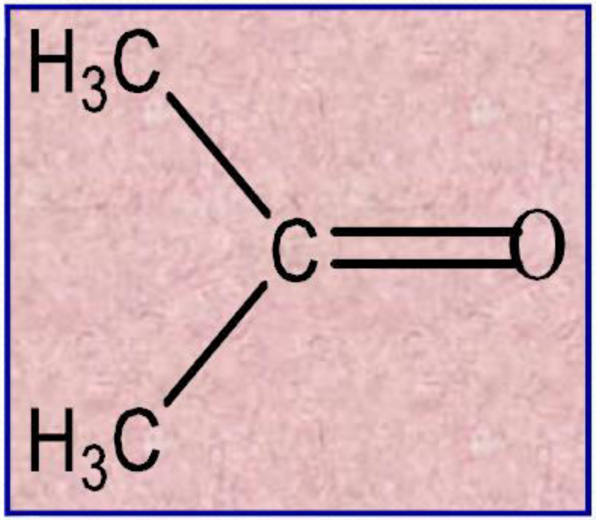




Chemical shifts are measured relative to the peak produced by a standard substance, called **TMS**. By definition, δ is 0 for TMS.

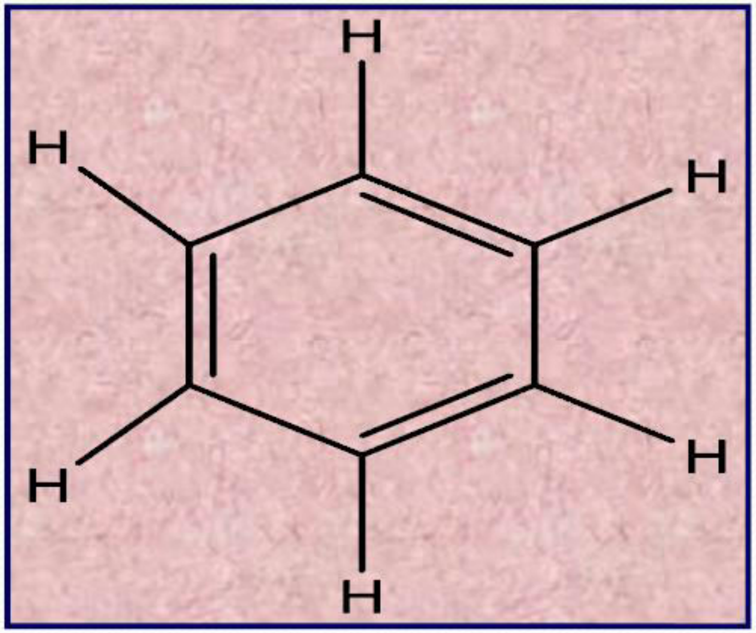
Prediction of Signal Number

Acetone



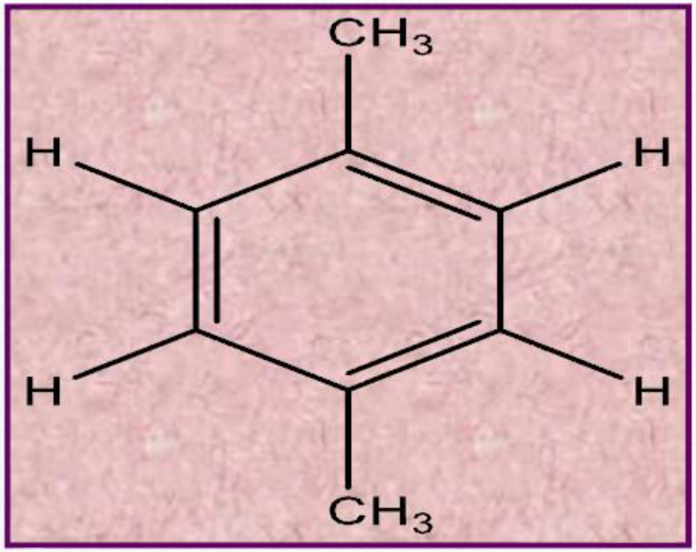
(one signal)

Benzene



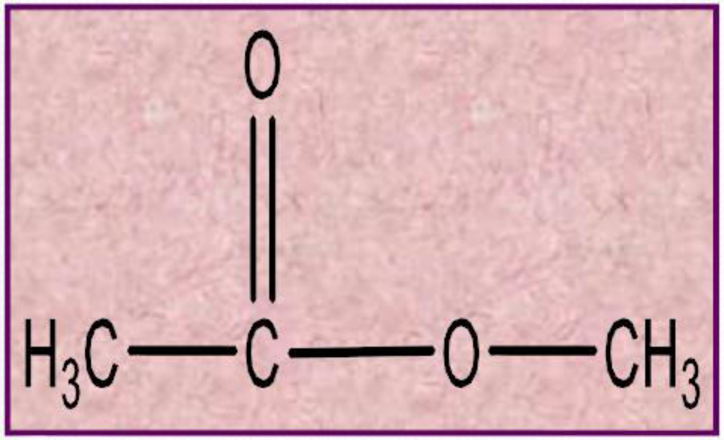
(one signal)

p- xylene



(Two NMR signals)

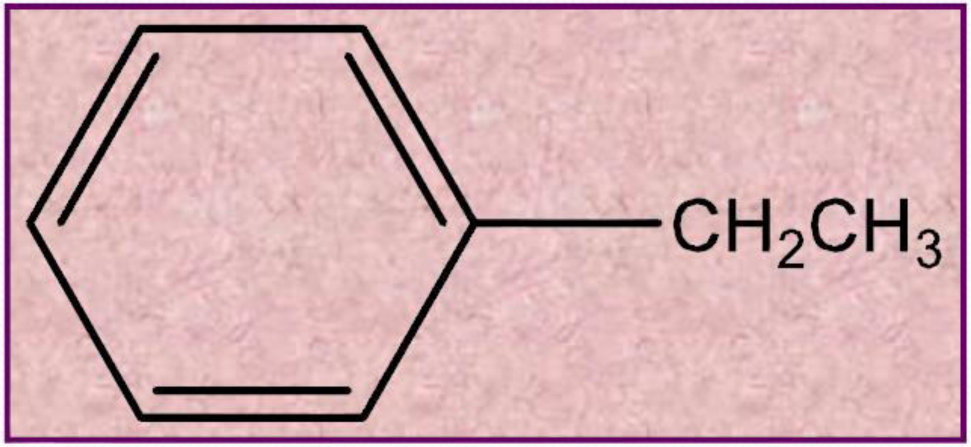
Methyl Acetate



$H_3C-C(=O)-O-CH_3$

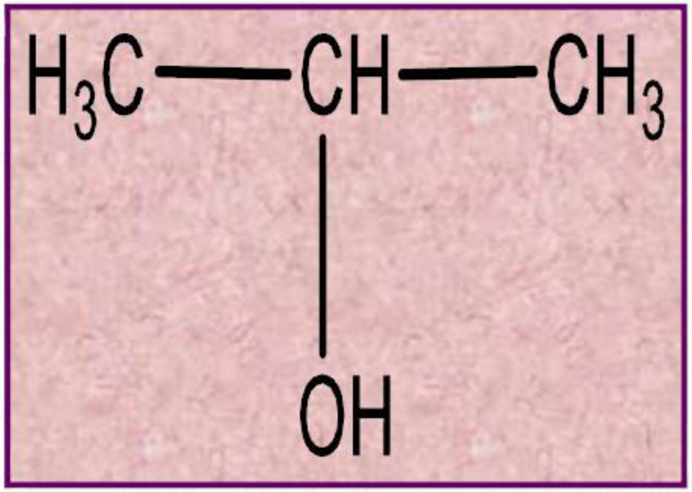
(Two NMR signals)

Ethyl benzene



(Three NMR signals)

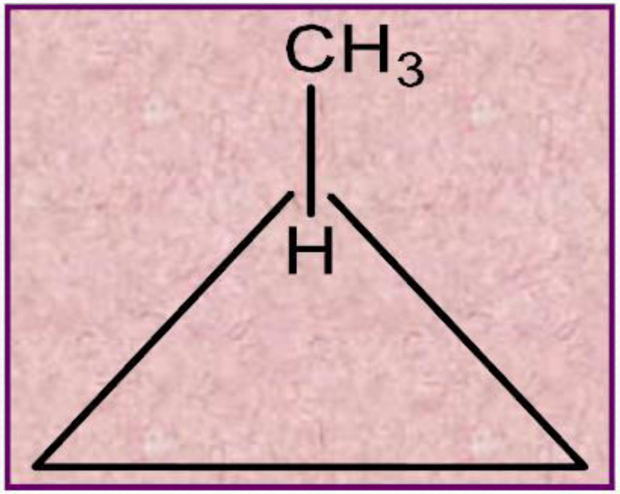
Propane2-ol



$H_3C-CH(OH)-CH_3$

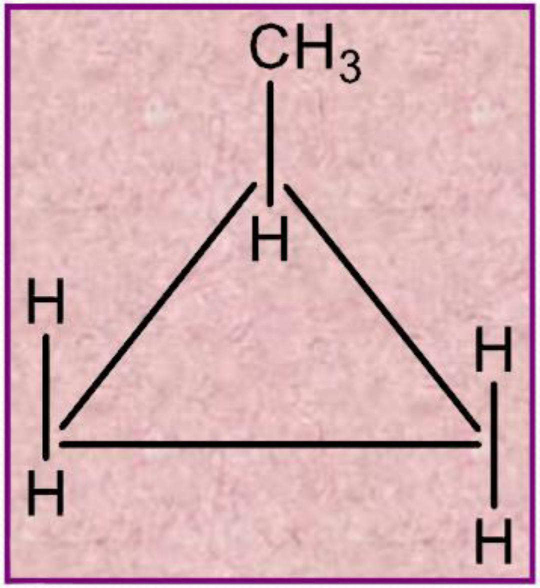
(3 NMR signals)

Methyl cyclopropane



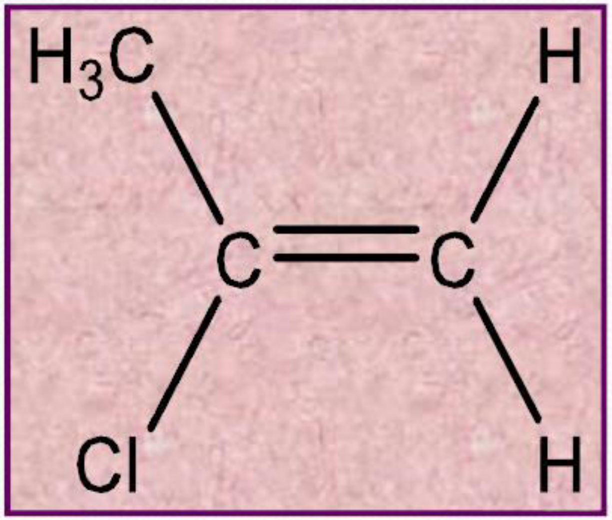
(Three signals)

Wrong



(4 signals)

2- chloropropene



Three signal

INTEGRATION

INTEGRATION OF A PEAK

Not only does each different type of hydrogen give a distinct peak in the NMR spectrum, but we can also tell the relative numbers of each type of hydrogen by a process called integration.

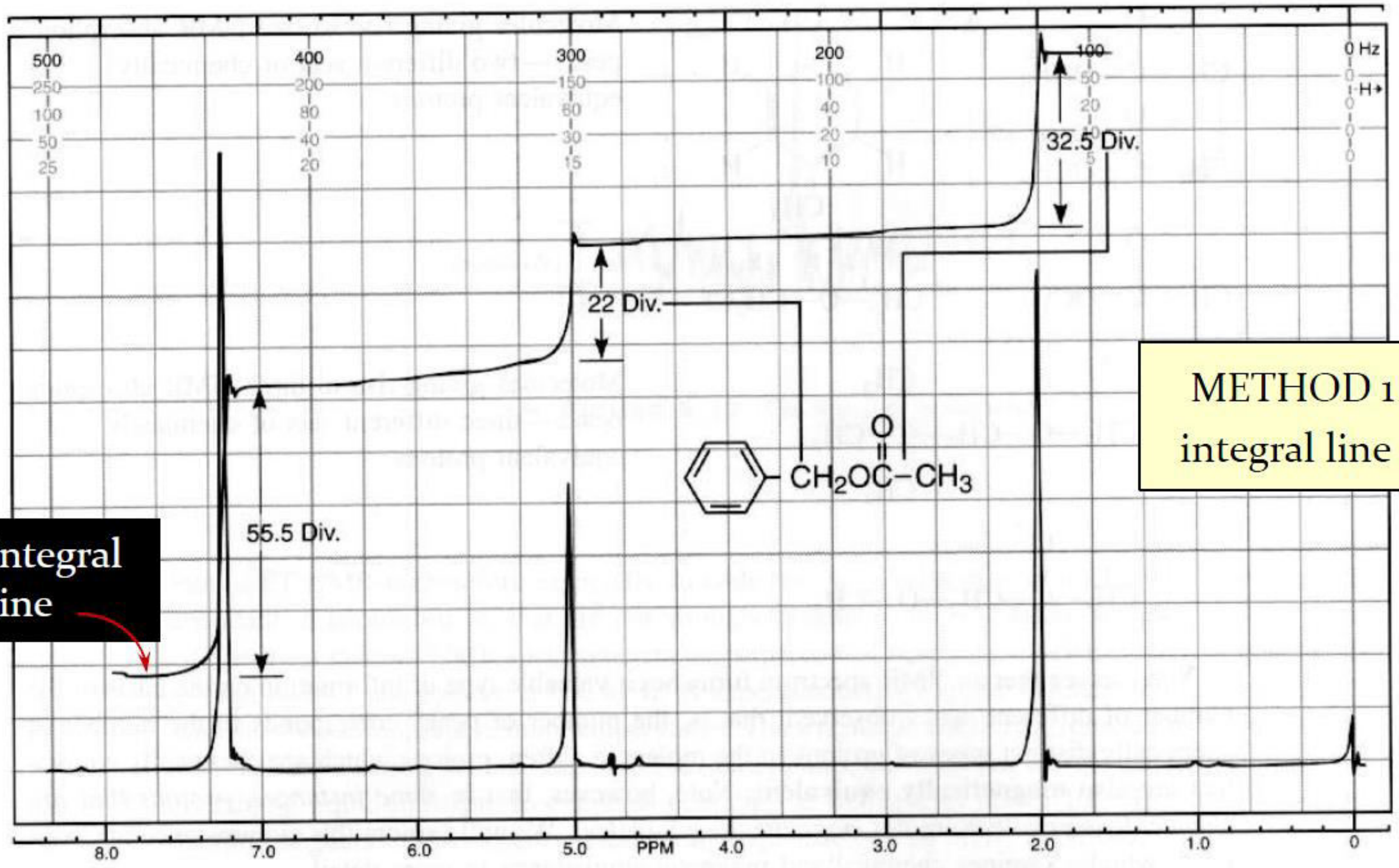
Integration = determination of the area under a peak

The area under a peak is proportional to the number of hydrogens that generate the peak.

Integration of Peak

Benzyl Acetate

The integral line rises an amount proportional to the number of H in each peak



METHOD 1
integral line

integral line

55 : 22 : 33 = 5 : 2 : 3

simplest ratio
of the heights

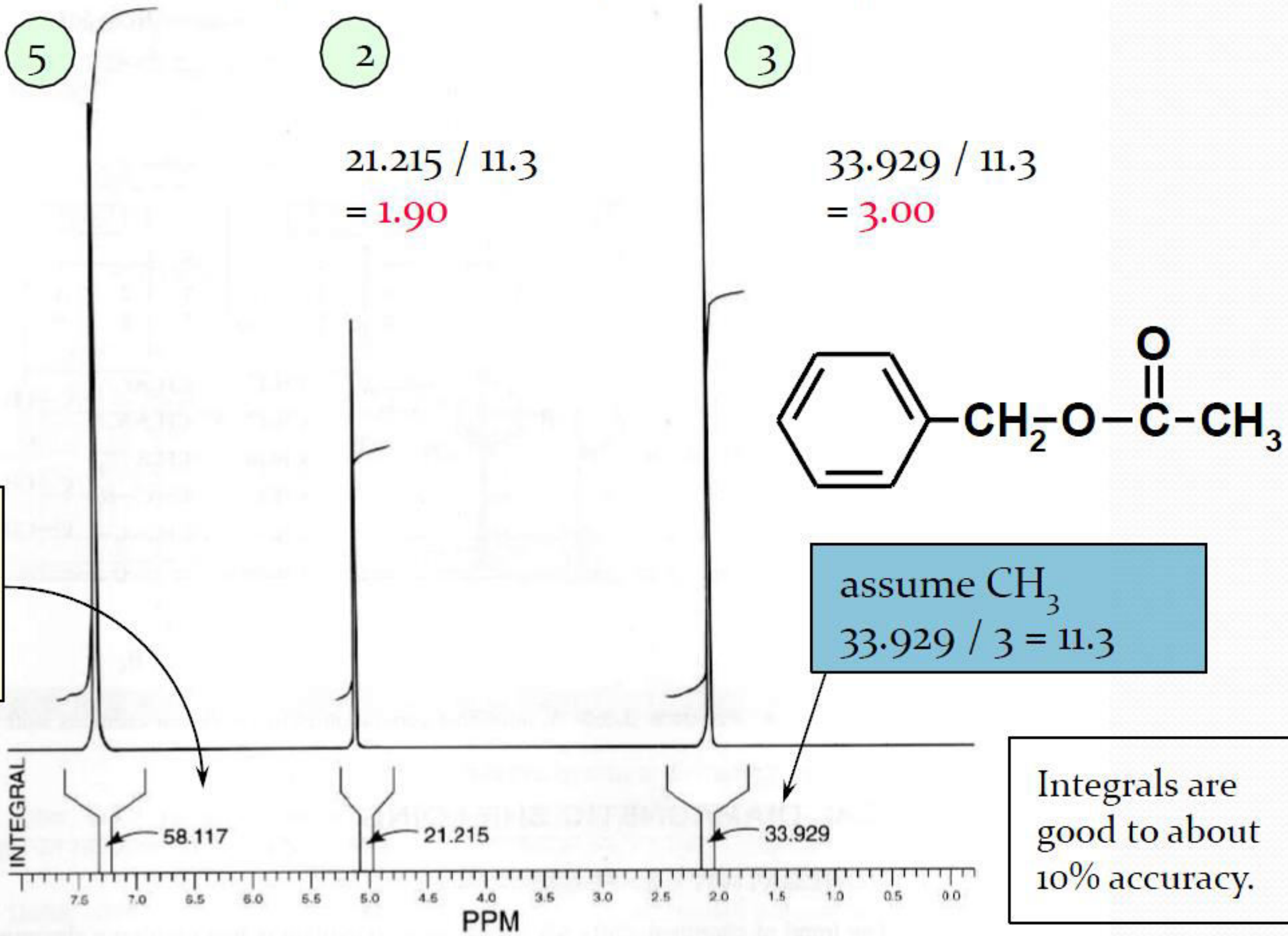
Benzyl Acetate (FT-NMR)

Actually :

58.117 / 11.3
= 5.14

21.215 / 11.3
= 1.90

33.929 / 11.3
= 3.00

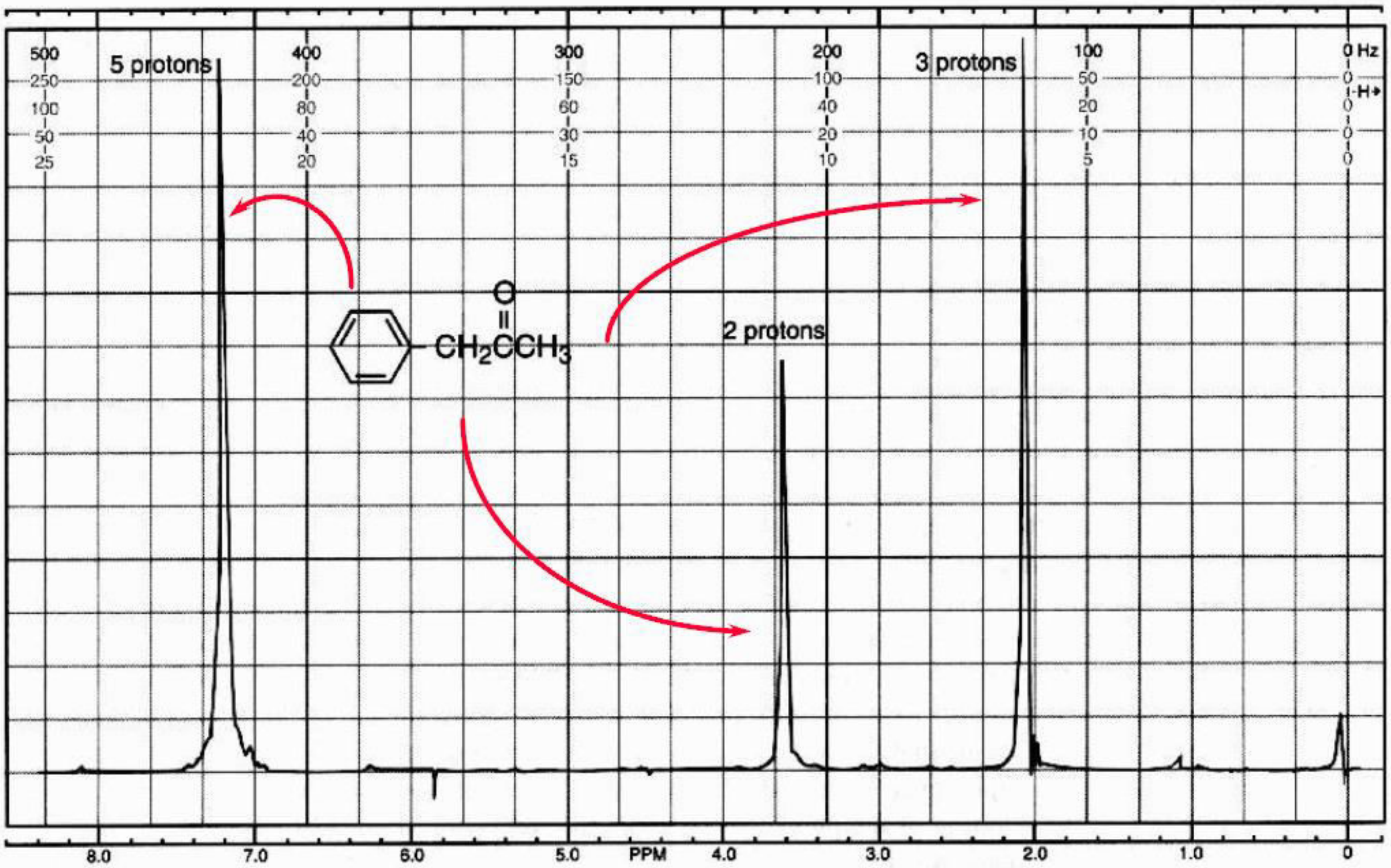


METHOD 2
digital
integration

assume CH_3
33.929 / 3 = 11.3

Integrals are good to about 10% accuracy.

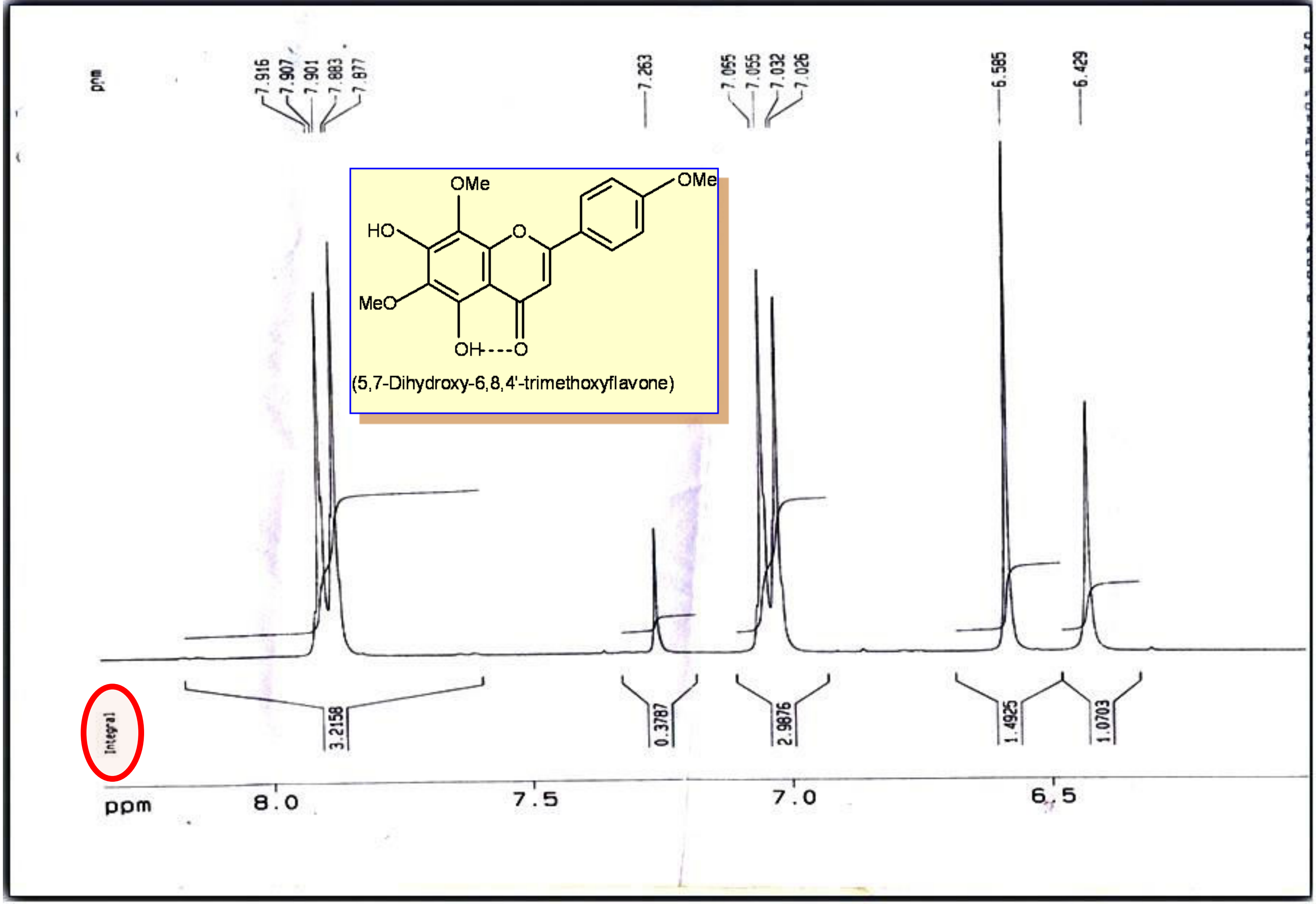
Modern instruments report the integral as a number.



Each different type of proton comes at a different place .

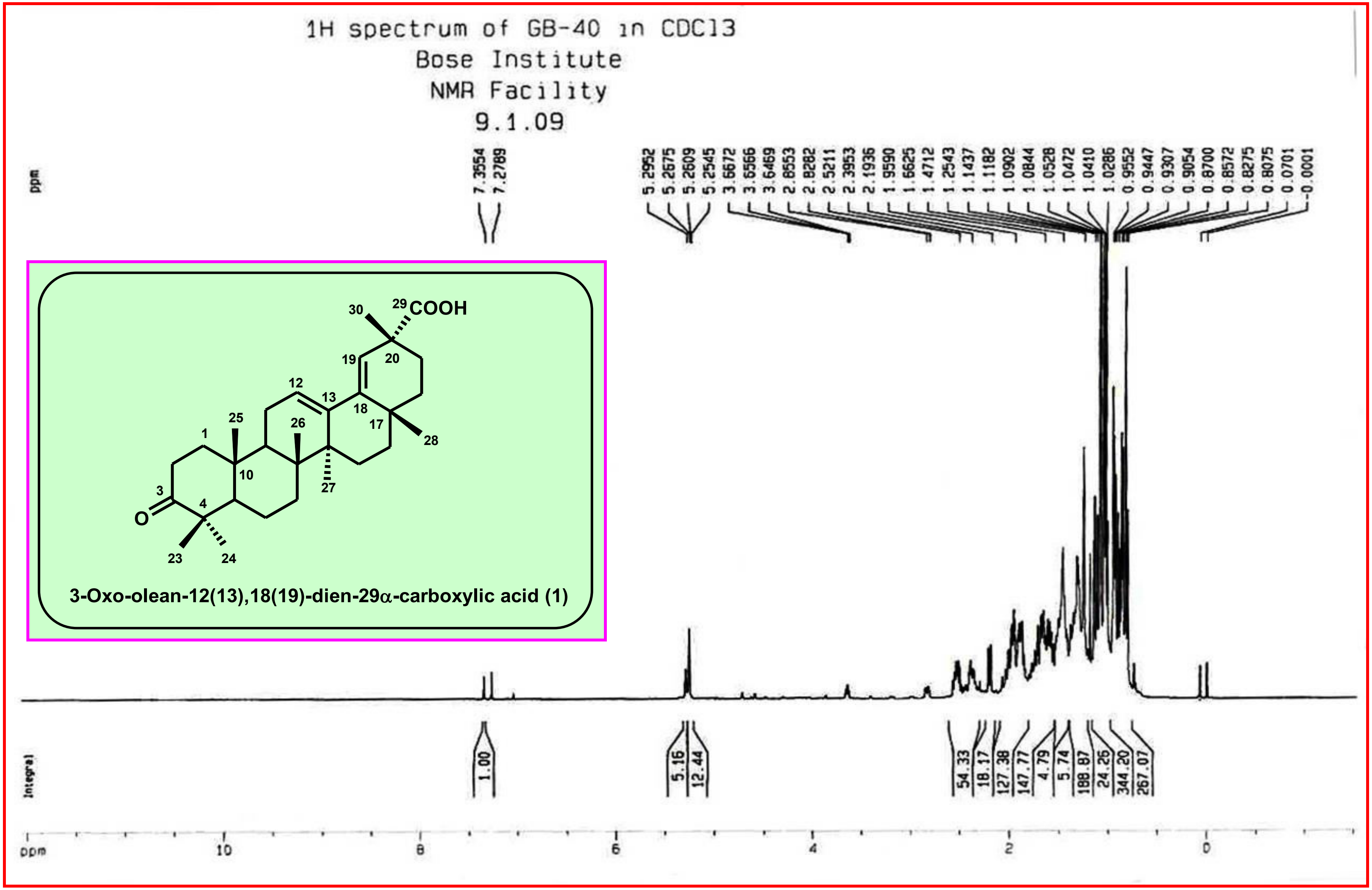
NMR Spectrum of Phenyl acetone

ORIGINAL SPECTURM OF A FLAVONE



(5,7-Dihydroxy-6,8,4'-trimethoxyflavone)

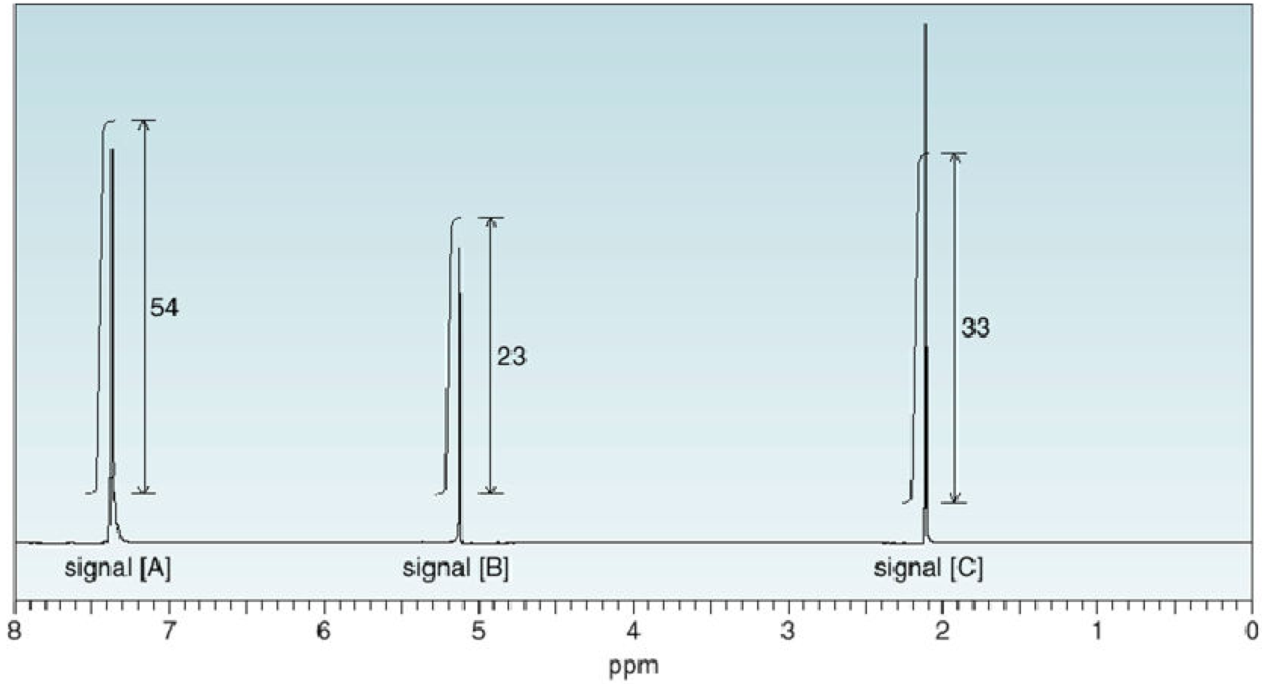
ORIGINAL SPECTURM OF A TRITERPENOID



3-Oxo-olean-12(13),18(19)-dien-29α-carboxylic acid (1)

How To Determine the Number of Protons Giving Rise to an NMR Signal

Example A compound of molecular formula $C_9H_{10}O_2$ gives the following integrated ^1H NMR spectrum. How many protons give rise to each signal?



Step [1] **Determine the number of integration units per proton by dividing the total number of integration units by the total number of protons.**

- Total number of integration units: 54 + 23 + 33 = 110 units
- Total number of protons = 10
- Divide: 110 units/10 protons = **11 units per proton**

Step [2] **Determine the number of protons giving rise to each signal.**

- To determine the number of H atoms giving rise to each signal, divide each integration value by the answer of Step [1] and round to the nearest whole number.

Signal [A]: Signal [B]: Signal [C]:

Answer: $\frac{54}{11} = 4.9 \approx \boxed{\mathbf{5\ H}}$ | $\frac{23}{11} = 2.1 \approx \boxed{\mathbf{2\ H}}$ | $\frac{33}{11} = \boxed{\mathbf{3\ H}}$

SPIN-SPIN SPLITTING

SPLITTING OF THE SIGNALS

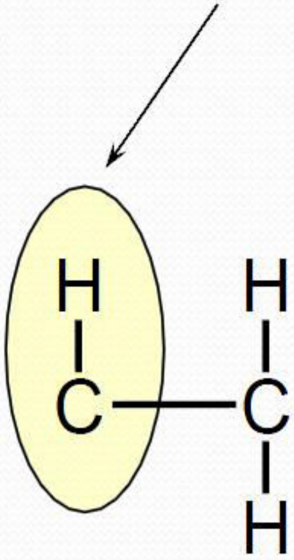
- Each signals in NMR spectrum represents one kind or one set of protons in the molecule.
- In certain molecules, instead of a single peak a group of peaks are observed.
- This phenomena of splitting of proton signals into two or more sub-peaks are referred as splitting.
- The splitting pattern of a given nucleus can be predicted by the ***n+1* rule**, where ***n*** is the number of protons on the neighboring carbon.
- The simplest multiplicities are **singlet** ($n = 0$), **doublets** ($n = 1$ or coupling to just one proton), **triplets** ($n = 2$), **quartets** ($n = 3$), **quintets** ($n = 4$), **sextets** ($n = 5$) and **septets** ($n = 6$).

$n + 1$ RULE

Where “n” mean neighboring Hydrogen

MULTIPLETS

this hydrogen's peak
is split by its two neighbors

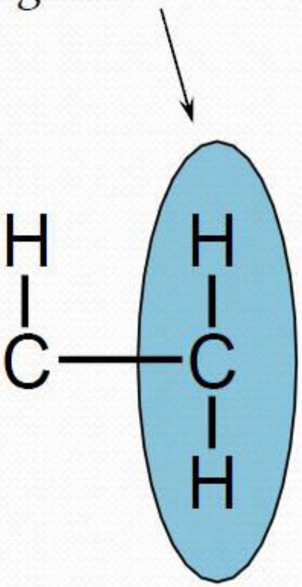


two neighbors

n+1 = 3

triplet

these hydrogens are
split by their single
neighbor



one neighbor

n+1 = 2

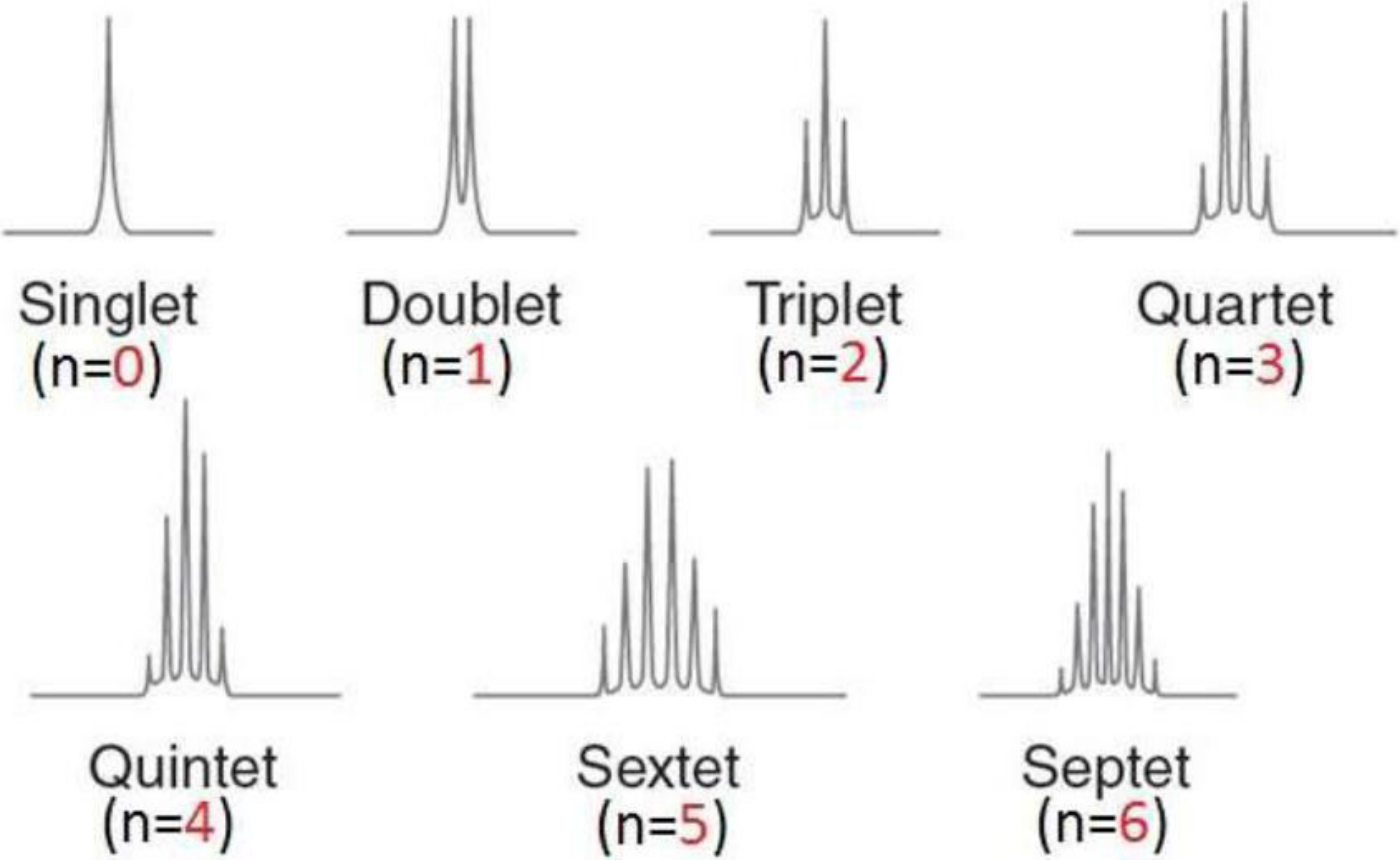
doublet

- singlet
- doublet
- triplet
- quartet
- quintet
- sextet
- septet

PASCAL'S TRIANGLE

The interior entries are the sums of the two numbers immediately above.

Intensities of multiplet peaks	
1	singlet
1 1	doublet
1 2 1	triplet
1 3 3 1	quartet
1 4 6 4 1	quintet
1 5 10 10 5 1	sextet
1 6 15 20 15 6 1	septet
1 7 21 35 35 21 7 1	octet

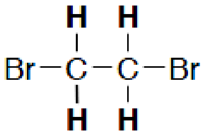

Singlet
(n=0)
Doublet
(n=1)
Triplet
(n=2)
Quartet
(n=3)
Quintet
(n=4)
Sextet
(n=5)
Septet
(n=6)

One proton on an adjacent carbon will split a proton into a **doublet** (d), two peaks of 1:1 relative intensity

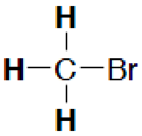
Two proton on an adjacent carbon will split a proton into a **triplet** (t), three peaks of 1:2:1 relative intensity

Three proton on an adjacent carbon will split a proton into a **quartet** (q), four peaks of 1:3:3:1 relative intensity

Equivalent protons do not show spin-spin coupling

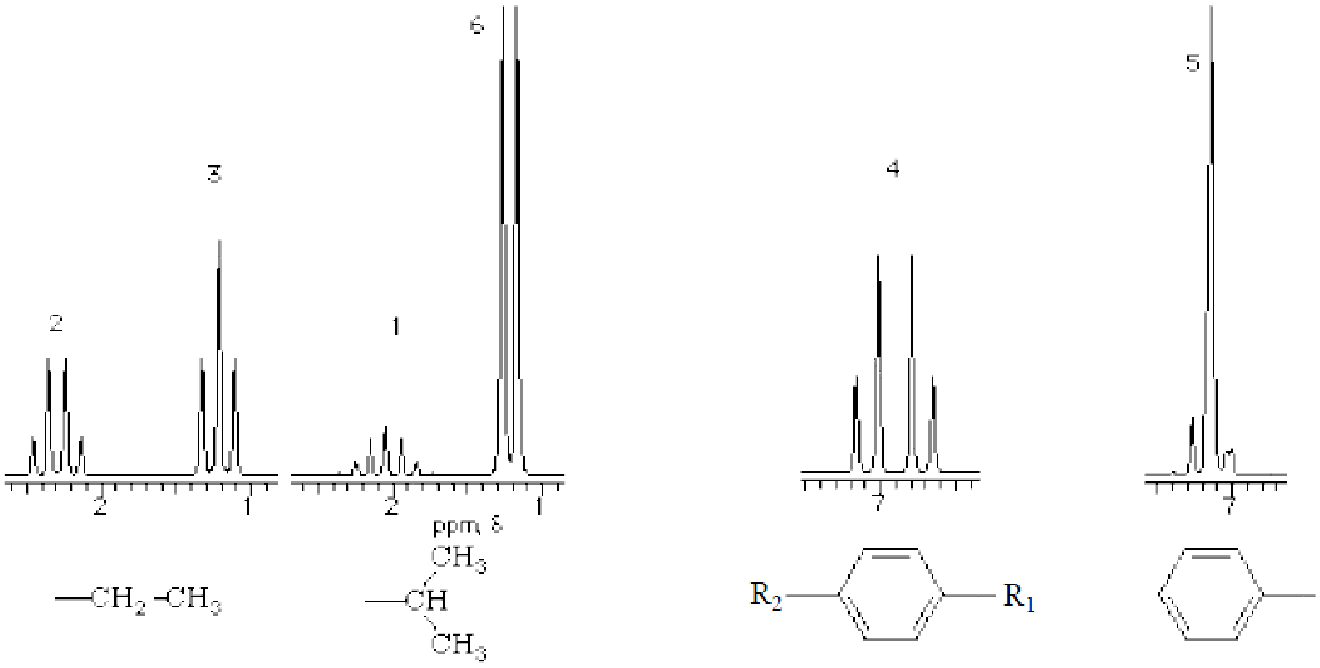


$BrCH_2CH_2Br$



CH_3Br

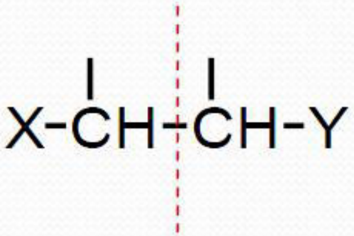
Singlet (s)



EXCEPTIONS TO THE N+1 RULE

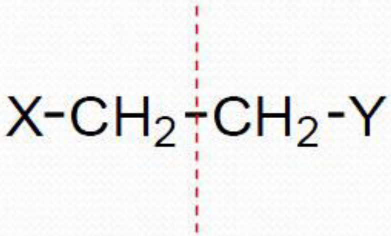
IMPORTANT !

1) Protons that are <u>equivalent by symmetry</u> usually do not split one another



$X-\overset{|}{C}H-\overset{|}{C}H-Y$

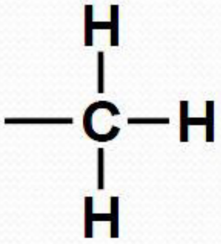
no splitting if x=y



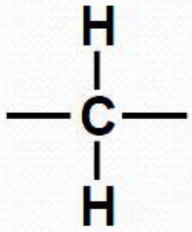
$X-CH_2-CH_2-Y$

no splitting if x=y

2) Protons in the <u>same group</u> usually do not split one another



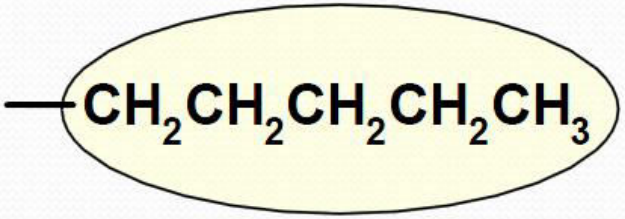
or



more detail later

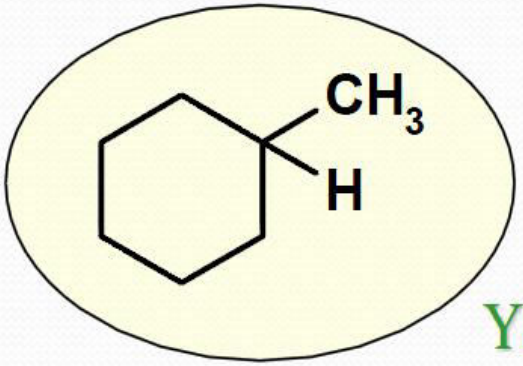
EXCEPTIONS TO THE N+1 RULE

3) The n+1 rule applies principally to protons in aliphatic (saturated) chains or on saturated rings.



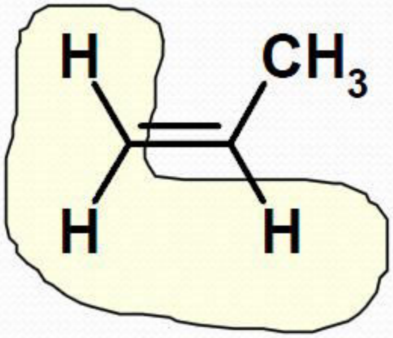
YES

or

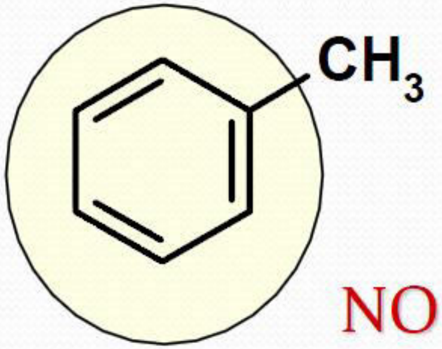


YES

but does not apply (in the simple way shown here) to protons on double bonds or on benzene rings.

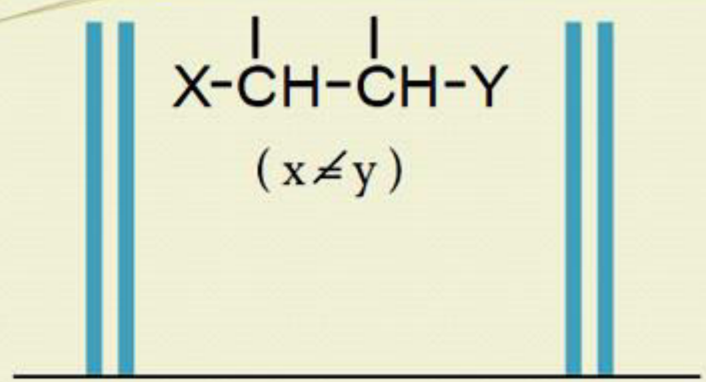


NO



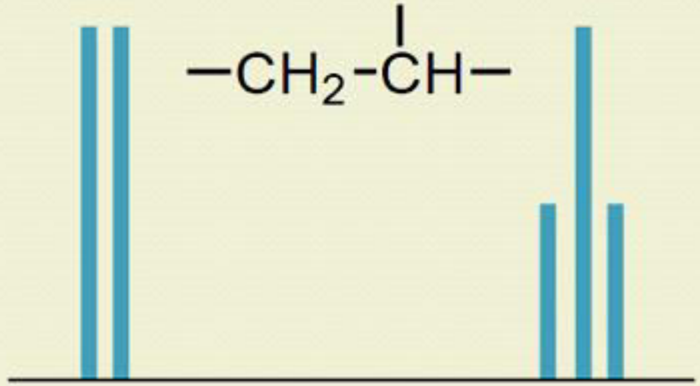
NO

SOME COMMON SPLITTING PATTERNS

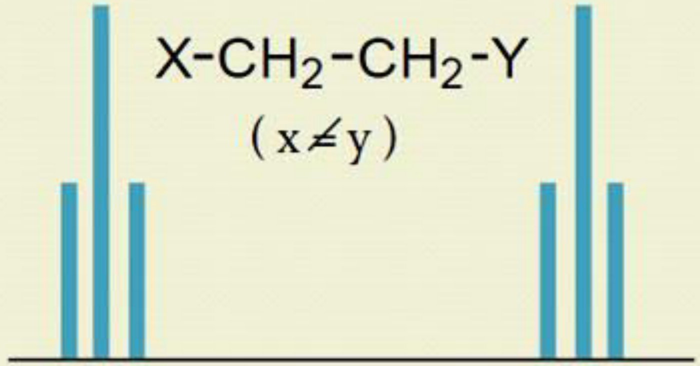


$X\text{-}\overset{|}{C}H\text{-}\overset{|}{C}H\text{-}Y$

(x≠y)

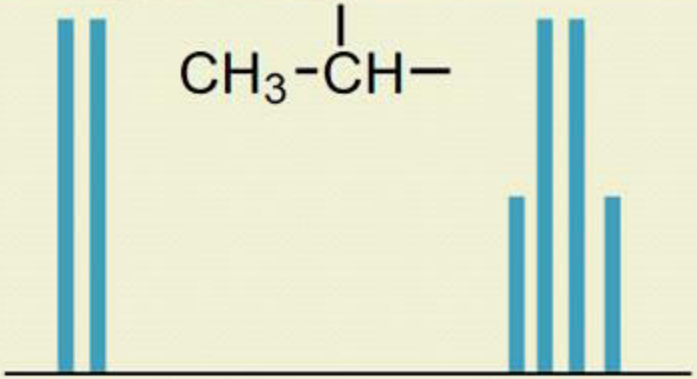


$-CH_2\text{-}\overset{|}{C}H-$

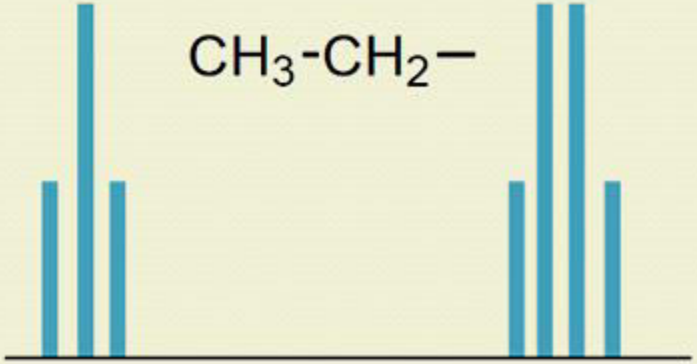


$X\text{-}CH_2\text{-}CH_2\text{-}Y$

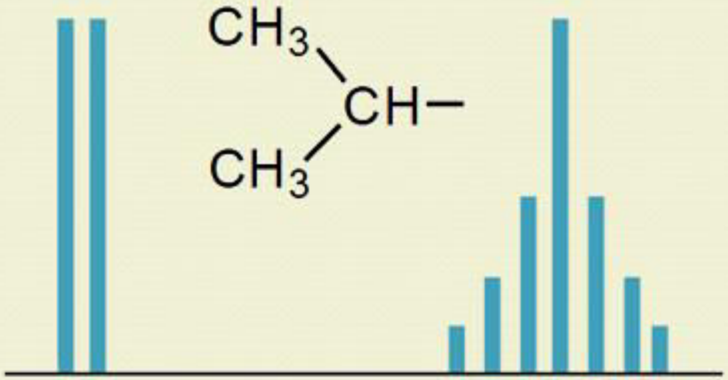
(x≠y)



$CH_3\text{-}\overset{|}{C}H-$

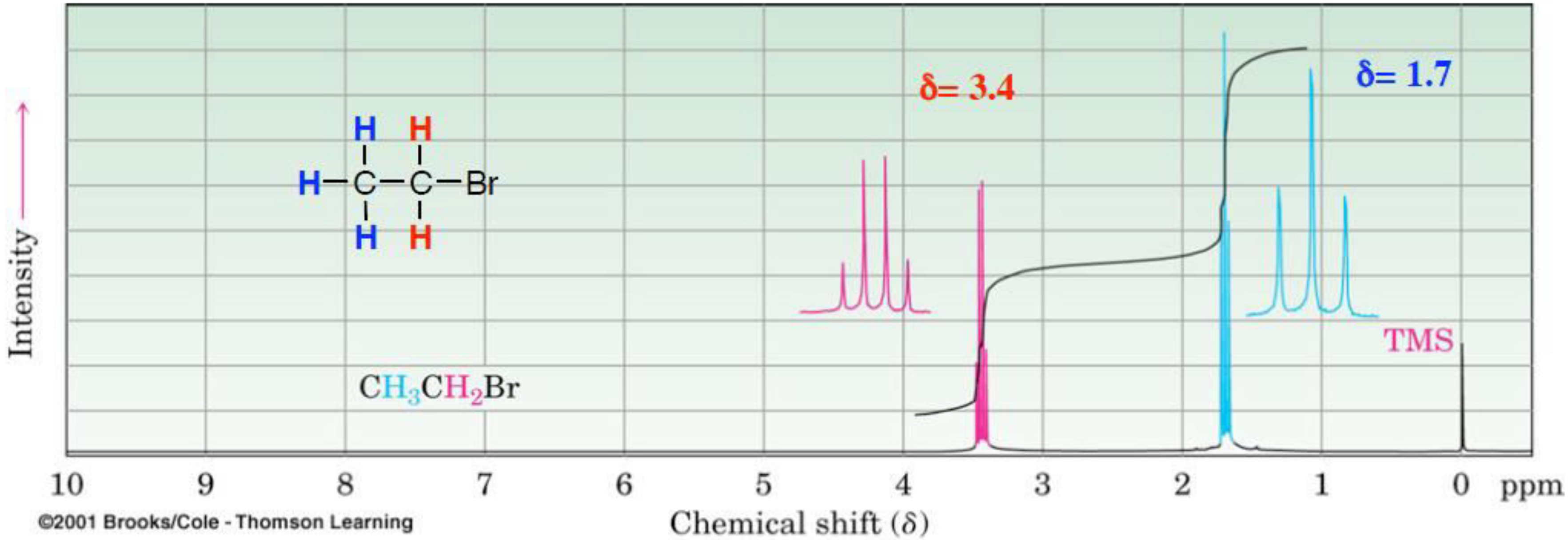


$CH_3\text{-}CH_2-$

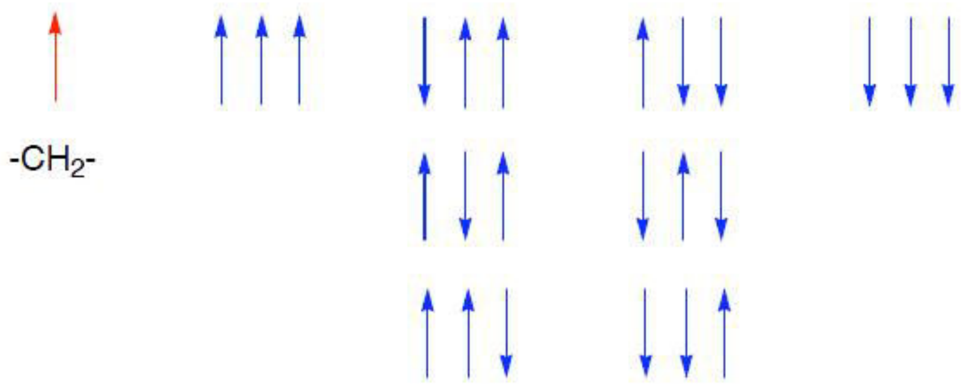


$(CH_3)_2CH-$

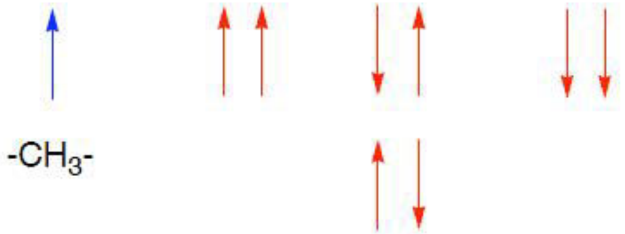
The *multiplicity* is defined by the number of peaks and the pattern



©2001 Brooks/Cole - Thomson Learning



-CH$_2$-



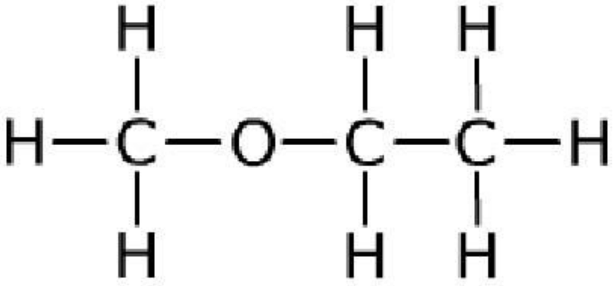
-CH$_3$-

1 : 3 : 3 : 1

1 : 2 : 1

SOME EXAMPLE SPECTRA WITH SPLITTING

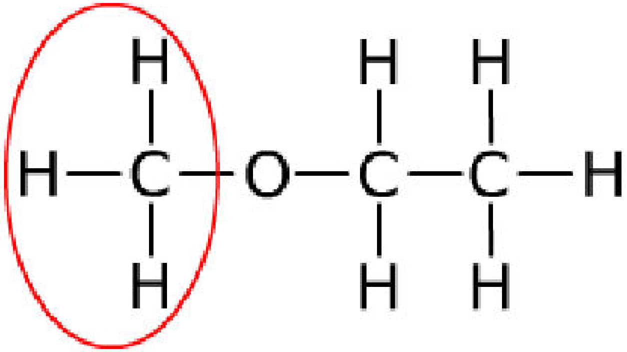
Proton n.m.r. spectroscopy



methoxyethane

How many peaks should appear in the proton n.m.r. spectrum of methoxyethane?

Proton n.m.r. spectroscopy

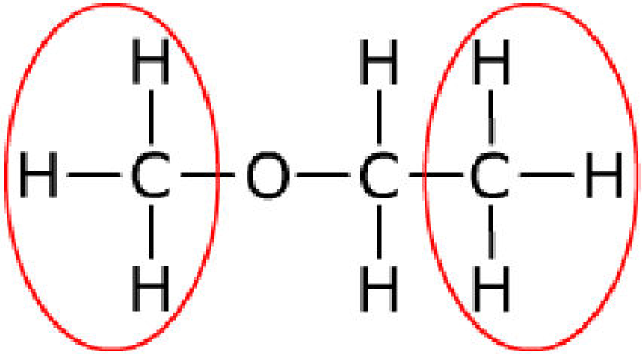


$$\mathrm{H-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$$

methoxyethane

Methoxyethane has a methyl group here.

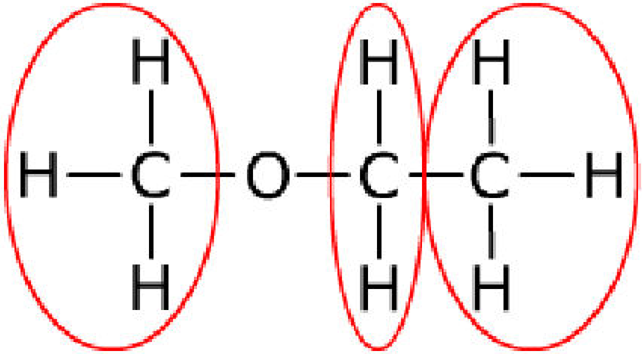
Proton n.m.r. spectroscopy



methoxyethane

It also has a methyl group here, but it is in a different chemical environment.

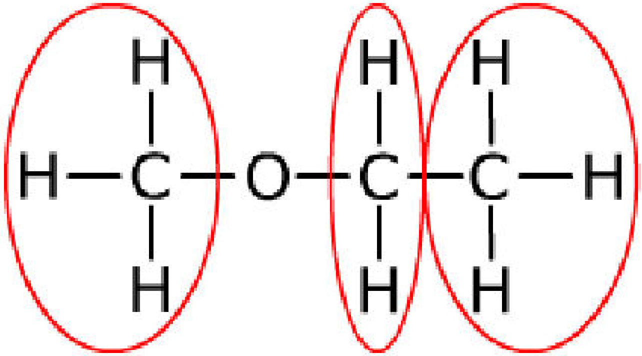
Proton n.m.r. spectroscopy



methoxyethane

It has a methylene group, CH_3.

Proton n.m.r. spectroscopy

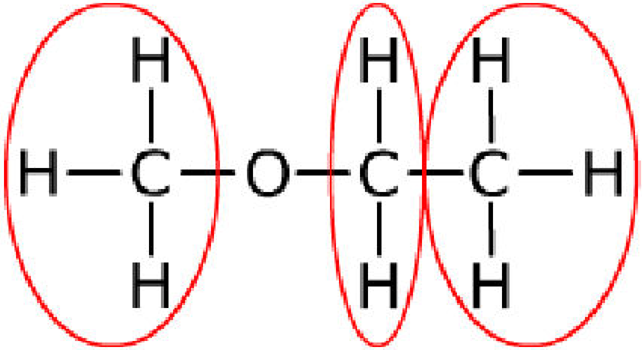


methoxyethane

three peaks

There are three different chemical environments, so there are three peaks in the spectrum.

Proton n.m.r. spectroscopy



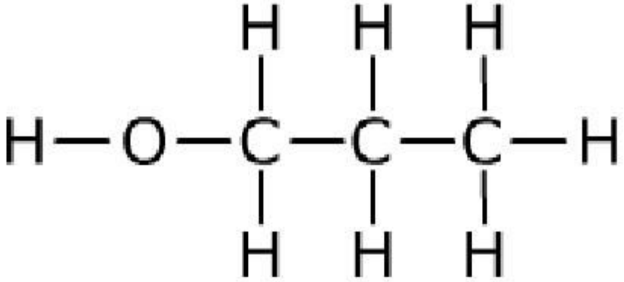
methoxyethane

three peaks

ratio 3:2:3

If we count up each equivalent hydrogen atom in the three chemical environments, we expect peak areas in the ratio 3:2:3.

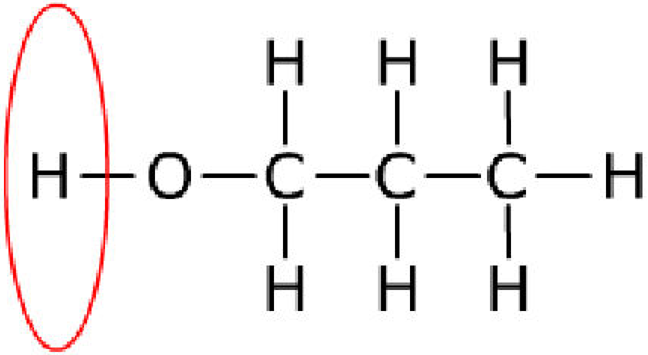
Proton n.m.r. spectroscopy



propan-1-ol

Propan-1-ol is an isomer of methoxyethane. How many peaks should appear in its proton n.m.r. spectrum?

Proton n.m.r. spectroscopy

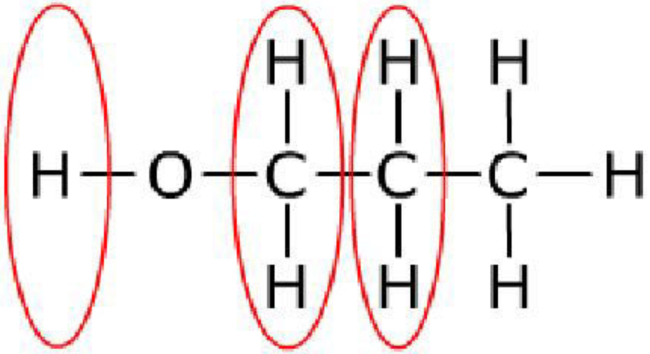


$$\begin{array}{ccccccccccc} & & & & H & & H & & H & & \\ & & & & | & & | & & | & & \\ H & - & O & - & C & - & C & - & C & - & H \\ & & & & | & & | & & | & & \\ & & & & H & & H & & H & & \end{array}$$

propan-1-ol

Propan-1-ol has a hydrogen atom in its hydroxyl group.

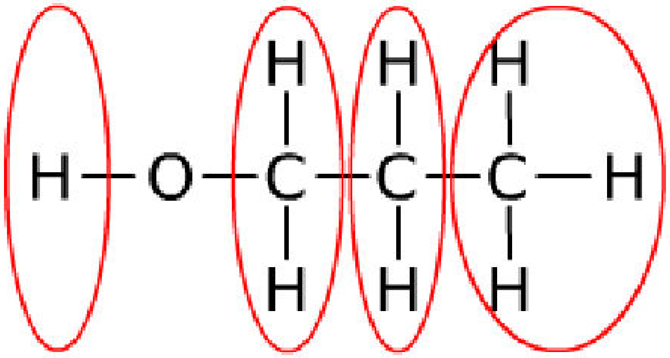
Proton n.m.r. spectroscopy



propan-1-ol

It has two methylene groups, CH_3 , but they are in different chemical environments.

Proton n.m.r. spectroscopy

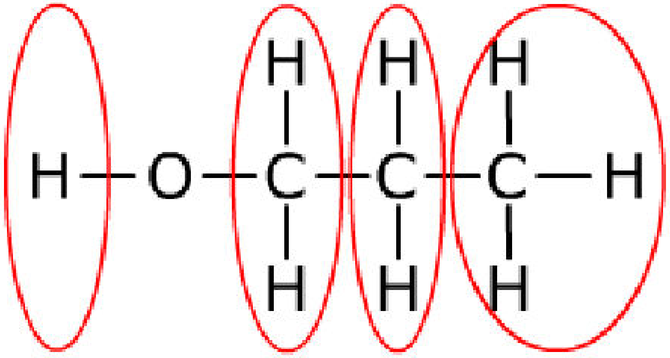


$H-O-CH_2-CH_2-CH_3$

propan-1-ol

It has a methyl group here.

Proton n.m.r. spectroscopy

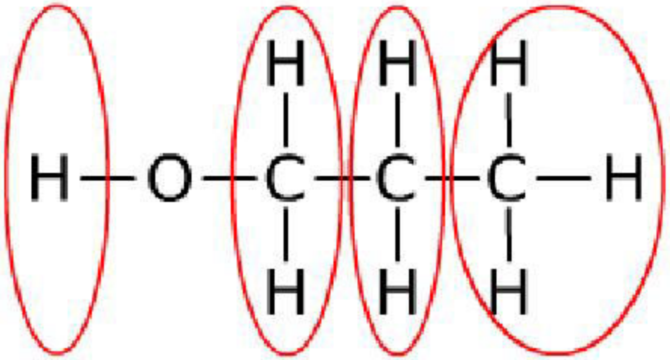


propan-1-ol

four peaks

There are four different chemical environments, so there are four peaks in the spectrum.

Proton n.m.r. spectroscopy



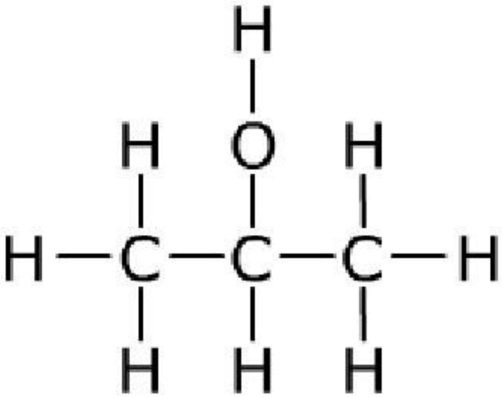
propan-1-ol

four peaks

ratio 1:2:2:3

If we count up each equivalent hydrogen atom in the four chemical environments, we expect peak areas in the ratio 1:2:2:3.

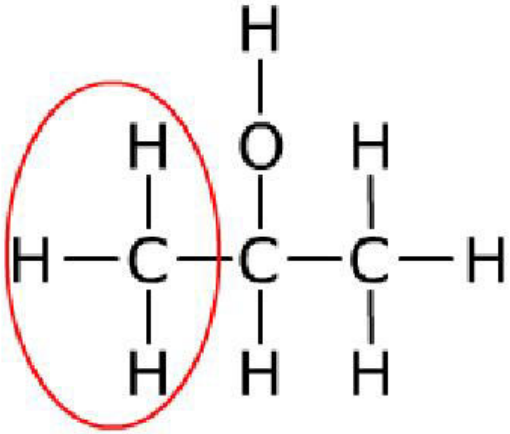
Proton n.m.r. spectroscopy



propan-2-ol

Propan-2-ol is an isomer of methoxyethane and propan-1-ol. How many peaks should appear in its proton n.m.r. spectrum?

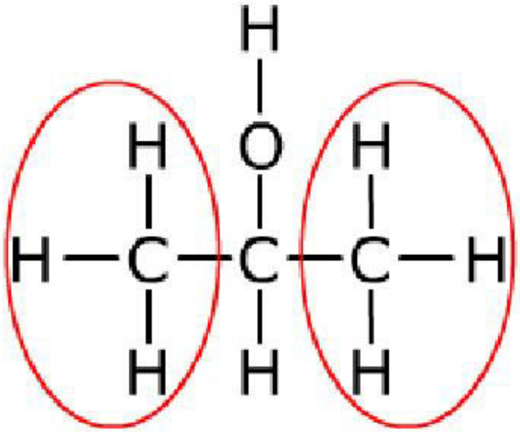
Proton n.m.r. spectroscopy



propan-2-ol

Propan-2-ol has a methyl group here.

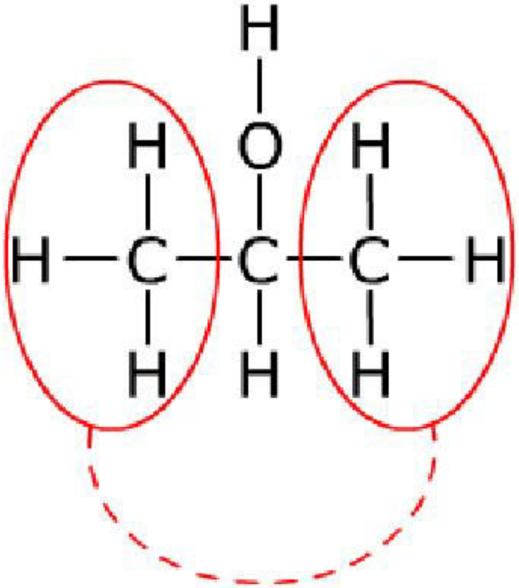
Proton n.m.r. spectroscopy



propan-2-ol

It also has a methyl group here.

Proton n.m.r. spectroscopy

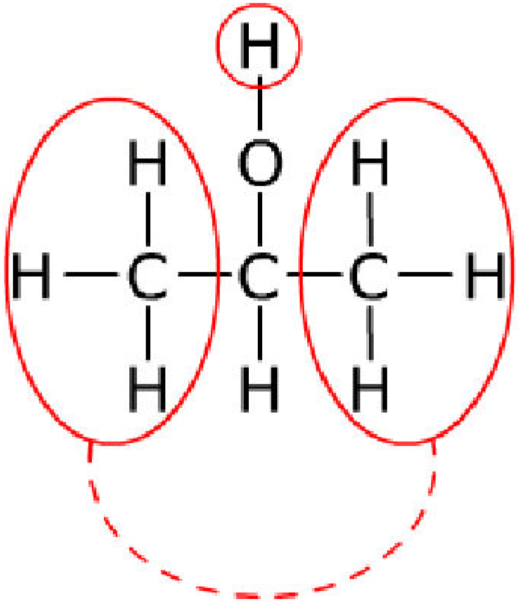


same chemical environment

propan-2-ol

Both methyl groups are in the same chemical environment. Their hydrogen atoms are all equivalent and will produce a single peak in the n.m.r. spectrum.

Proton n.m.r. spectroscopy

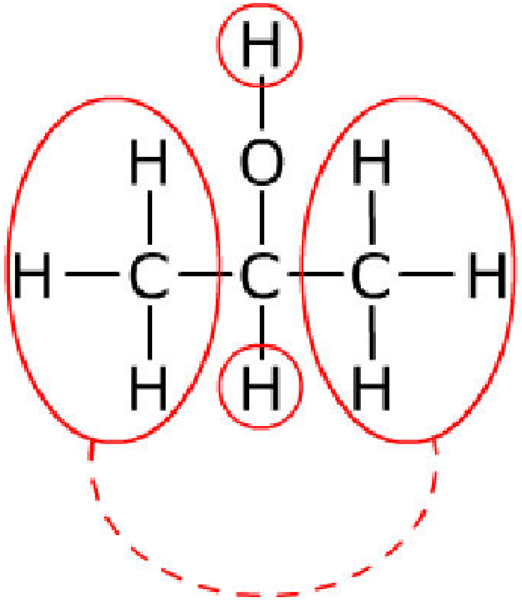


same chemical environment

propan-2-ol

Propan-2-ol has a hydrogen atom in the hydroxyl group.

Proton n.m.r. spectroscopy

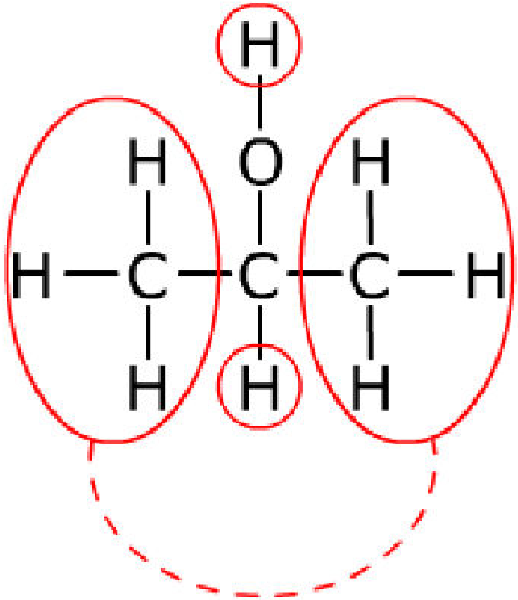


same chemical environment

propan-2-ol

It has another hydrogen atom here, but this is in a different chemical environment to the one in the hydroxyl group.

Proton n.m.r. spectroscopy



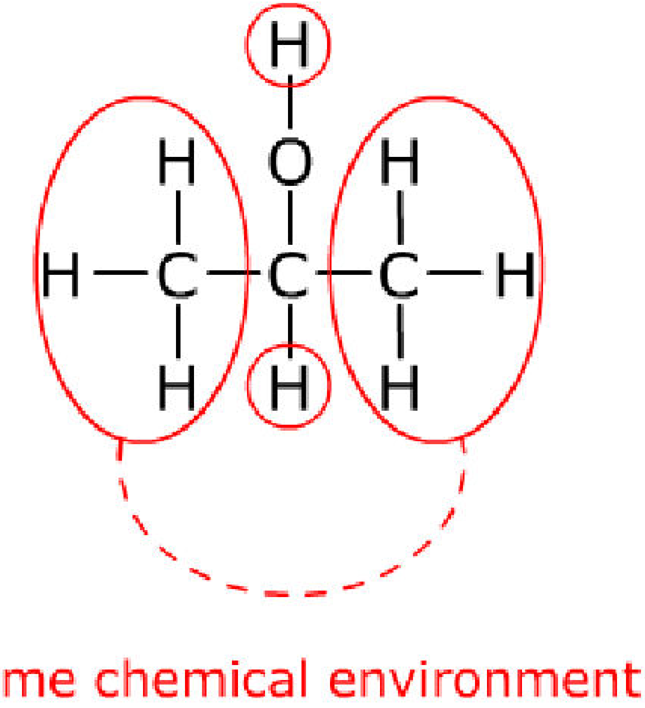
same chemical environment

propan-2-ol

three peaks

There are three different chemical environments, so there are three peaks in the spectrum.

Proton n.m.r. spectroscopy



propan-2-ol

three peaks
ratio 6:1:1

If we count up each equivalent hydrogen atom in the three chemical environments, we expect peak areas in the ratio 6:1:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights

Some of the peaks are split into clusters of smaller peaks in **high-resolution** proton n.m.r. spectra, because of **spin-spin coupling**.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1		

This happens if non-equivalent hydrogen atoms are adjacent to each other. No splitting occurs otherwise.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms n	Number of peaks produced by splitting $n+1$	Name	Ratio of peak heights
0	1	singlet	1

Without spin-spin coupling a single peak forms, called a singlet, just as in a low-resolution spectrum.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n+1***	Name	Ratio of peak heights
0	1	singlet	1
1	2		

If hydrogen atoms in one chemical environment are adjacent to one hydrogen atom in another chemical environment, the peak they produce will split into two.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1

This is called a doublet, with a ratio of peak areas of 1:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3		

If hydrogen atoms in one chemical environment are adjacent to two hydrogen atoms in another chemical environment, the peak they produce will split into three.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1

This is called a triplet, with a ratio of peak areas of 1:2:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4		

If hydrogen atoms in one chemical environment are adjacent to three hydrogen atoms in another chemical environment, the peak they produce will split into four.

Proton n.m.r. spectroscopy

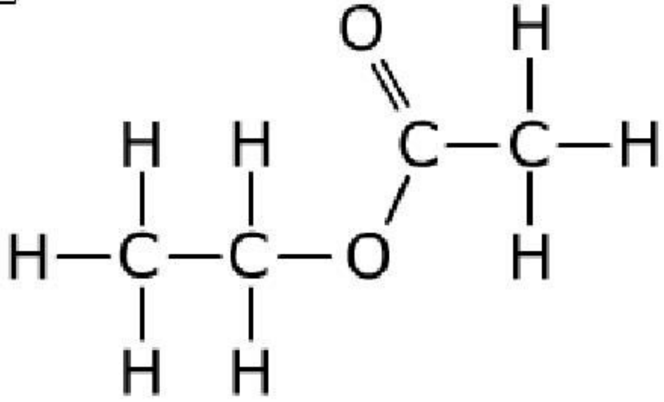
Number of neighbouring non-equivalent H atoms n	Number of peaks produced by splitting $n+1$	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

This is called a quartet, with a ratio of peak areas of 1:3:3:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate

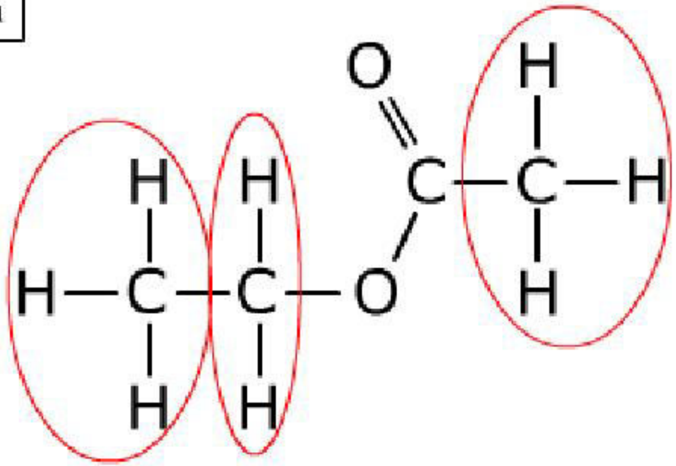


This is ethyl ethanoate.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting *n*+1	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate

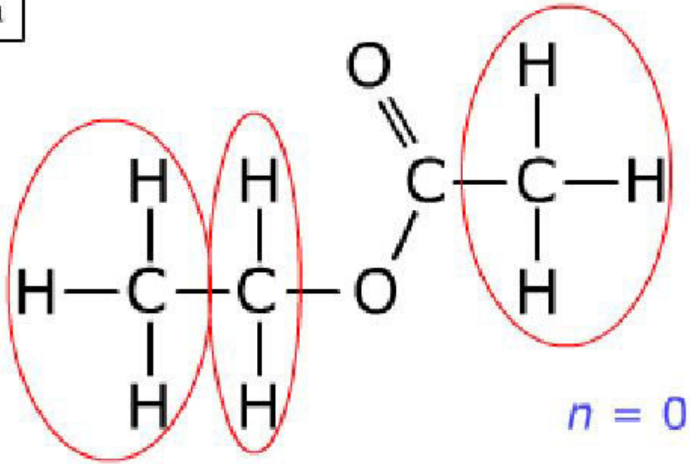


Its low-resolution proton n.m.r. spectrum would show three peaks in the ratio 3:2:3.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate



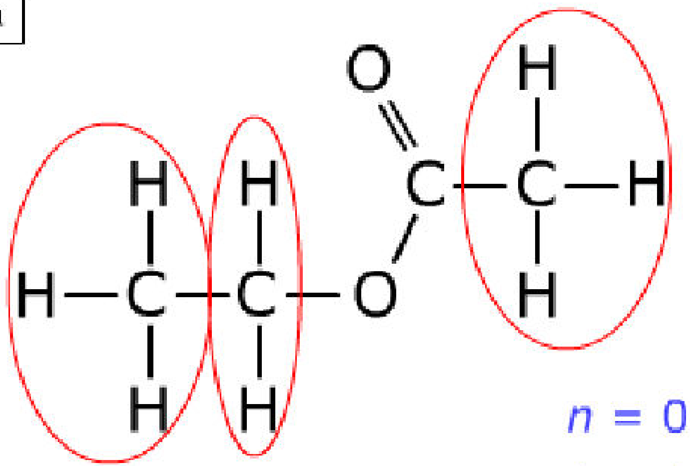
$n = 0$

The hydrogen atoms in this methyl group have no adjacent non-equivalent hydrogen atoms.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate



n = 0

n + 1 = 1

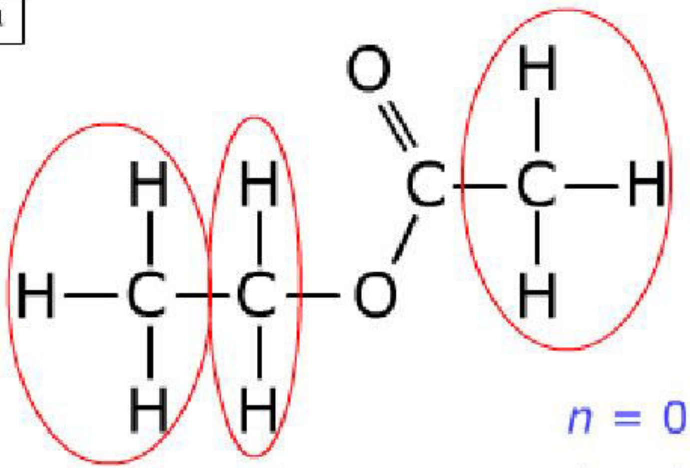
singlet

In a high-resolution spectrum, they would still produce a single peak.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms ***n***	Number of peaks produced by splitting ***n*+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate



$n = 2$

$n = 0$

$n + 1 = 1$

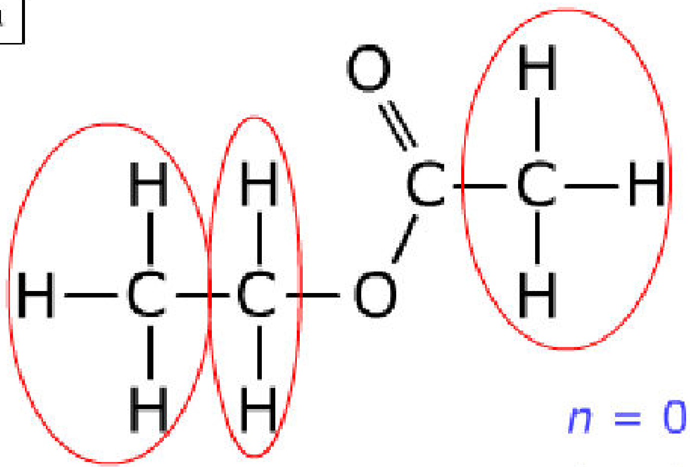
singlet

The hydrogen atoms in this methyl group have two adjacent non-equivalent hydrogen atoms.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms n	Number of peaks produced by splitting $n+1$	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

ethyl ethanoate



$n = 0$

$n + 1 = 1$

singlet

$n = 2$

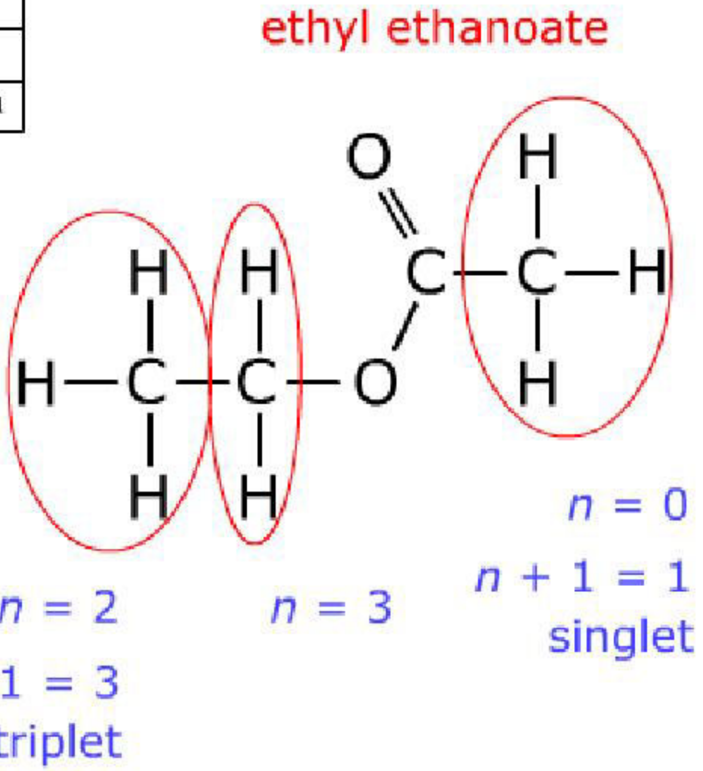
$n + 1 = 3$

triplet

In a high-resolution spectrum, they would produce a triplet of peaks, with a ratio of 1:2:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting *n*+1	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

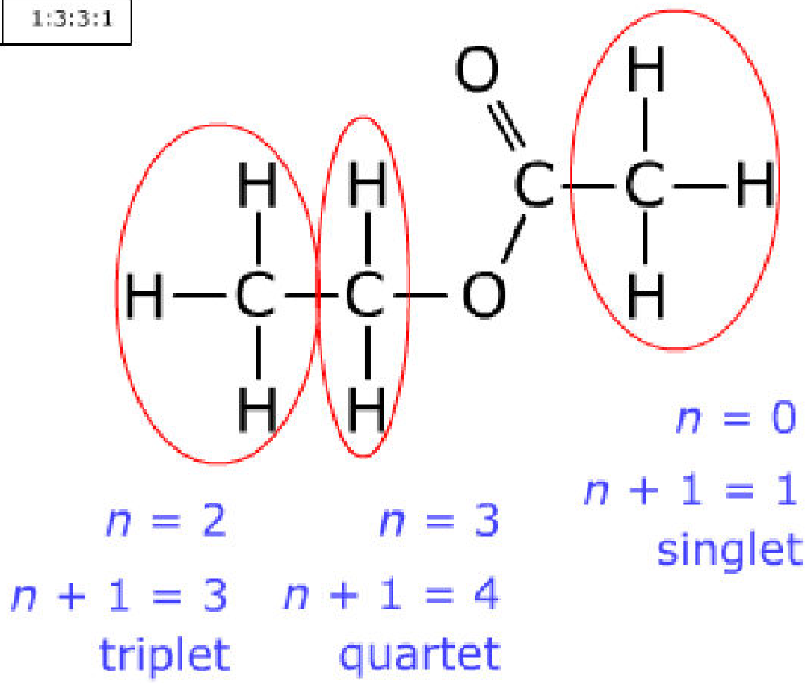


The hydrogen atoms in this methylene group have three adjacent non-equivalent hydrogen atoms.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms n	Number of peaks produced by splitting $n+1$	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

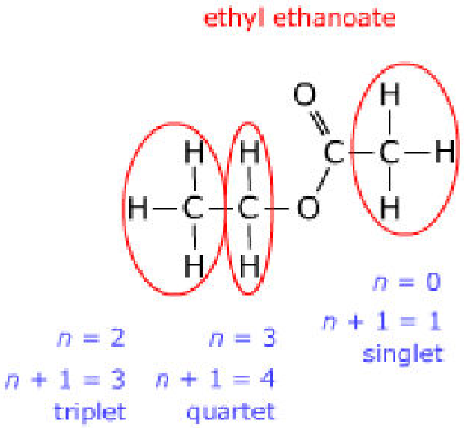
ethyl ethanoate



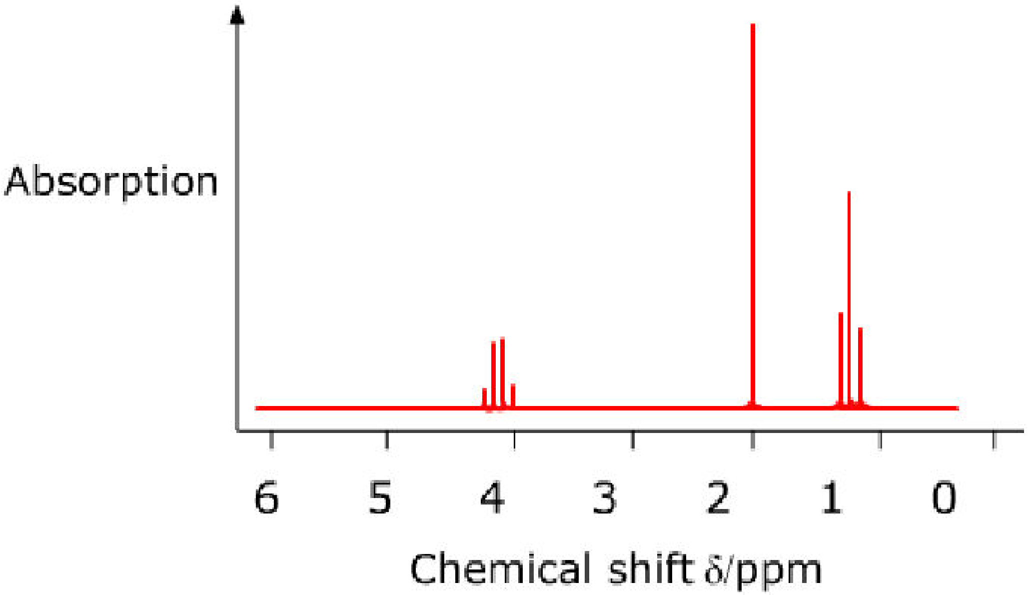
In a high-resolution spectrum, they would produce a quartet of peaks, with a ratio of 1:3:3:1.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting *n*+1	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1



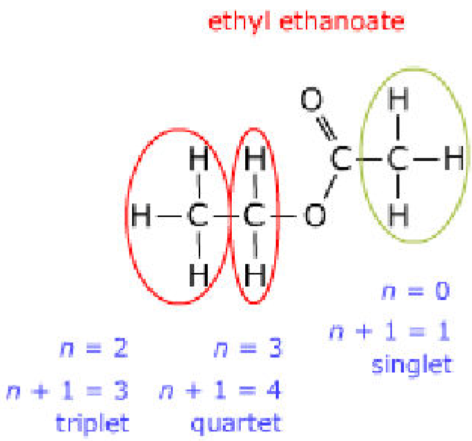
Simplified high-resolution spectrum of ethyl ethanoate



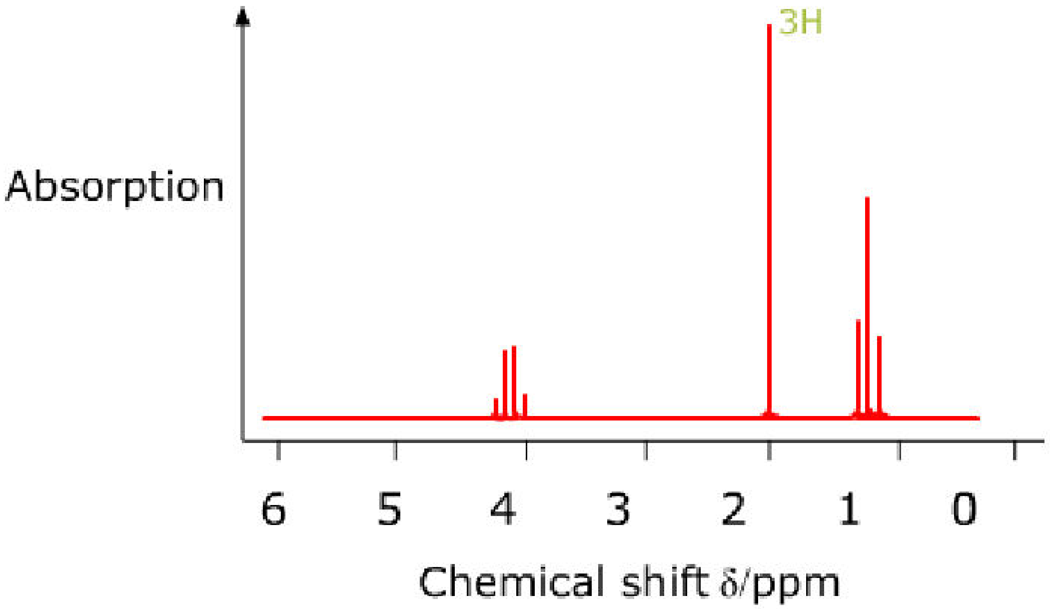
This is a simplified high-resolution proton n.m.r. spectrum of ethyl ethanoate.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting *n*+1	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1



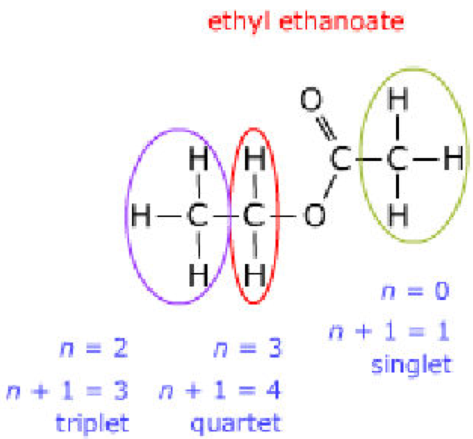
Simplified high-resolution spectrum of ethyl ethanoate



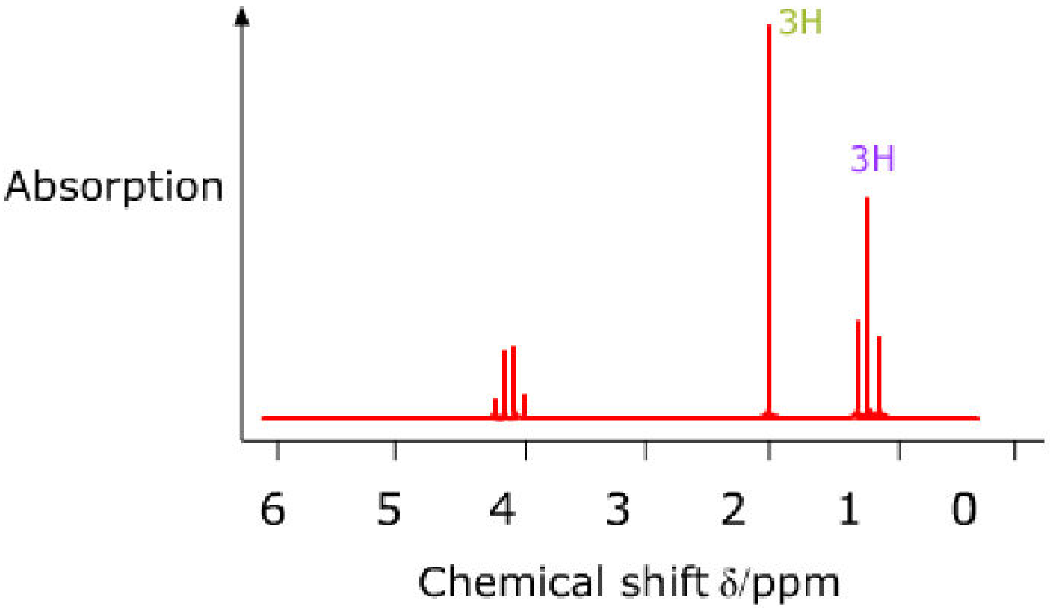
These are the equivalent hydrogen atoms in the different chemical environments and the peaks they produce.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms *n*	Number of peaks produced by splitting *n*+1	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1



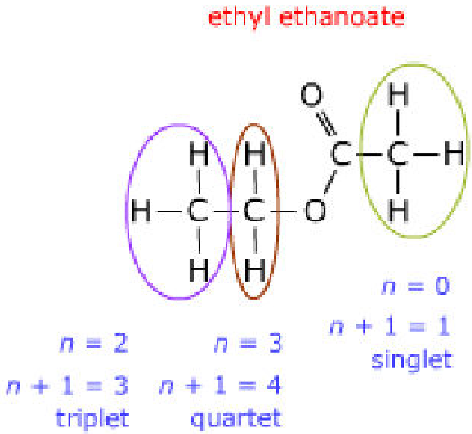
Simplified high-resolution spectrum of ethyl ethanoate



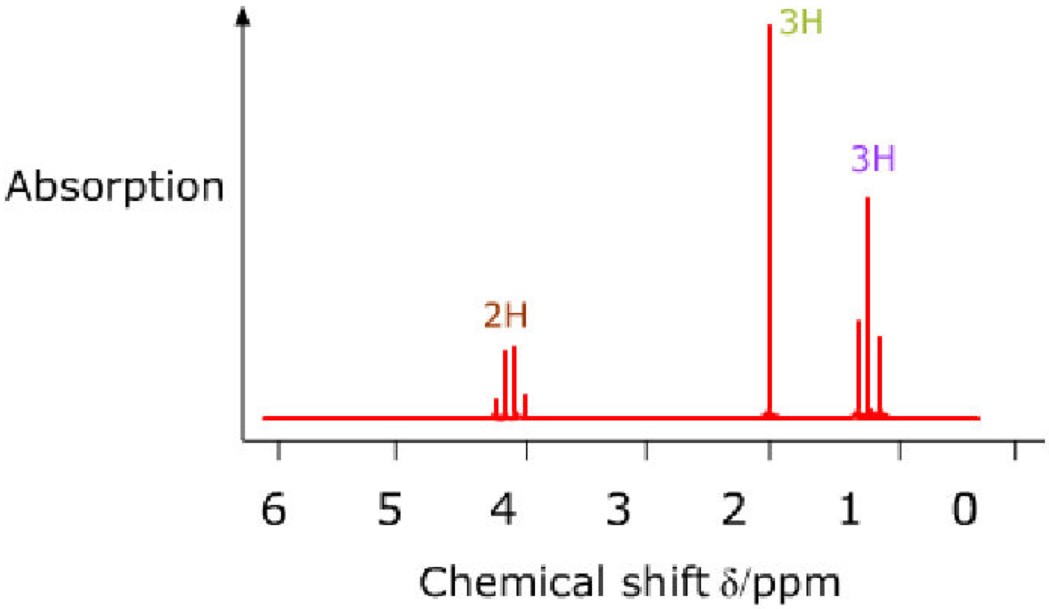
These are the equivalent hydrogen atoms in the different chemical environments and the peaks they produce.

Proton n.m.r. spectroscopy

Number of neighbouring non-equivalent H atoms **n**	Number of peaks produced by splitting **n+1**	Name	Ratio of peak heights
0	1	singlet	1
1	2	doublet	1:1
2	3	triplet	1:2:1
3	4	quartet	1:3:3:1

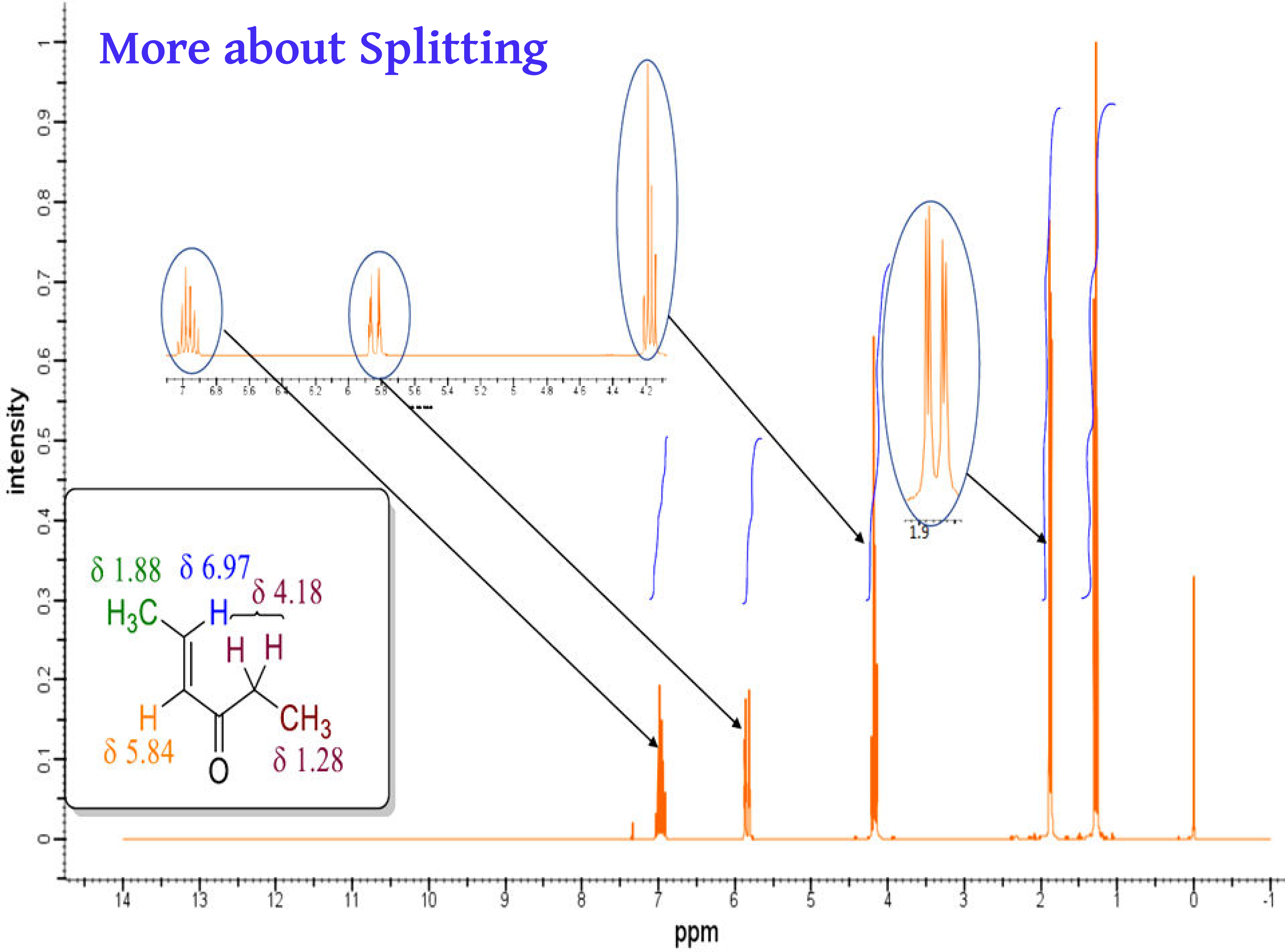


Simplified high-resolution spectrum of ethyl ethanoate

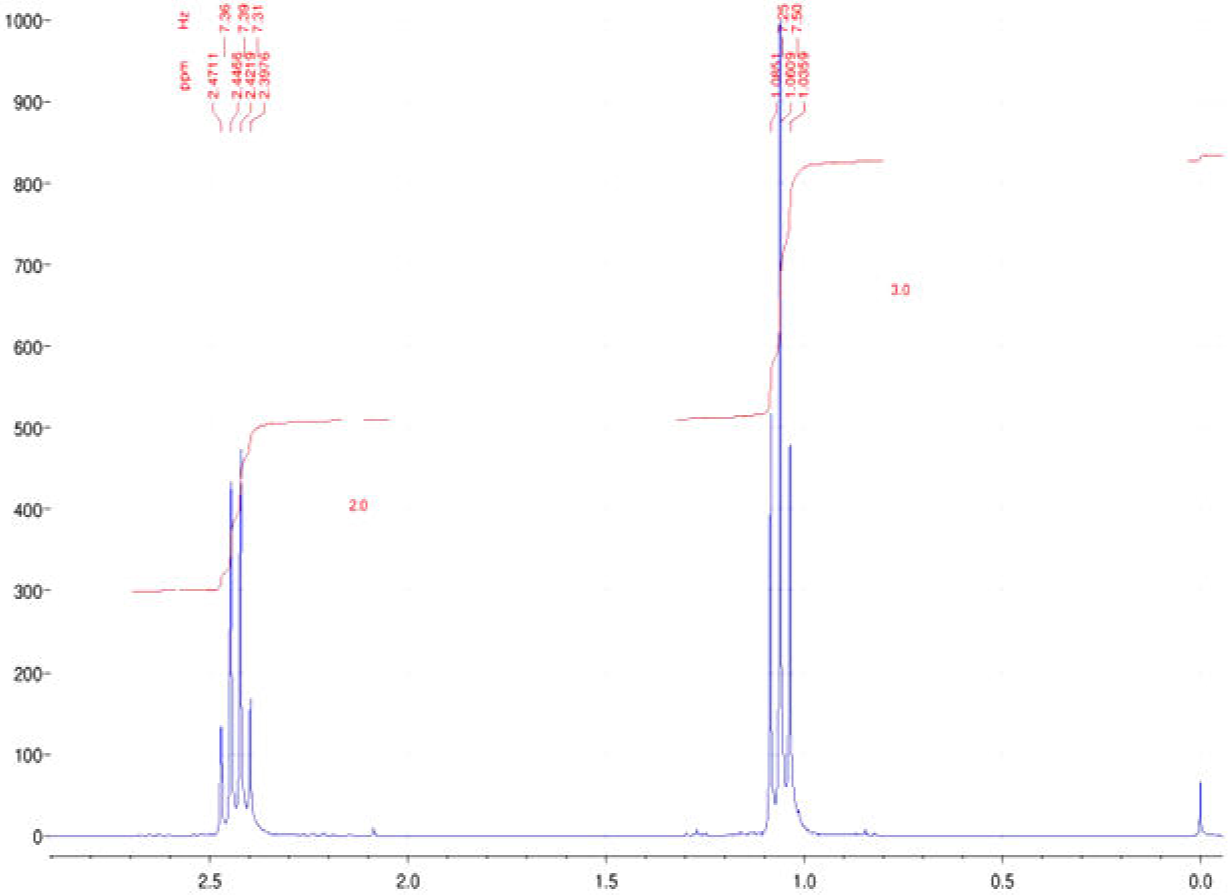


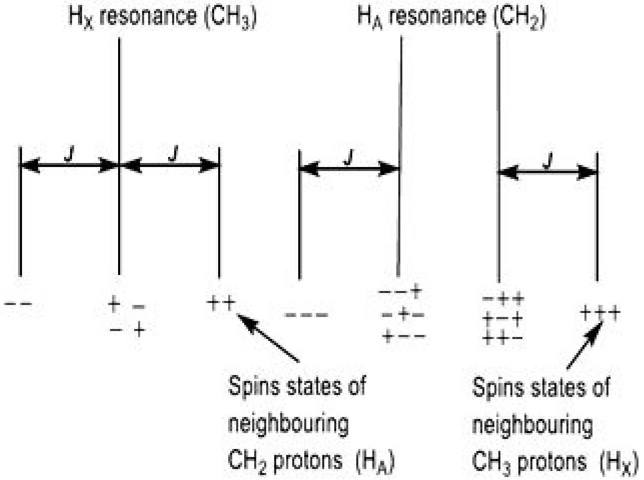
These are the equivalent hydrogen atoms in the different chemical environments and the peaks they produce.

More about Splitting



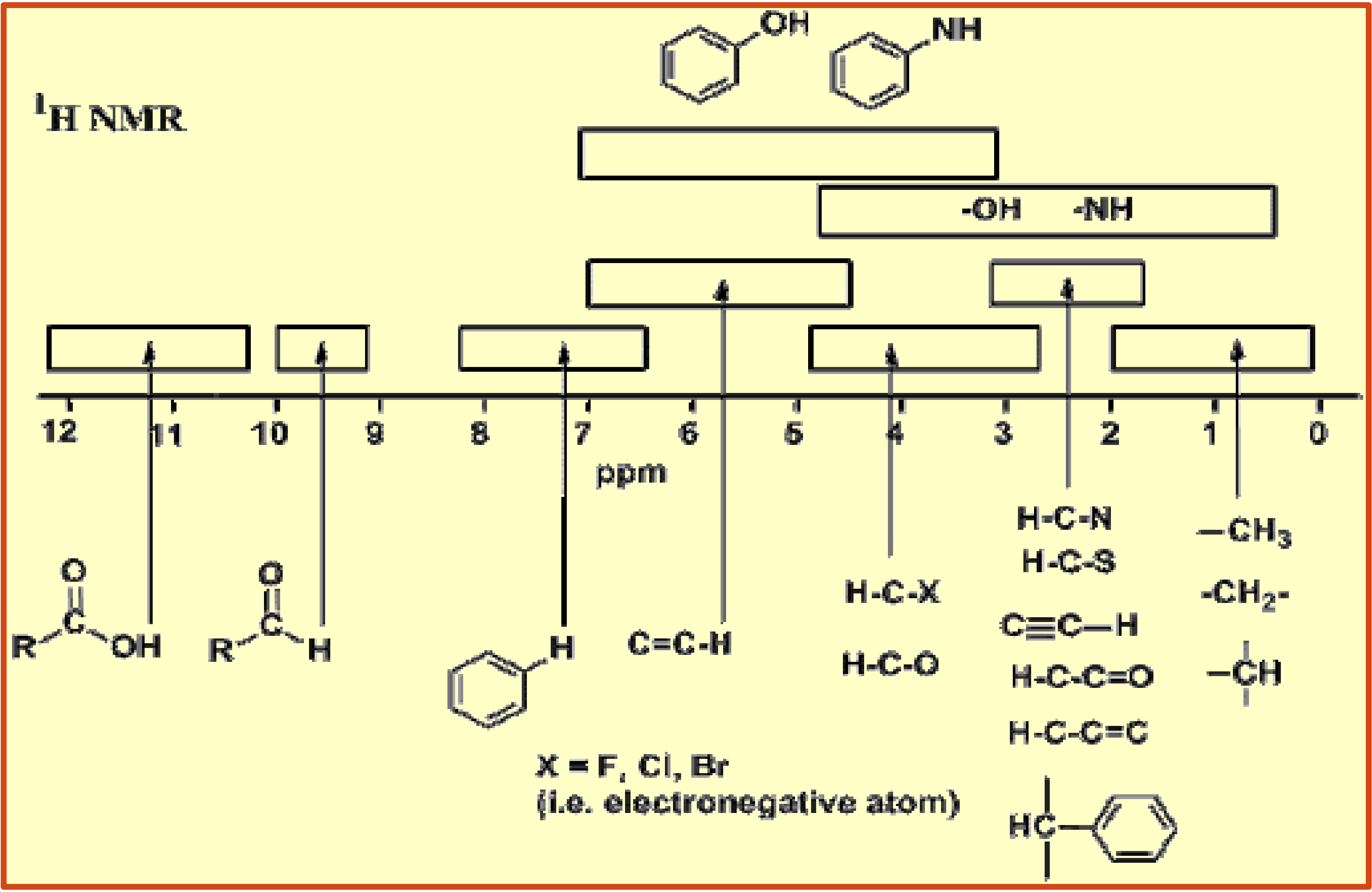
3-Pentanone molecule



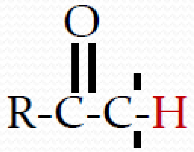
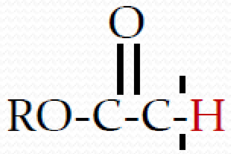
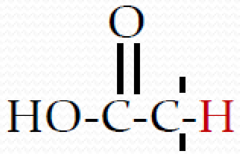
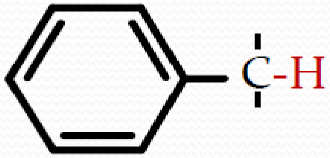


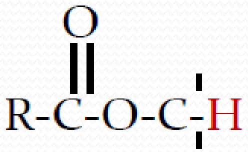
- With the increase in numbers of neighbouring spins the complexity in splitting pattern increases. Thus for a A_2X_3 system (e.g. the ethyl group of 3-pentanone) we have a triplet-quartet pattern.
- The methyl protons labelled H_X split into three peaks (triplet) as it is influenced by the two methylene protons labelled as H_A.
- On the other hand the methylene signal splits into four peaks (quartet) because four different magnetic environment created depending upon the four possible spins of H_X nucleus as shown. Hence results in a 1:3:3:1 quartet.

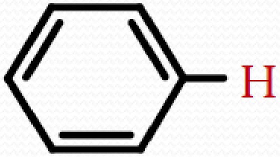
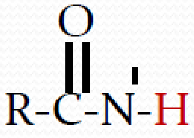
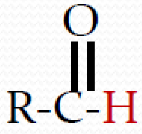
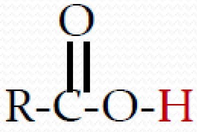
Standard Chemical Shift Data of PMR



Standard Chemical Shift Data of PMR

$R-CH_3$	0.7 - 1.3
$R-CH_2-R$	1.2 - 1.4
R_3CH	1.4 - 1.7
$R-C=C-C-H$	1.6 - 2.6
 $R-\overset{O}{\overset{\|}{C}}-C-H$	2.1 - 2.4
 $RO-\overset{O}{\overset{\|}{C}}-C-H$	2.1 - 2.5
 $HO-\overset{O}{\overset{\|}{C}}-C-H$	2.1 - 2.5
$N\equiv C-C-H$	2.1 - 3.0
$R-C\equiv C-C-H$	2.1 - 3.0
 $C-H$	2.3 - 2.7
$R-C\equiv C-H$	1.7 - 2.7

$R-N-C-H$	2.2 - 2.9
$R-S-C-H$	2.0 - 3.0
$I-C-H$	2.0 - 4.0
$Br-C-H$	2.7 - 4.1
$Cl-C-H$	3.1 - 4.1
$RO-C-H$	3.2 - 3.8
$HO-C-H$	3.2 - 3.8
 $R-\overset{O}{\overset{\|}{C}}-O-C-H$	3.5 - 4.8
O_2N-C-H	4.1 - 4.3
$F-C-H$	4.2 - 4.8

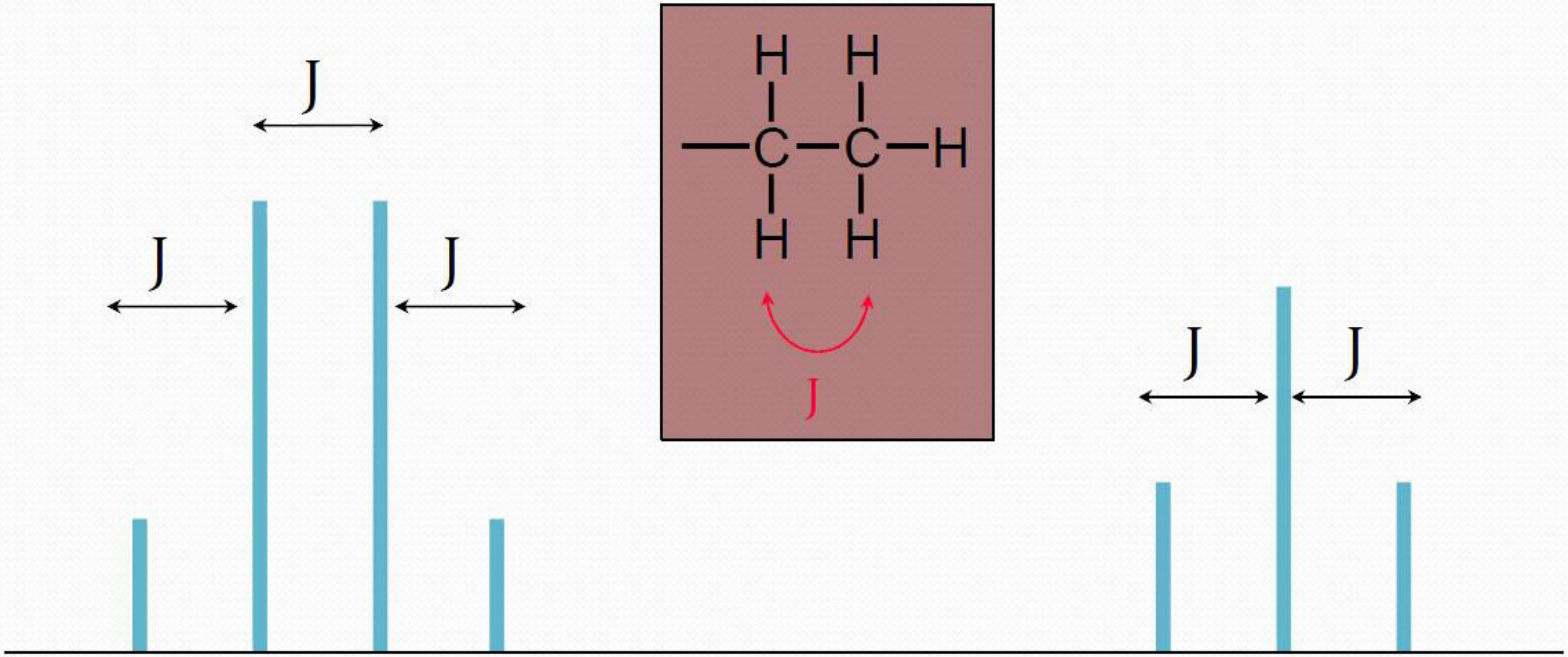
$R-C=C-H$	4.5 - 6.5
 H	6.5 - 8.0
 $R-\overset{O}{\overset{\|}{C}}-N-H$	5.0 - 9.0
 $R-\overset{O}{\overset{\|}{C}}-H$	9.0 - 10.0
 $R-\overset{O}{\overset{\|}{C}}-O-H$	11.0 - 12.0

$R-N-H$	0.5 - 4.0	$Ar-N-H$	3.0 - 5.0
$R-O-H$	0.5 - 5.0	$Ar-O-H$	4.0 - 7.0

$R-S-H$	1.0 - 4.0

THE COUPLING CONSTANT

THE COUPLING CONSTANT



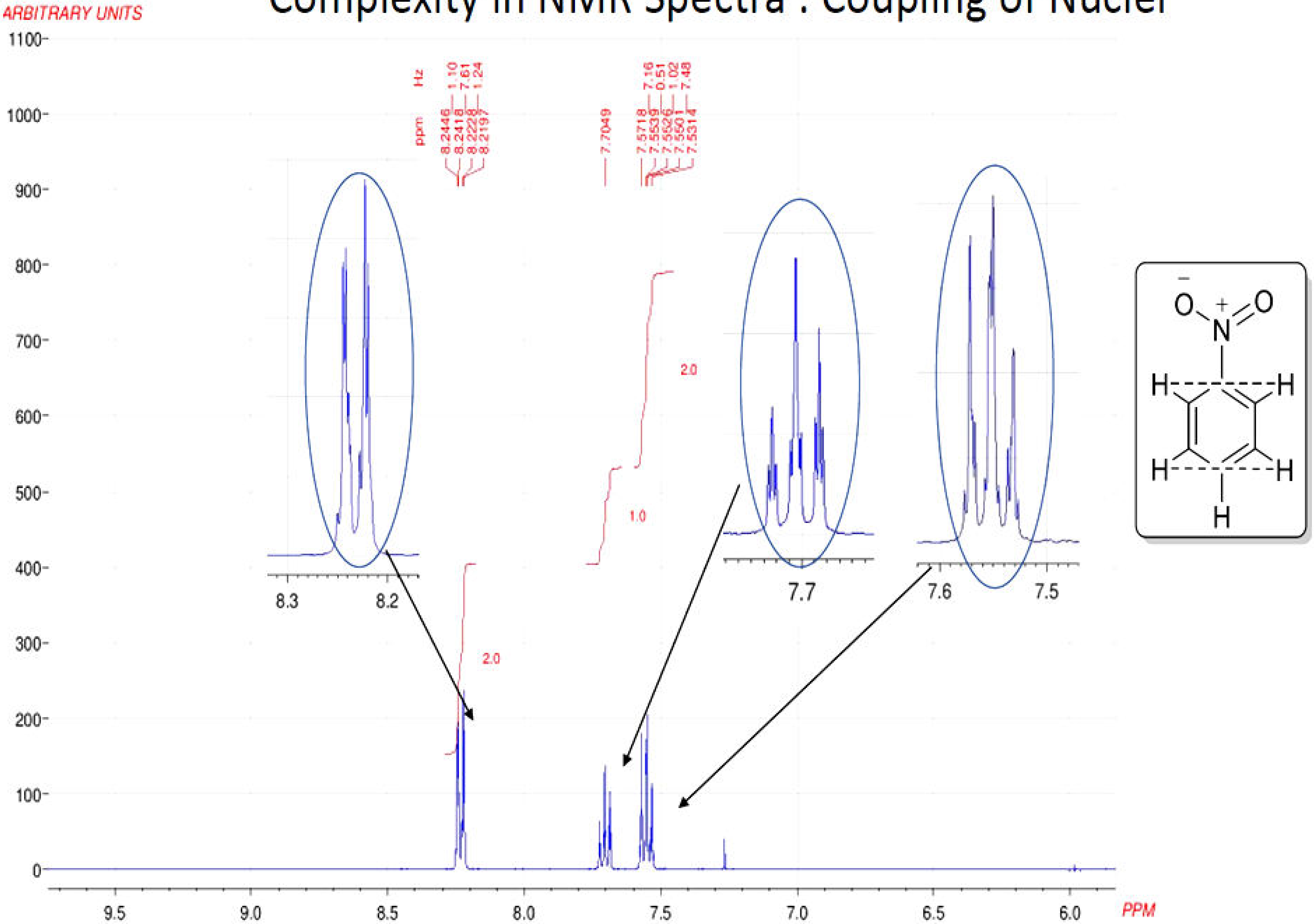
The coupling constant is the distance J (measured in Hz) between the peaks in a simple multiplet.

J is a measure of the amount of interaction between the two sets of hydrogens creating the multiplet.

- The coupling constant is a measure of how strongly a nucleus is affected by the spin states of its neighbor.
- Coupling constant is expressed in Hertz (Hz).

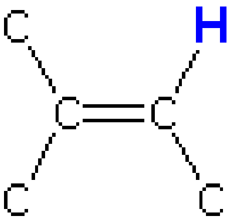
Calculation of Coupling Constant (*J*)

Complexity in NMR Spectra : Coupling of Nuclei

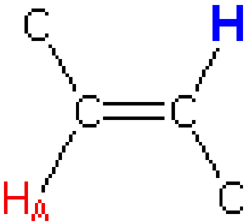


Number of Coupled Hydrogen & Their *J* Value

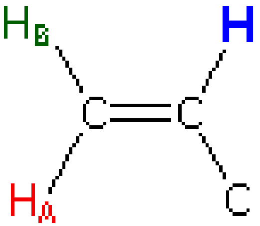
No Coupled Hydrogens



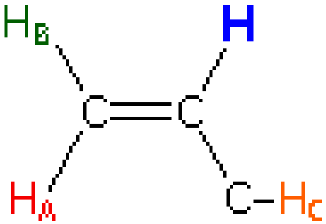
One Coupled Hydrogen

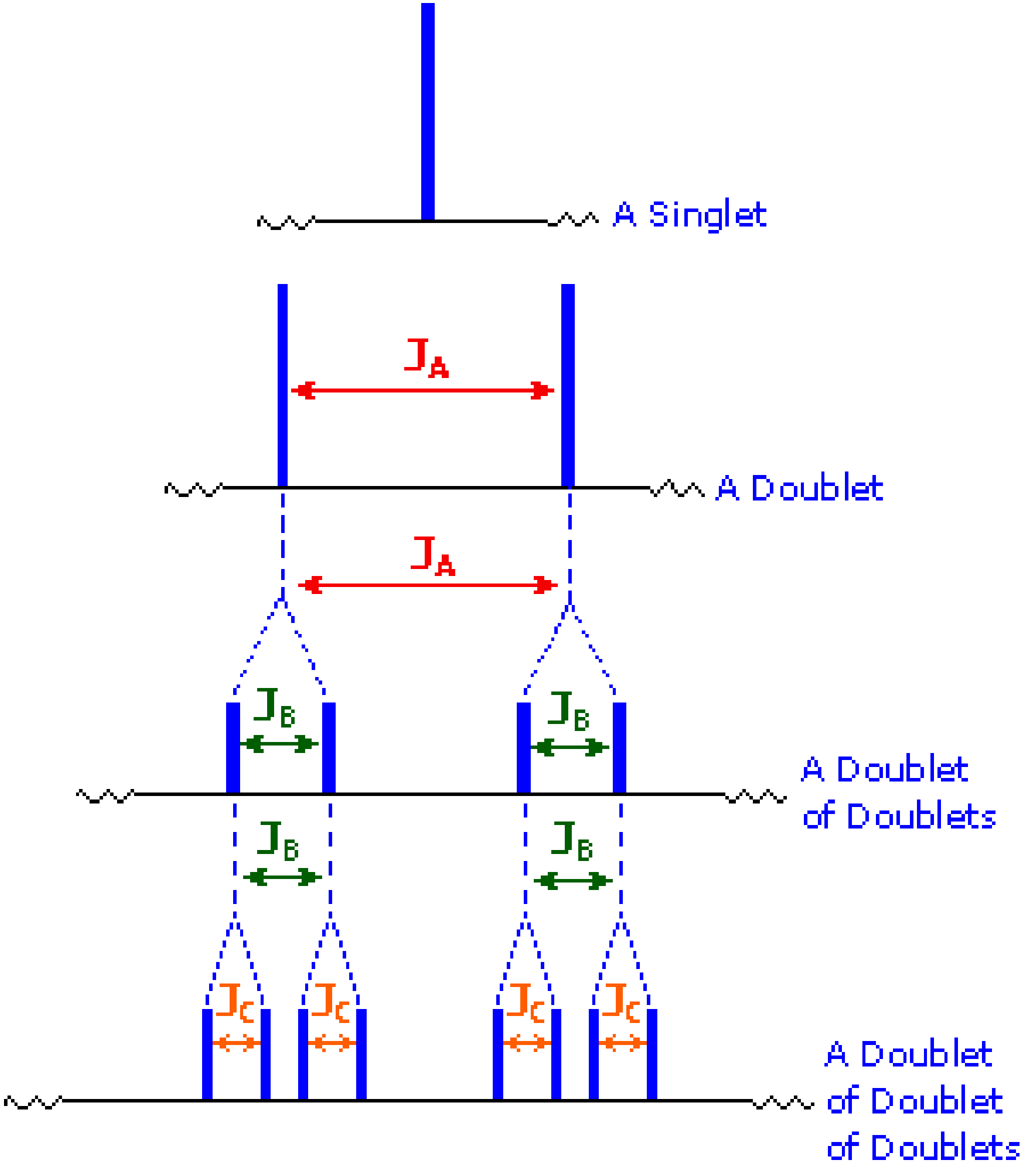


Two Coupled Hydrogens



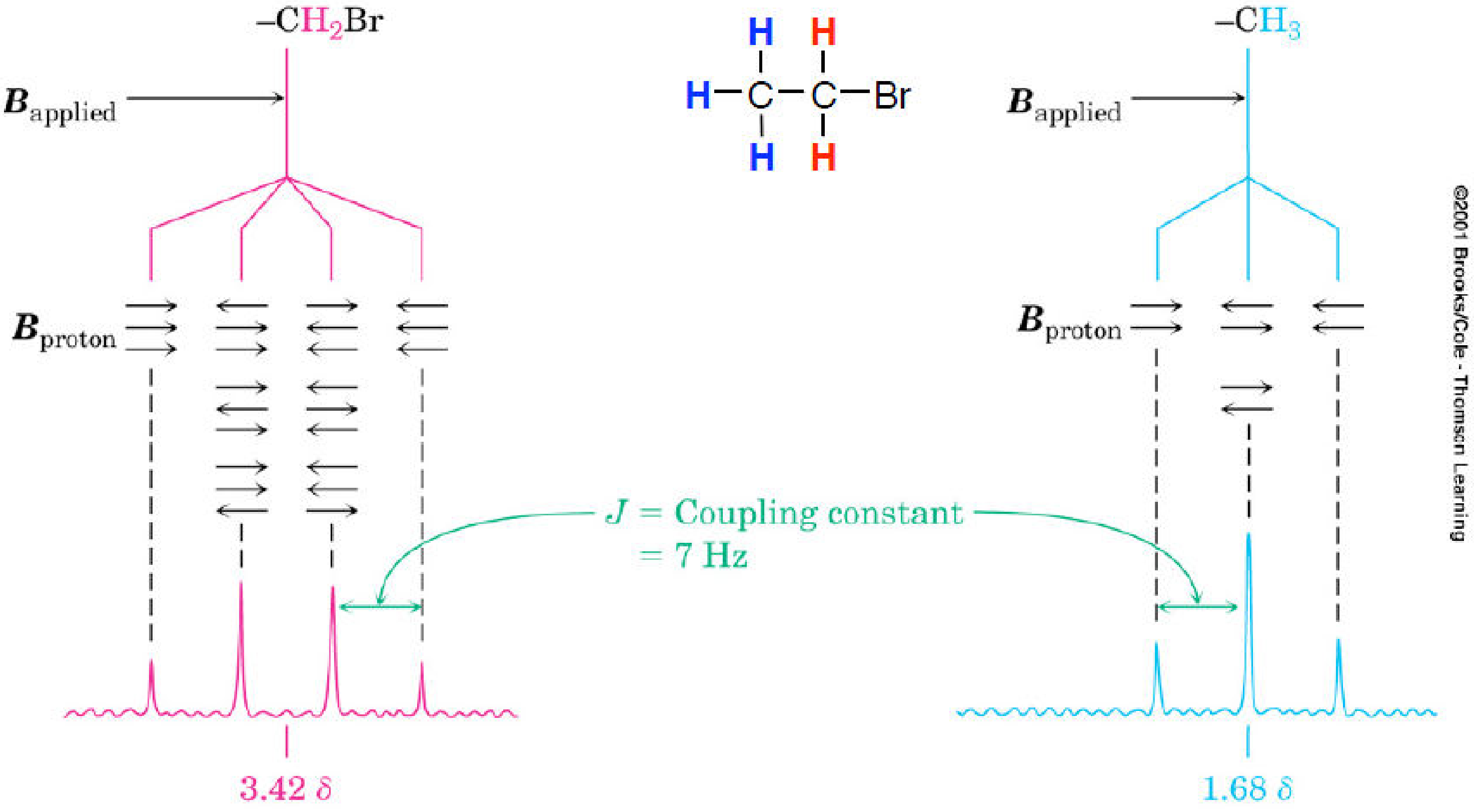
Three Coupled Hydrogens





The resonance of a proton with n equivalent protons on the adjacent carbon will be “split” into n + 1 peaks with a *coupling constant J*.

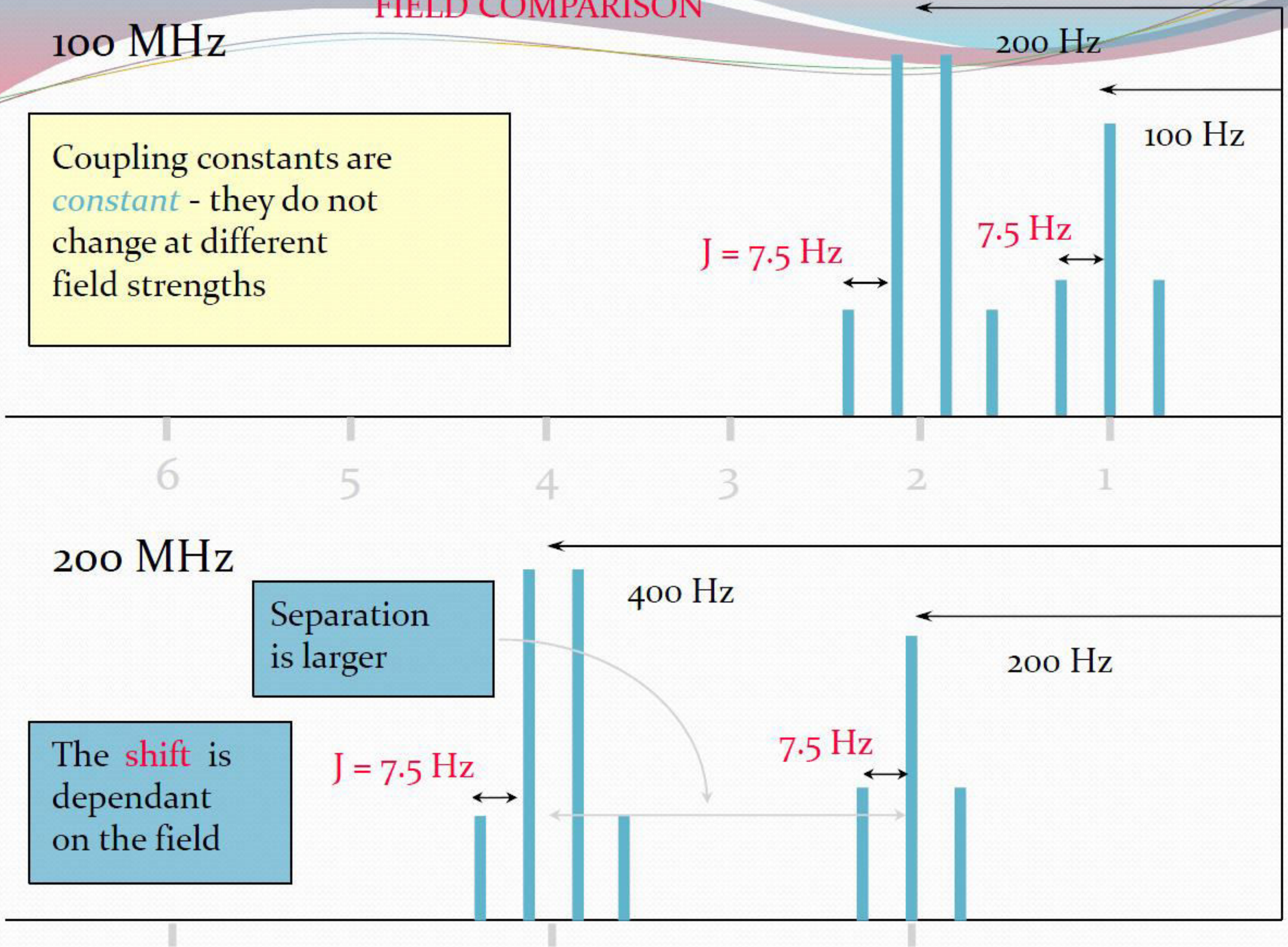
Coupling constant: distance between peaks of a split pattern; expressed in Hz. Protons coupled to each other have the same coupling constant J.



Quartet due to coupling with $-CH_3$

Triplet due to coupling with $-CH_2Br$

FIELD COMPARISON



Coupling constants are *constant* - they do not change at different field strengths

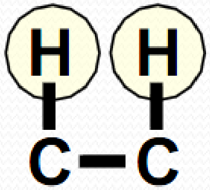
Separation is larger

The shift is dependant on the field

NOTATION FOR COUPLING CONSTANTS

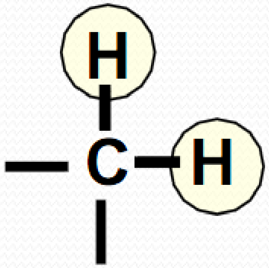
The most commonly encountered type of coupling is between hydrogens on adjacent carbon atoms.

^3J



This is sometimes called *vicinal* coupling. It is designated ^3J since three bonds intervene between the two hydrogens.

Another type of coupling that can also occur in special cases is



^2J

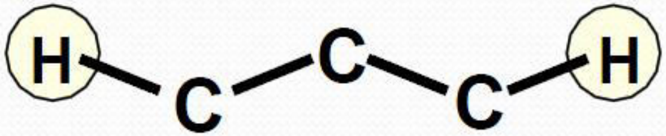
^2J or *geminal* coupling

(most often $^2J = 0$)

Geminal coupling does not occur when the two hydrogens are equivalent due to rotations around the other two bonds.

LONG RANGE COUPLINGS

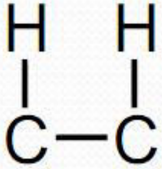
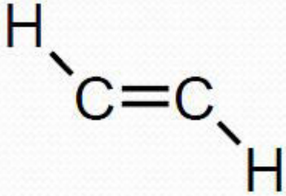
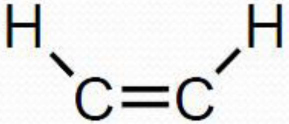
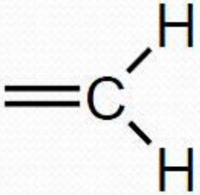
Couplings larger than ^2J or ^3J also exist, but operate only in special situations.

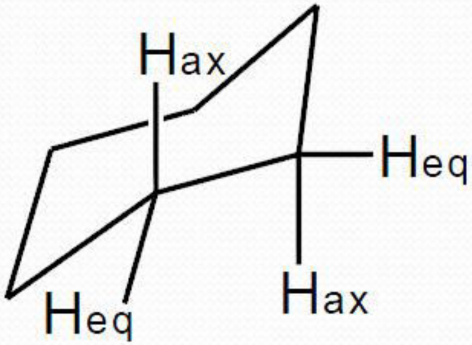


^4J , for instance, occurs mainly when the hydrogens are forced to adopt this "W" conformation (as in bicyclic compounds).

Couplings larger than ^3J (e.g., ^4J, ^5J, etc) are usually called "long-range coupling."

SOME REPRESENTATIVE COUPLING CONSTANTS

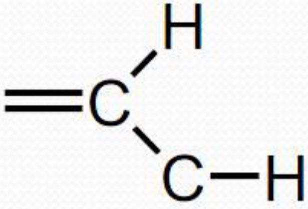
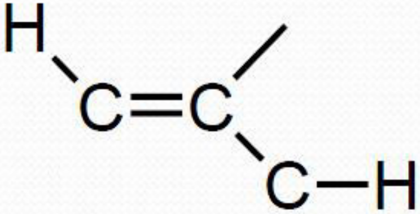
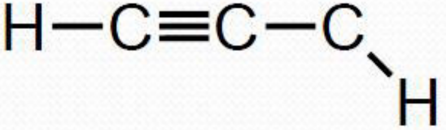
vicinal		6 to 8 Hz	three bond	^3J
trans		11 to 18 Hz	three bond	^3J
cis		6 to 15 Hz	three bond	^3J
geminal		0 to 5 Hz	two bond	^2J



H_{ax},H_{ax} = 8 to 14

H_{ax},H_{eq} = 0 to 7 three bond ^3J

H_{eq},H_{eq} = 0 to 5

	*cis* *trans*	6 to 12 Hz 4 to 8 Hz	three bond	^3J
		4 to 10 Hz	three bond	^3J
		0 to 3 Hz	four bond	^4J
		0 to 3 Hz	four bond	^4J

Couplings that occur at distances greater than three bonds are called long-range couplings and they are usually small (<3 Hz) and frequently nonexistent (0 Hz).

^{13}C NMR Spectra

Why ^{13}C NMR Required ??

- Proton NMR used for study of number of nonequivalent proton present in unknown compound.

- Carbon NMR can used to determine the number of non-equivalent carbons and to identify the types of carbon atoms(methyl, methylene, aromatic, carbonyl….) which may present in compound.

- ^{13}C signals are spread over a much wider range than ^{1}H signals making it easier to identify & count individual nuclei.

CHARACTERISTIC FEATURES OF ^{13}C NMR

- The chemical shift of the CMR is wider(δ is 0-220ppm relative to TMS) in comparison to PMR(δ is 0-12ppm relative toTMS).
- ^{13}C-^{13}C coupling is negligible because of low natural abundance of ^{13}C in the compound. Thus in one type ofCMR
- spectrum(proton de coupled) each magnetically non equivalent carbon gives a single sharp peak that does undergo further splitting.

CHARACTERISTIC FEATURES OF ^{13}C NMR

- The area under the peak in CMR spectrum is not necessary to be proportional to the number of carbon responsible for the signal. Therefore not necessary to consider the area under ratio.
- Proton coupled spectra the signal for each carbon or a group of magnetically equivalent carbon is split by proton bonded directly to that carbon & the n+1 rule is follwed.
- ^{13}C nucleus is about one-fourth the frequency required to observe proton resonance.
- The chemical shift is greater for ^{13}C atom than for proton due to direct attachment of the electronegative atom to ^{13}C

Gurdeep R. Chatwal, Sham K.Anand; Instrumental Methods Of Chemical Analysis, Enlarge edition 2002,Pg. no. 2.31-2.32

^{13}C Chemical Shifts

are measured in ppm (δ) from the carbons of TMS

- The correlation chart is here divided into sections

1)the saturated carbon atom which appear at Upfield,nearest to TMS(8-60ppm).

2) effect of electronegative atom(40-80ppm)

3) Alkenes and aromatic carbon atom(100-170)

4)It contain carbonyl carbon bond. which appear at Downfield value(155-200ppm).

Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 177

Correlation Chart

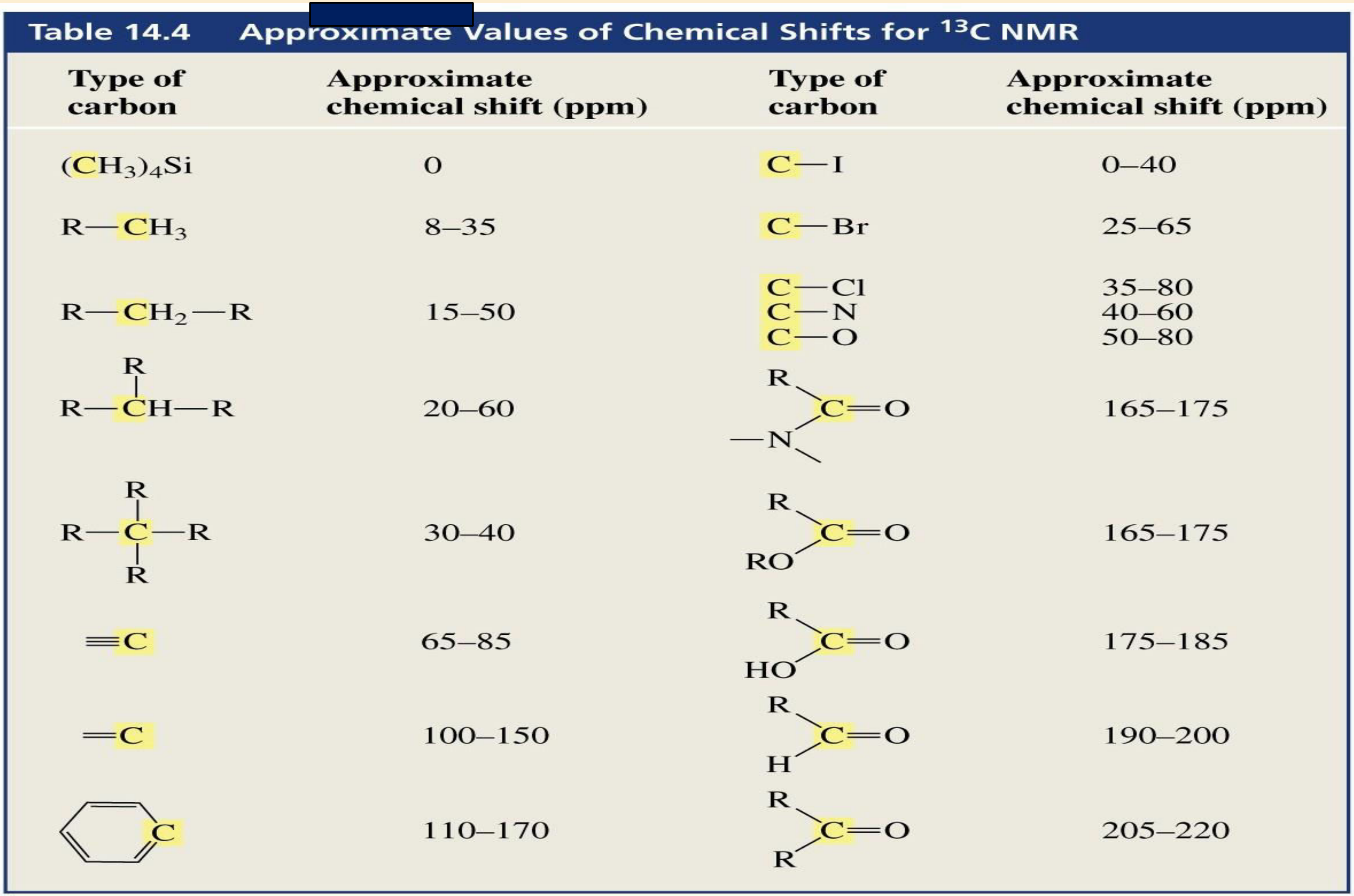
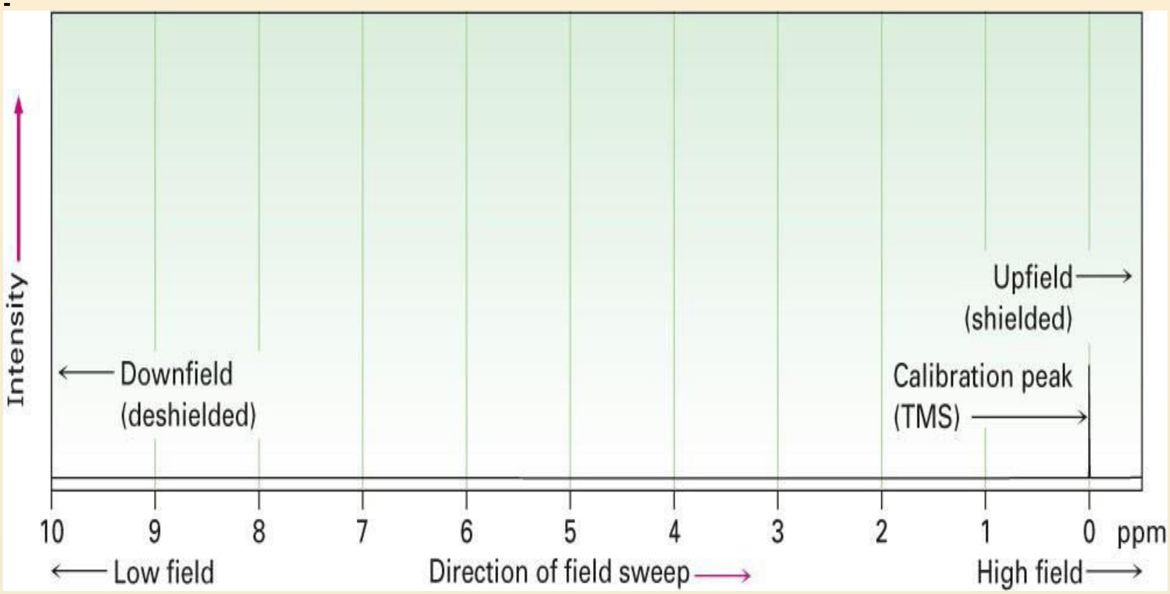


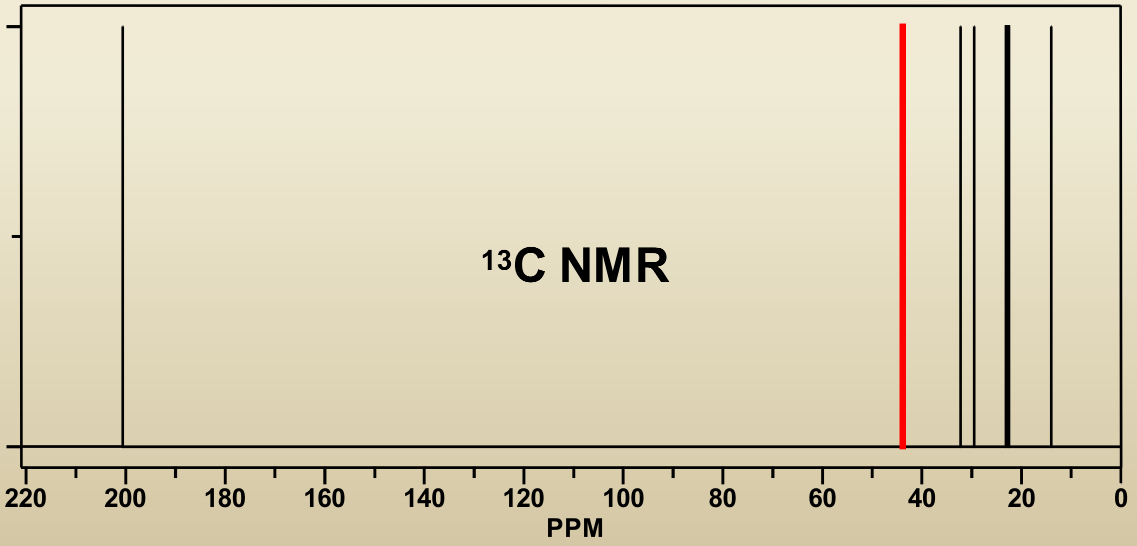
Table 14.4 Approximate Values of Chemical Shifts for ^{13}C NMR

Type of carbon	Approximate chemical shift (ppm)	Type of carbon	Approximate chemical shift (ppm)
$(CH_3)_4Si$	0	$C-I$	0–40
$R-CH_3$	8–35	$C-Br$	25–65
$R-CH_2-R$	15–50	$C-Cl$ $C-N$ $C-O$	35–80 40–60 50–80
$R-\overset{R}{\overset{\vert}{C}}H-R$	20–60	$\begin{matrix}R & \\ & C=O \\ -N & \end{matrix}$	165–175
$R-\overset{R}{\underset{R}{\overset{\vert}{\underset{\vert}{C}}}}-R$	30–40	$\begin{matrix}R & \\ & C=O \\ RO & \end{matrix}$	165–175
$\equiv C$	65–85	$\begin{matrix}R & \\ & C=O \\ HO & \end{matrix}$	175–185
$=C$	100–150	$\begin{matrix}R & \\ & C=O \\ H & \end{matrix}$	190–200
C	110–170	$\begin{matrix}R & \\ & C=O \\ R & \end{matrix}$	205–220

Chemical Shift



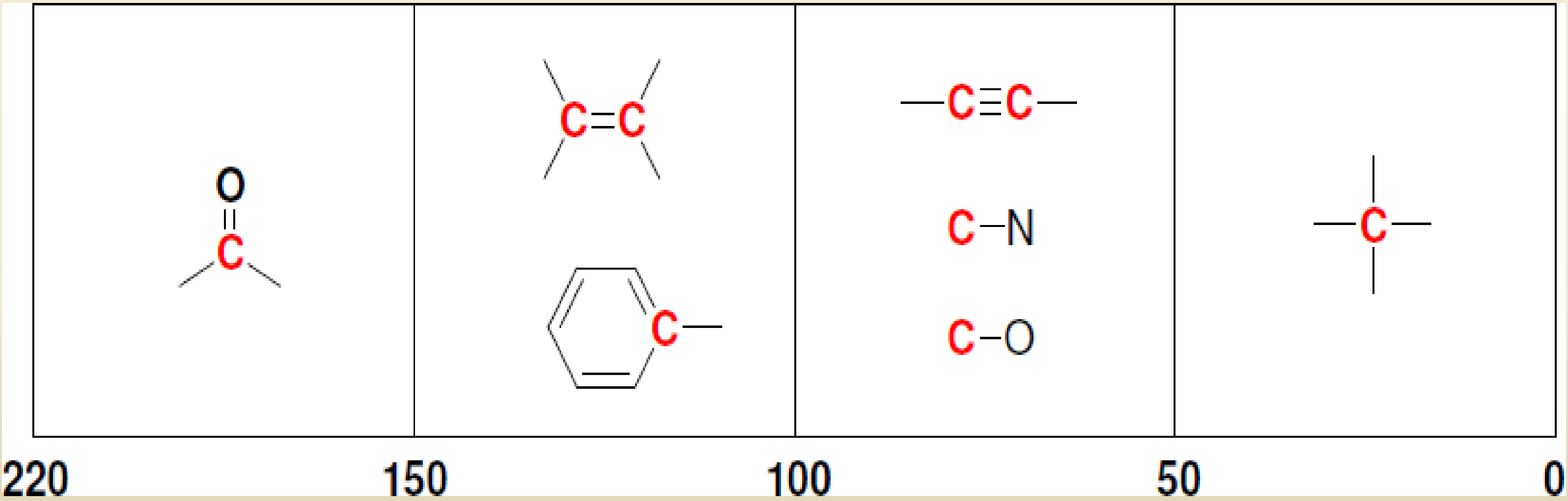
^1H range = 0 to ~ 12 ppm



^{13}C range = 0 to ~ 220 ppm

^{13}C Chemical shifts are most affected by

- hybridization state of carbon-
- electronegativity of groups attached to carbon-



Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 176-178

^{1}H and ^{13}C NMR compared

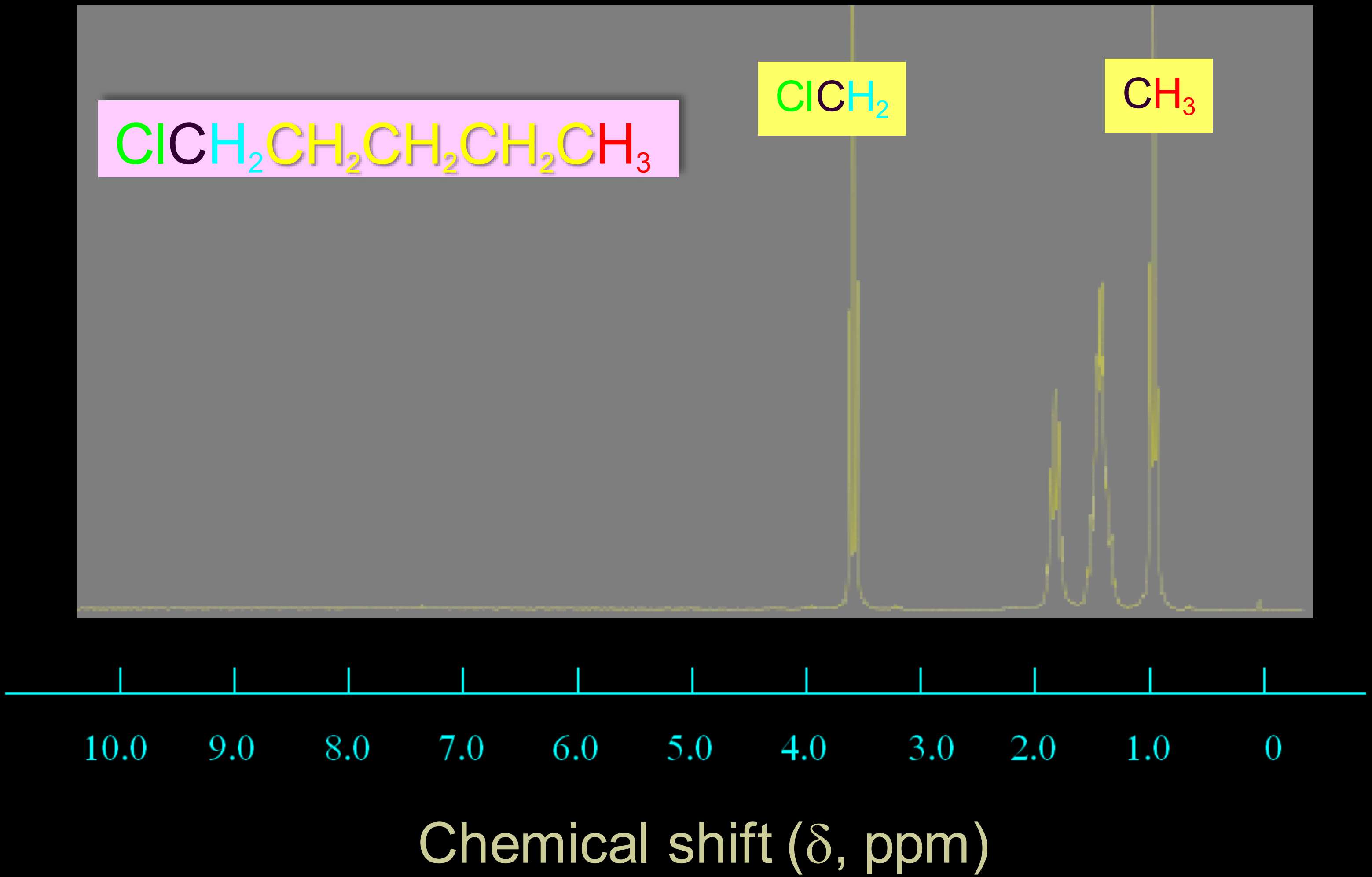
^{13}C signals are spread over a much wider range than ^{1}H signals making it easier to identify and count individual nuclei

Figure #1 shows the ^{1}H NMR spectrum of 1-chloropentane;

Figure #2 shows the ^{13}C spectrum. It is much easier to identify the compound as 1-chloropentane by its ^{13}C spectrum than by its ^{1}H spectrum.

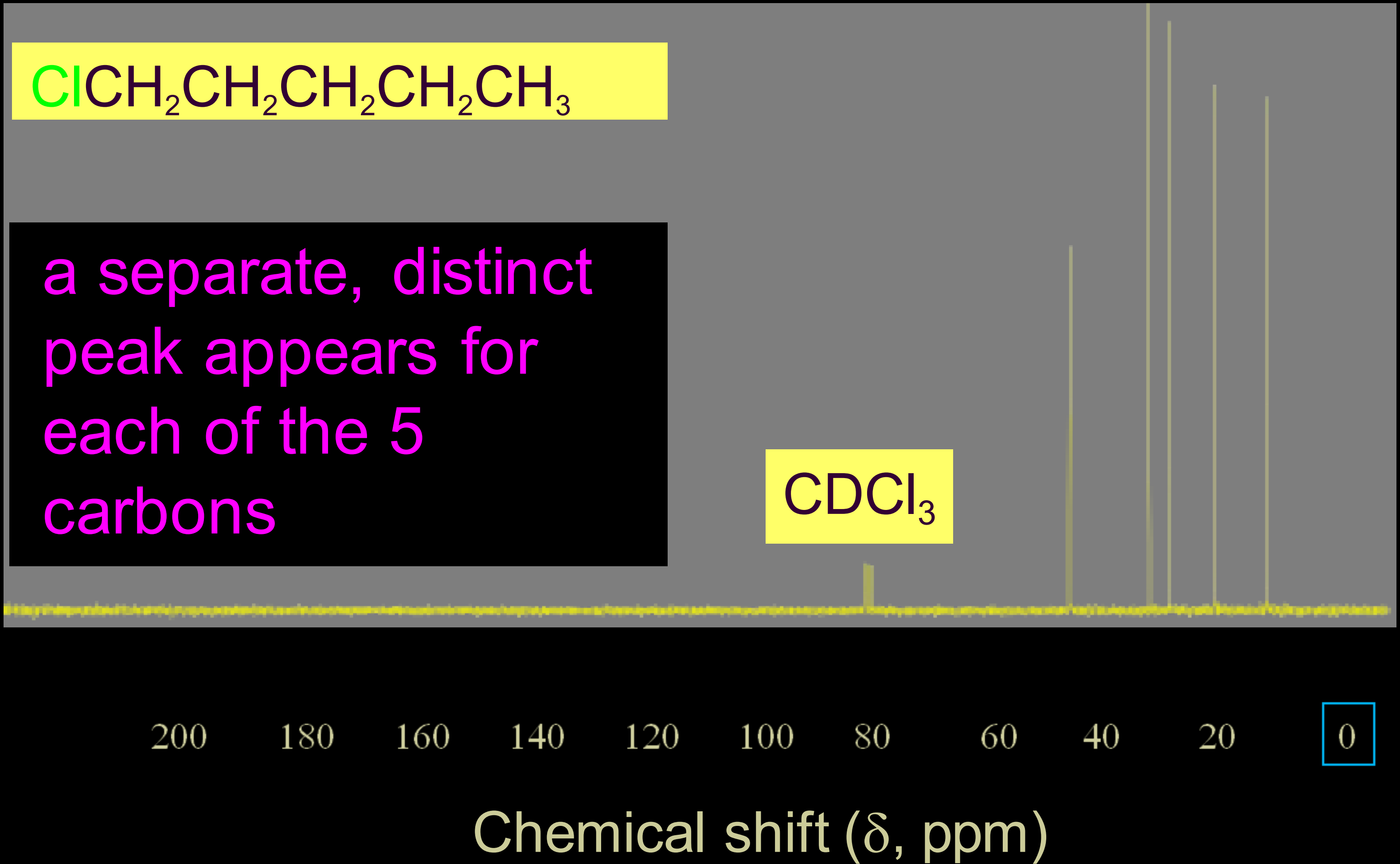
1-Chloropentane

^1H



1-Chloropentane

^{13}C



$ClCH_2CH_2CH_2CH_2CH_3$

a separate, distinct peak appears for each of the 5 carbons

Problems of ^{13}C

- **Natural abundance-**

  ^{13}C natural abundance is **very low (1.1%).**

- **Gyro magnetic ratio-**

  ^{13}C nucleus gyro magnetic ratio is much lesser than proton nucleus. **^{13}C-1.404; ^{1}H-5.585.**

- **Coupling phenomenon-**

  ^{13}C & ^{1}H have I=1/2 so that coupling between them probably occur.

Y.R.Sharma,S.Chand; Elementary Organic Spectroscopy, India edition, 2009,Pg. no. 71

PROBLEMS IN NMR CAN BE OVERCOME BY

- Fourier Transform Technique-

- Decoupling Technique-
    1) Broad Band Decoupling
    2) Off Resonance Decoupling
    3) DEPT (Pulse) Decoupling

- Nuclear Overhauser Phenomenon-

Signal Averaging and FT-NMR

- Low abundance of ^{13}C is overcome by *signal averaging* and *Fourier-transform NMR* (**FT-NMR**)
  - **Signal averaging**
    - Numerous individual runs are added together and averaged such that random background noise cancels to zero and NMR signals are enhanced, substantially increasing sensitivity.

SIGNAL AVERAGING AND FT-NMR

FT-NMR: (Pulse FT_NMR)

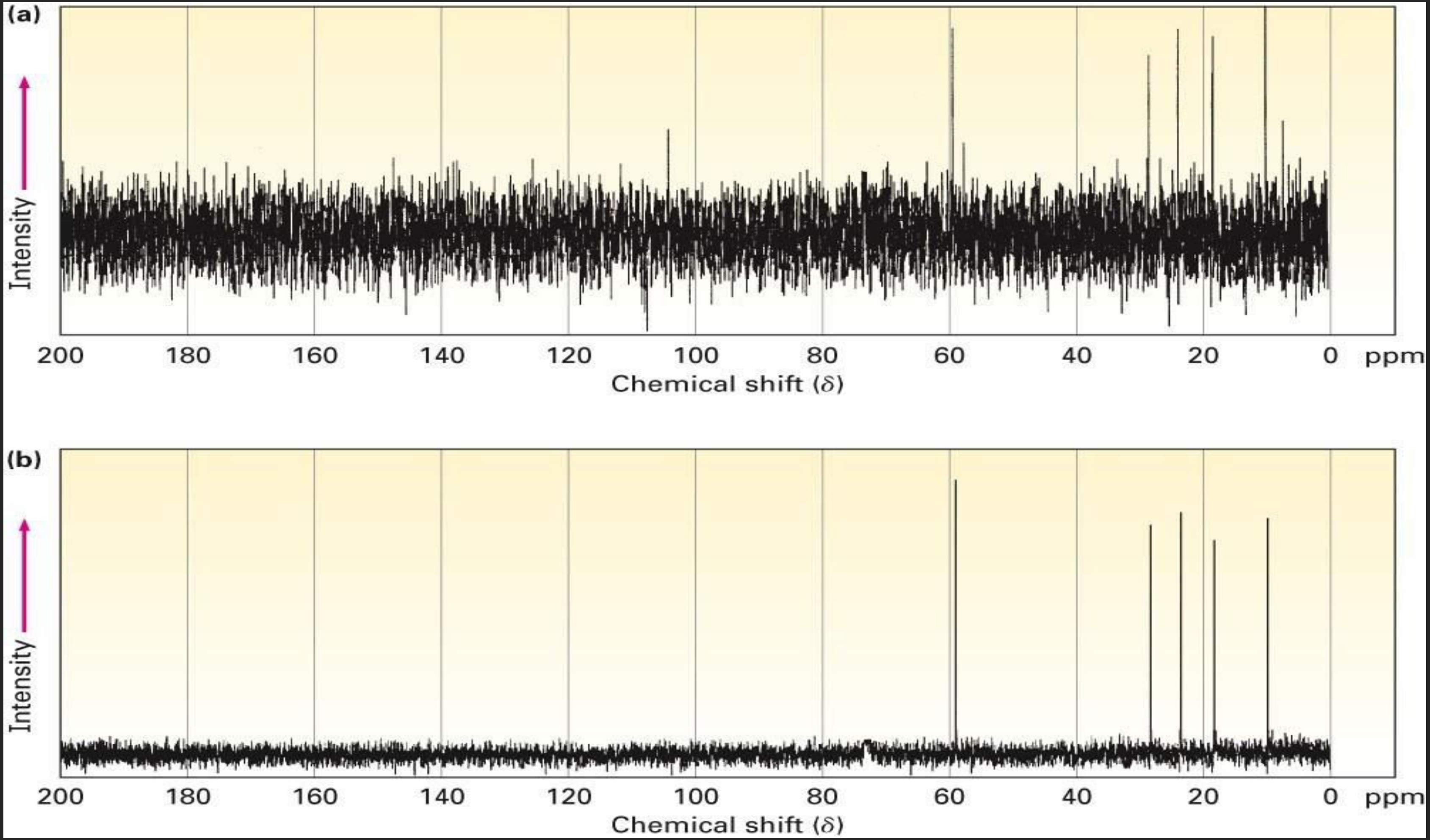
- Sample is irradiated with entire range of useful frequencies
- ^{13}C nuclei in the sample resonate at once giving complex, composite signal that is mathematically manipulated by Fourier transforms to segregate individual signals & convert them to frequencies.

Advantages-

- More sensitive-
- Very fast-

Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 121

Signal Averaging and FT-NMR, Pentan-1-ol

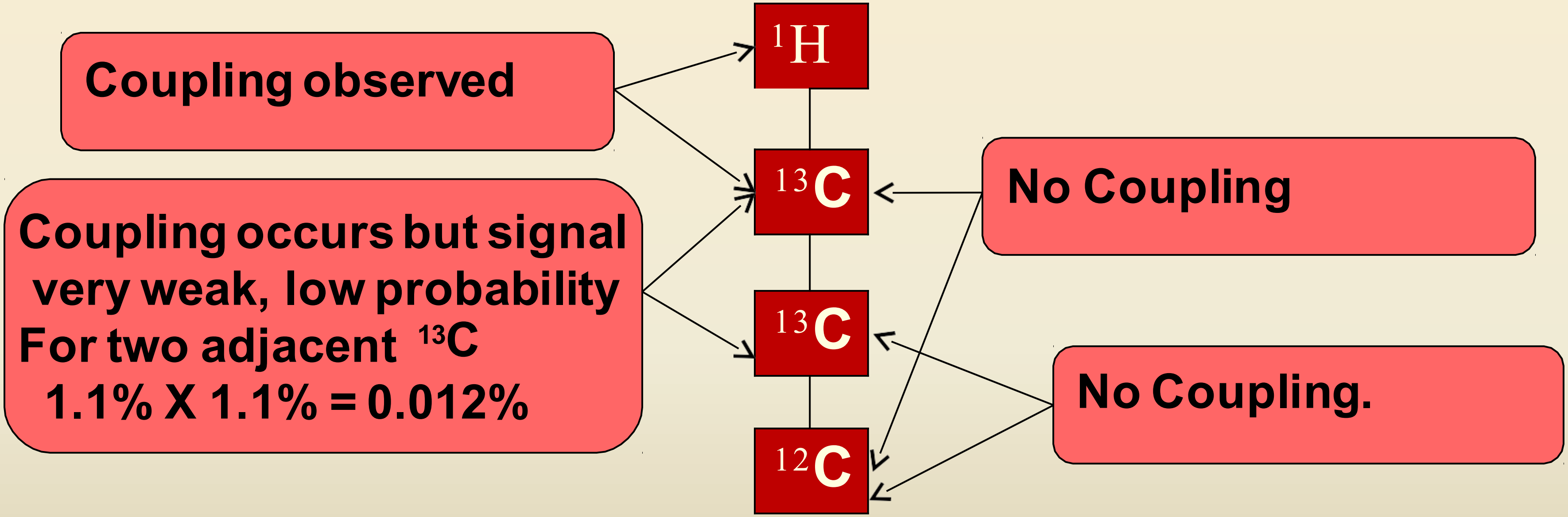


Carbon-13 NMR spectra of pentan-1-ol. Spectrum (a) is a single run, showing background noise. Spectrum (b) is an average of 200 runs

^{13}C-NMR Spin-Spin Coupling

- **^{1}H NMR:** Splitting reveals number of H neighbours.

  ^{13}C NMR: Limited to nuclei separated by just one sigma bond; no Pi bond.



Coupling observed

Coupling occurs but signal very weak, low probability For two adjacent ^{13}C 1.1% X 1.1% = 0.012%

^{1}H

^{13}C

^{13}C

^{12}C

No Coupling

No Coupling.

Decoupling Techniques

Proton or Noise Decoupling

- Irradiation of all ^1H nuclei by using decoupler
- ^1H nuclei are saturated & C nuclei see zero coupling

off Resonance Decoupling

- Provides multiplet information keeping the spectrum simple.
- Coupling between C & H attached directly to it

DEPT

- Involves complex program of pulse & delay times in C & H channel
- C atoms attached to varying no. of H exhibit different phases

Proton or Broadband Decoupling

a sample is irradiated with two different radiofrequencies.

1-to excite all C nuclei

2-to cause all protons -rapid transition

These rapid transition decoupled any spin-spin interaction between ^{1}H & ^{13}C nuclei.

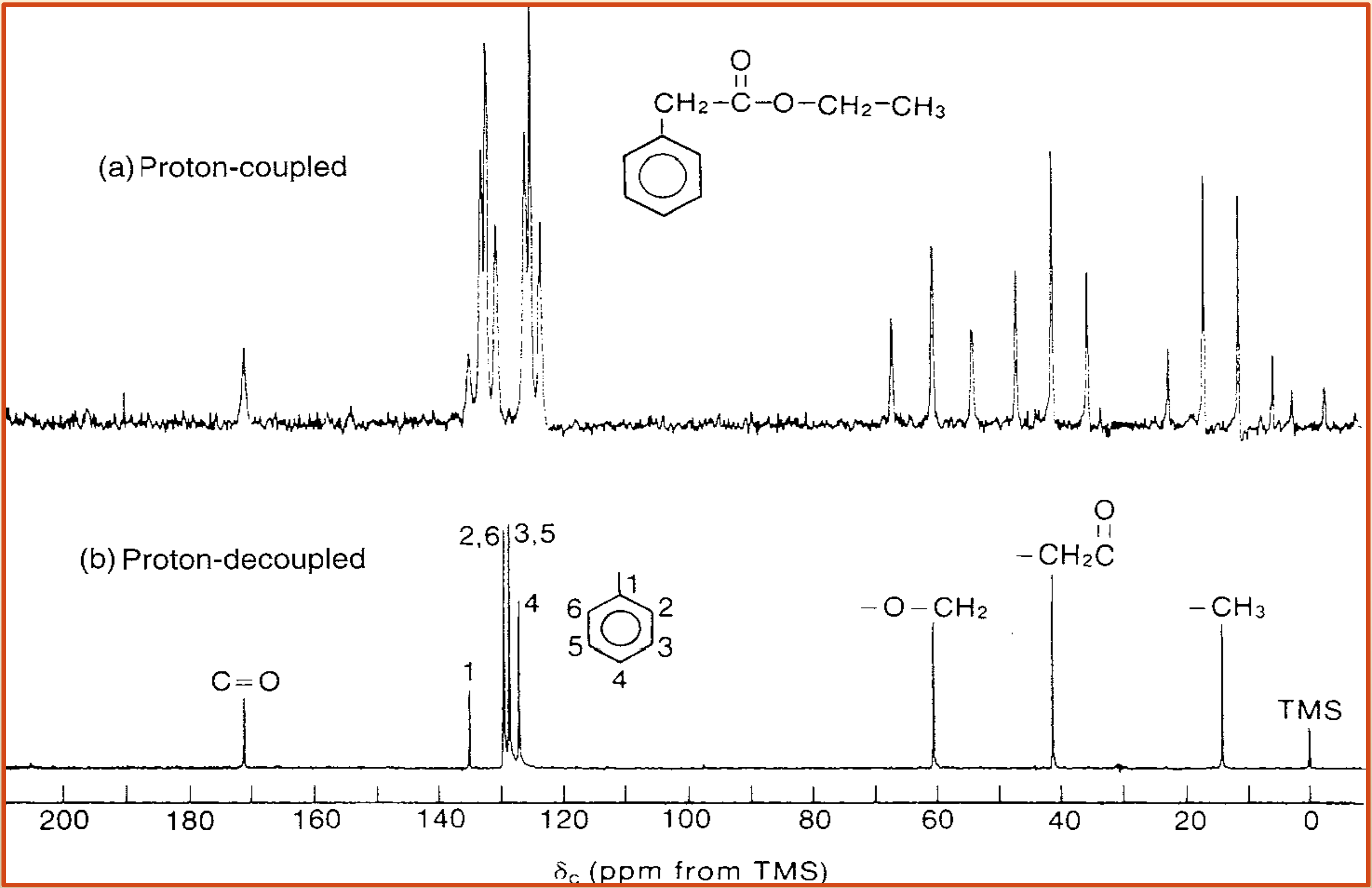
Due to rapid change, all spin interactions are averaged to zero.

Appear only ^{13}**C** spectrum

Disadvantage.-information on attached H is lost.

Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 181

Spectra of Ethyl phenyl acetate



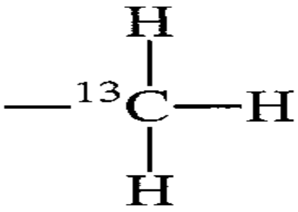
^{13}C off-resonance decoupling

- In this technique the ^{13}**C** nuclei are split only by the protons directly bonded to them as a result the multiplets become narrow & not removed altogether as in fully decoupled spectra.
- It simplifies the spectrum by allowing some of the splitting information to be retained.
- The N + 1 rule applies: a carbon with N number of protons gives a signal with N + 1 peaks.

P.S.Kalsi; Spectroscopy Of Organic Compounds, Sixth Edition:2004, Page no.-377

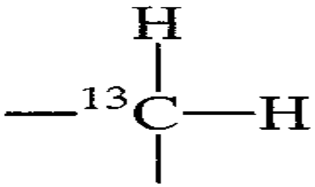
^{13}C off-resonance decoupled spectrum

3 protons



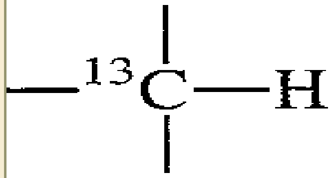
n+1=4

2 protons



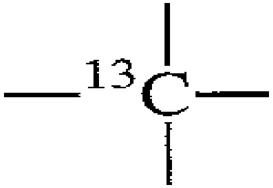
n+1=3

1 proton

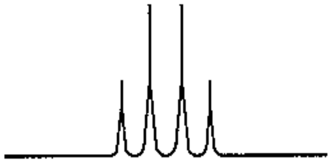


n+1=2

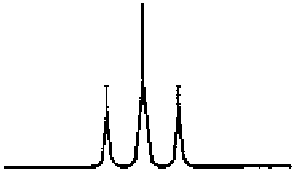
0 protons



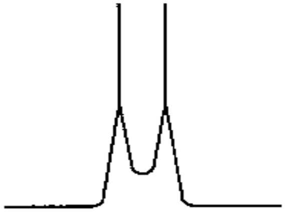
n+1=1



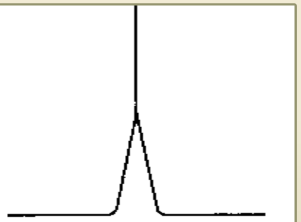
Methyl ‘C’



Methylene ‘C’



Methine ‘C’

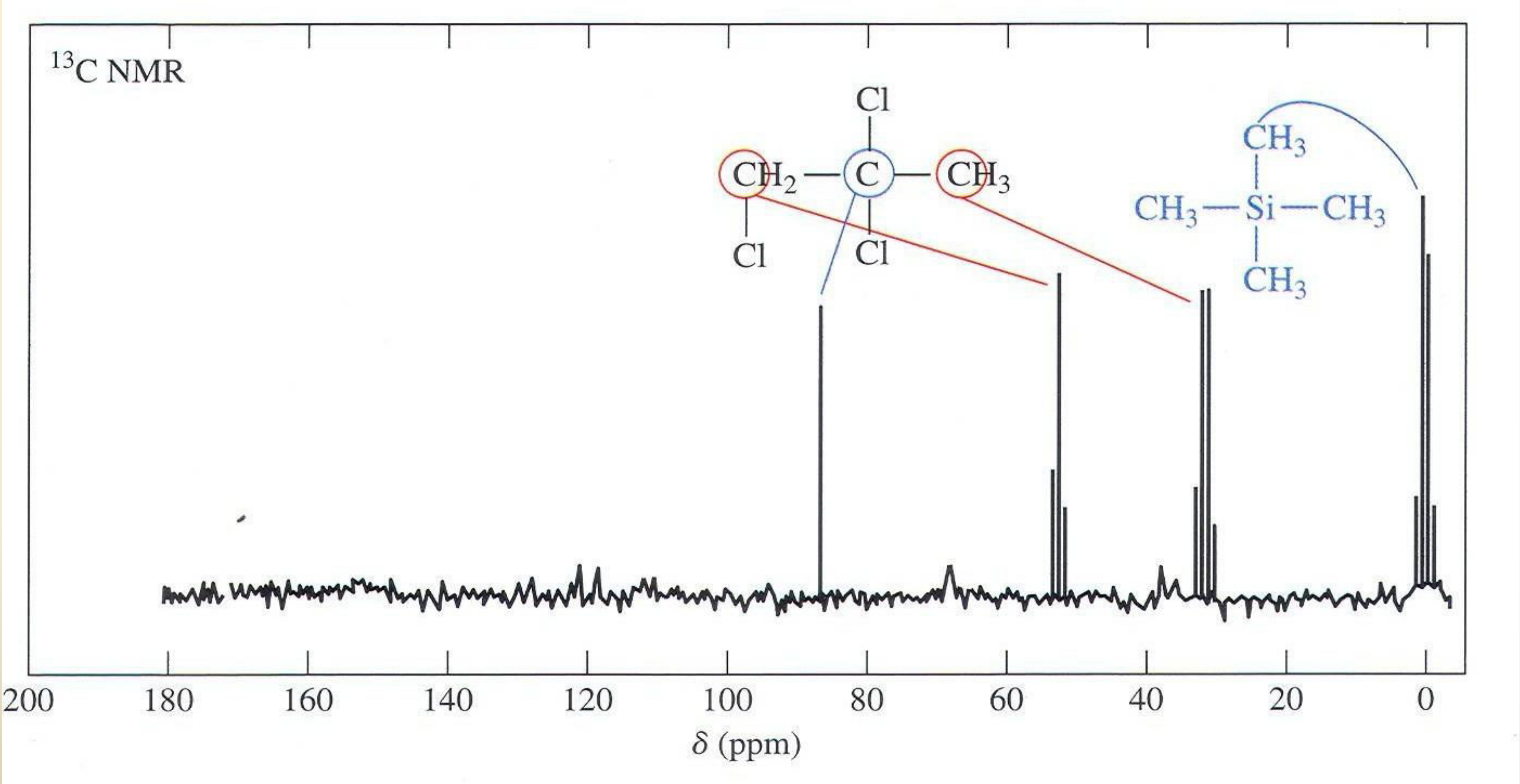


Quaternary‘C’

P.S.Kalsi; Spectroscopy Of Organic Compounds, Sixth Edition:2004, Page no.-377

^{13}C Off-resonance decoupled spectrum

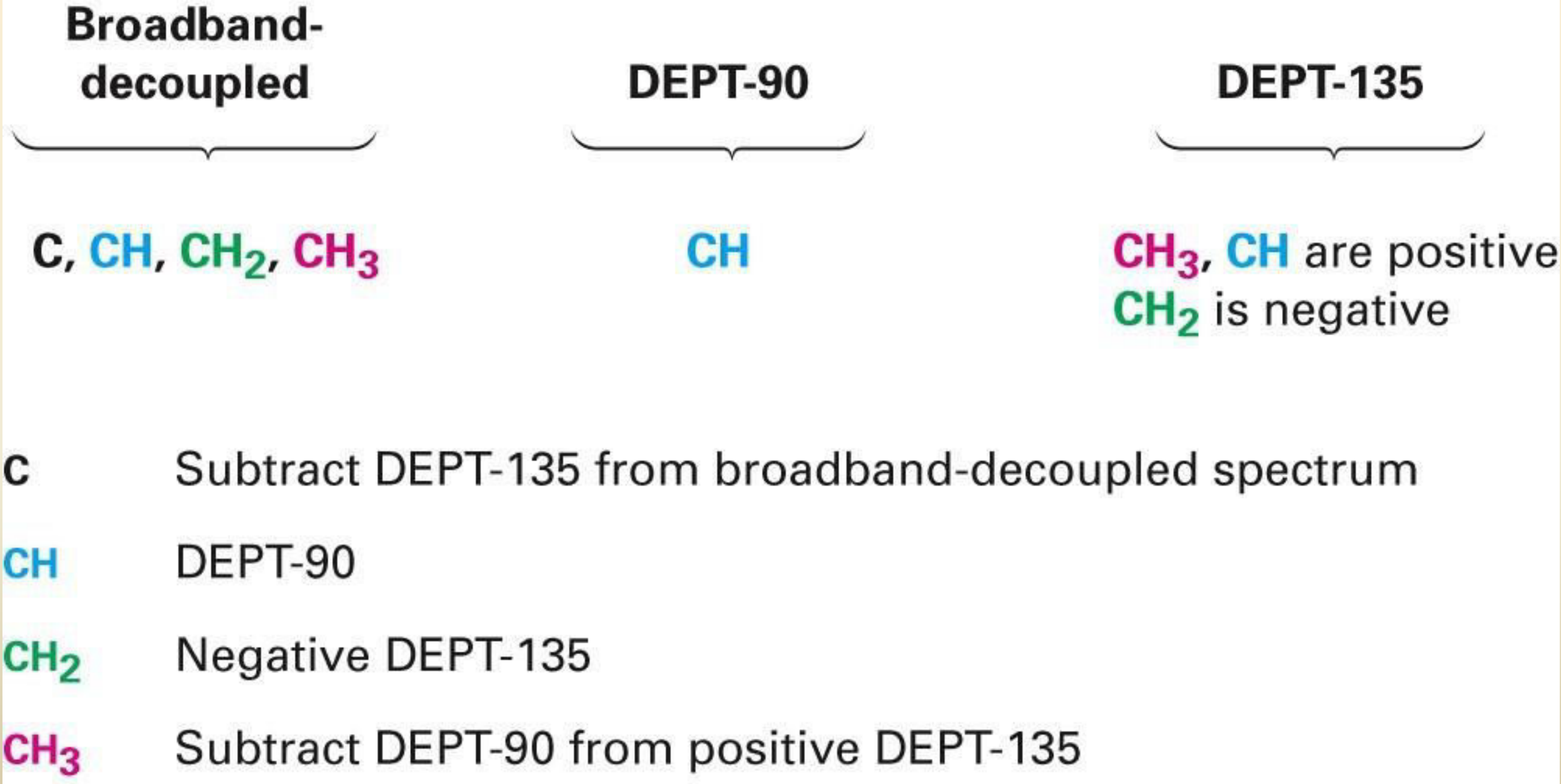
1,2,2-trichloropropane



P.S.Kalsi; Spectroscopy Of Organic Compounds, Sixth Edition:2004, Page no.-379

DEPT ^{13}C NMR Spectroscopy

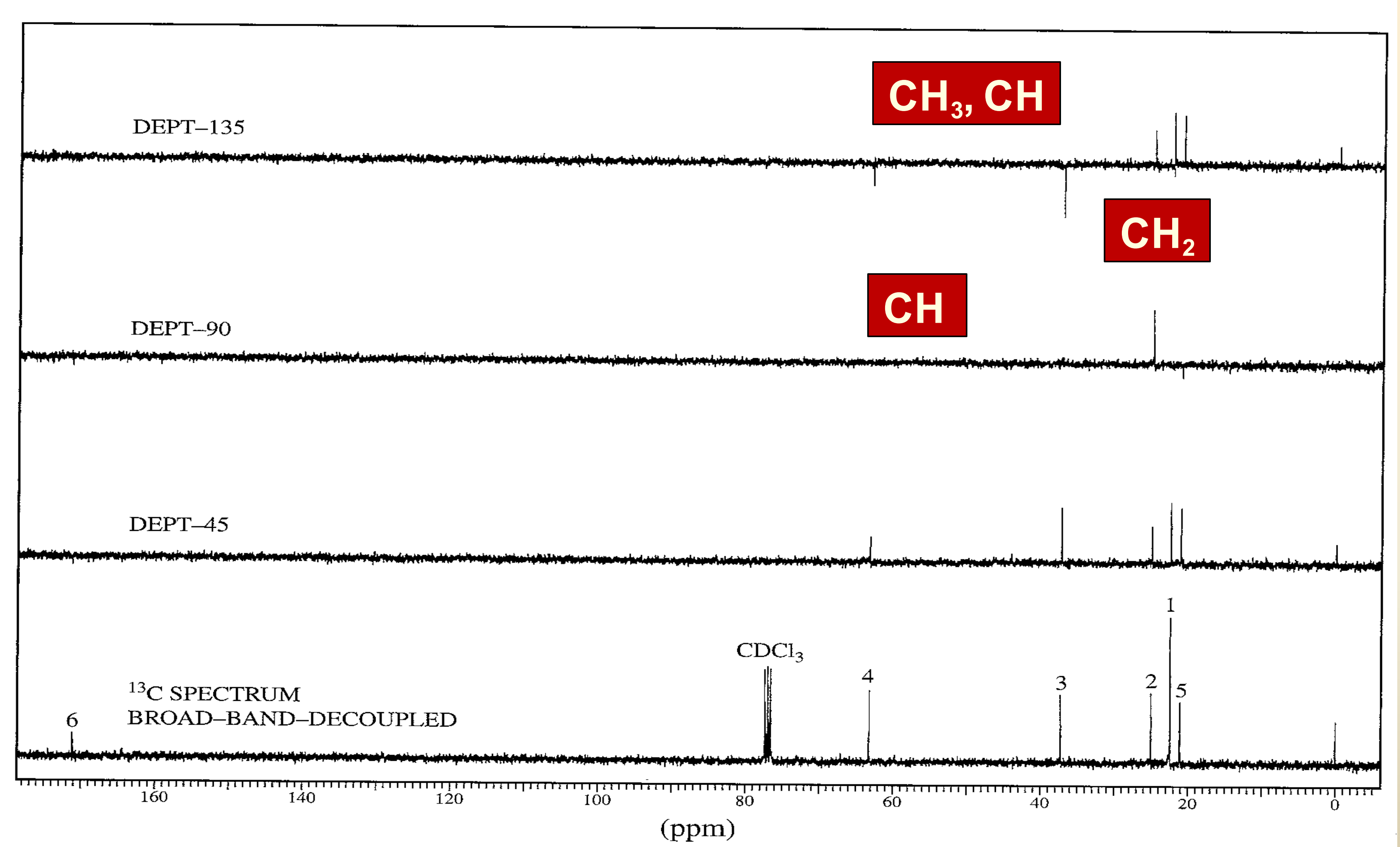
Three stages in DEPT experiment



Broadband-decoupled	DEPT-90	DEPT-135
C, CH, CH_2, CH_3	CH	CH_3, CH are positive CH_2 is negative

C	Subtract DEPT-135 from broadband-decoupled spectrum
CH	DEPT-90
CH_2	Negative DEPT-135
CH_3	Subtract DEPT-90 from positive DEPT-135

DEPT Spectra for isopentyl acetate



DEPT spectra of isopentyl acetate

^{13}C Interpretation with Other NMR Spectra

NUCLEAR OVERHAUSER ENHANCEMENT

- NOE effect for heteronuclear nuclei: when one of two different types of atoms irradiated & NMR spectrum of other type is determined they show change in absorption intensities of the observed atom, enhancement occurred, is called nuclear overhauser effect & the degree of increase in the signal is called nuclear overhauser enhancement.
- Effect can be either positive or negative.
- in ^{13}**C** interacting with ^{1}**H** effect is positive.
- NOE is enhancement of signals,it add in to original signal strength.

Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 180

^{13}C Interpretation

- Count how many lines- how many types of carbons
- Symmetry duplicates give same line- if there are more carbons in your spectrum – symmetry
- Check chemical shift window-
- Check splitting pattern-
- Signal height size-

^{13}C Interpretation

^{13}C NMR spectroscopy provides information about:

- The number of nonequivalent carbons atoms in a molecule
- The electronic environment of each carbon
- How many protons are bonded to each carbon

HETCOR Technique

Heteronuclear Chemical Shift Correlation :

- **Carbon - Hydrogen**

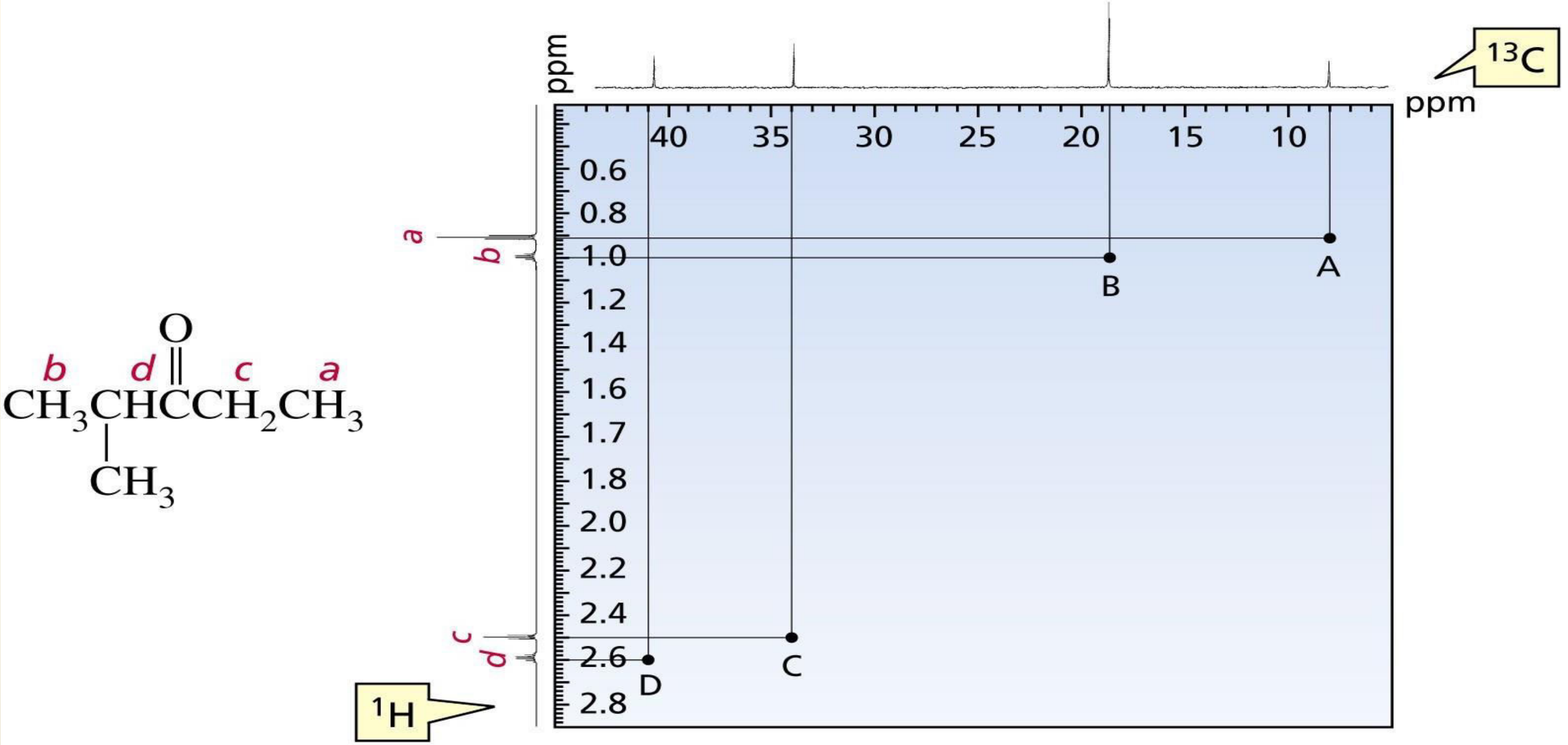
^{1}H and ^{13}C spectra plotted separately on two frequency axes.
Coordinates of cross peak connect signal of carbon to protons that are bonded to it.

- Other HETCOR technique-
- **Carbon to Deuterium**
- **^{13}C to ^{19}F**
- **^{13}C to ^{31}P**

Pavia, Lampman, Kriz, Vyvyan; Spectroscopy, Cengage Learning, India edition, 2007, Pg. no. 198

The HETCOR spectrum of 2-methyl-3-pentanone

indicates coupling between protons and the carbon to which they are attached

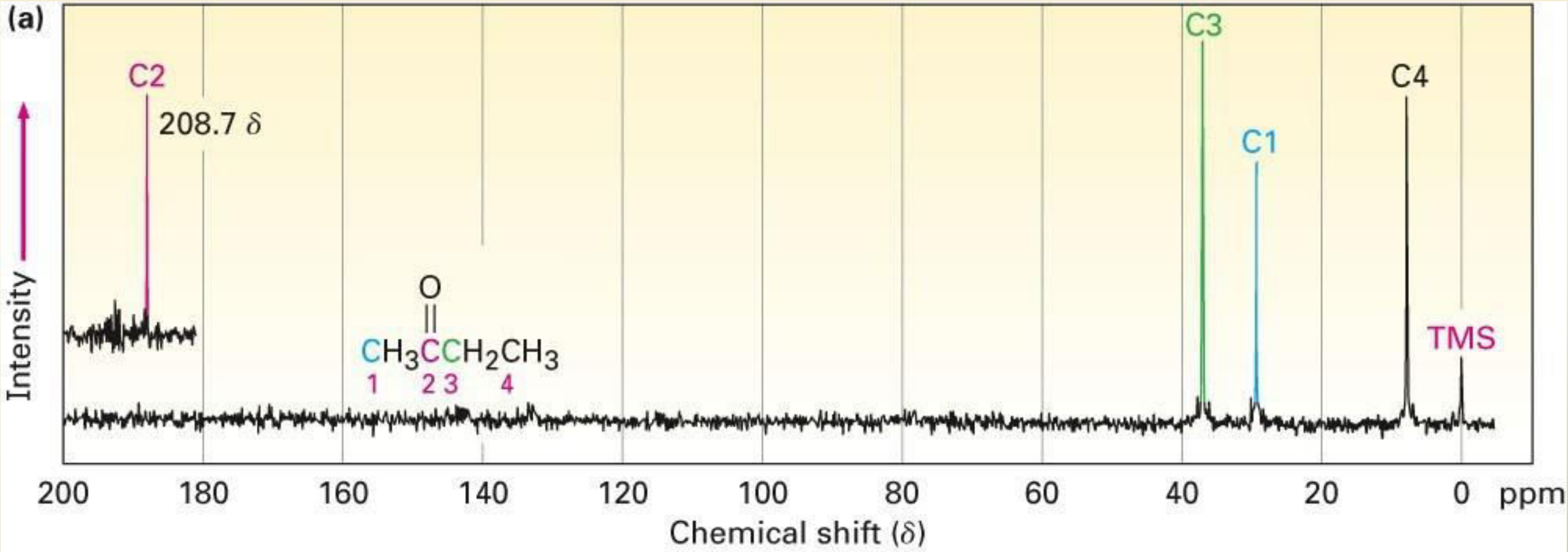


HETCOR: Heteronuclear Chemical Shift Correlation

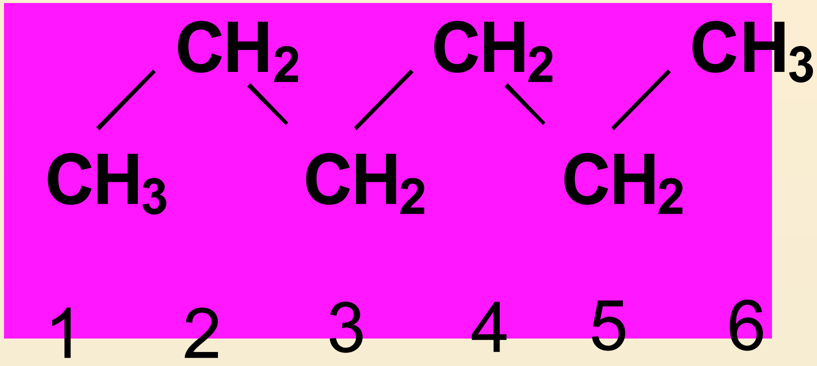
Example's

^{13}C spectrum for butan-2-one

- Butan-2-one contains 4 chemically nonequivalent carbon atoms
- Carbonyl carbons (C=O) are always found at the low-field end of the spectrum from 160 to 220 δ



n-Hexane

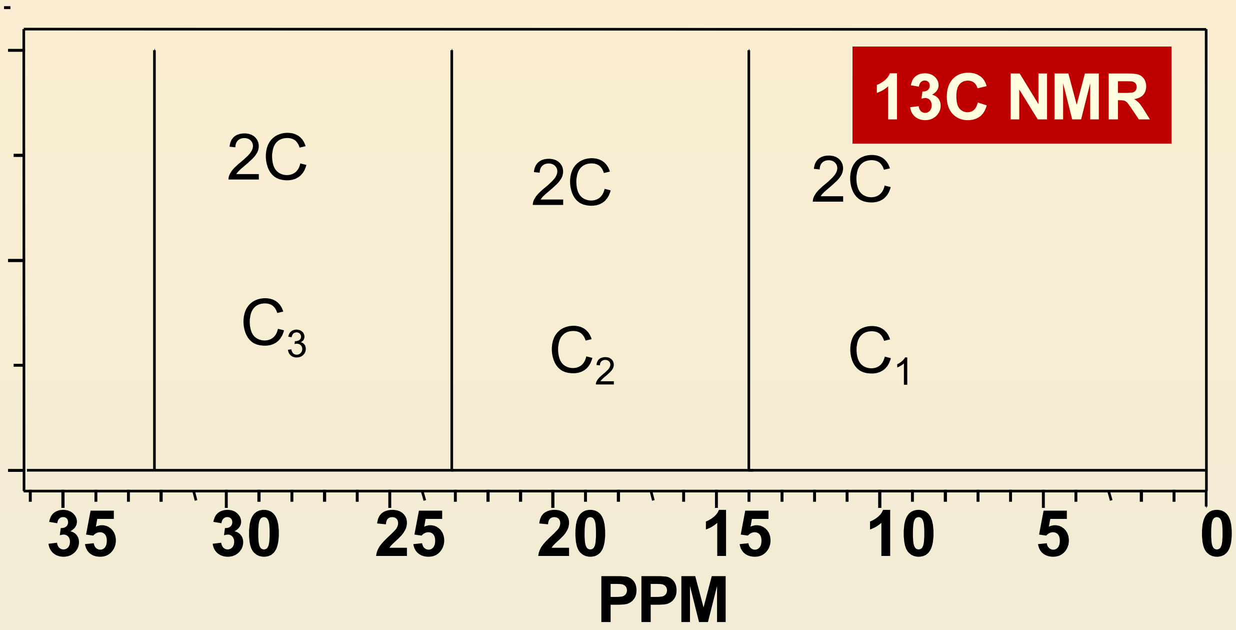


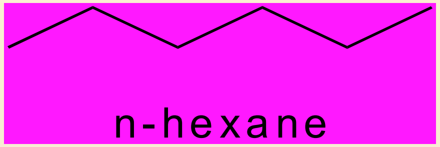
Three different kinds of carbon atoms in n-hexane: $C_1 = C_6$, $C_2 = C_5$, and $C_3 = C_4$

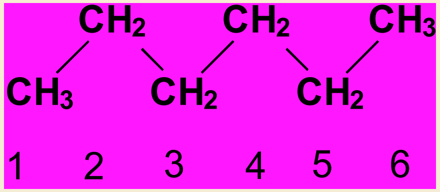
The signals in a 13C NMR are proportional to the relative number of carbon atoms in a structure

William Kemp, Organic Spectroscopy, Palgrave, Third edition, 2002, Pg. no. 135-144

n-Hexane







Task: Assign the 13C signals to the carbon atoms of n-hexane

Example

Predicting Chemical Shifts in ^{13}C NMR Spectra

At what approximate positions would you expect ethyl acrylate, $H_2C{=}CHCO_2CH_2CH_3$, to show ^{13}C NMR absorptions?

Worked Example

Predicting Chemical Shifts in ^{13}C NMR Spectra

Strategy

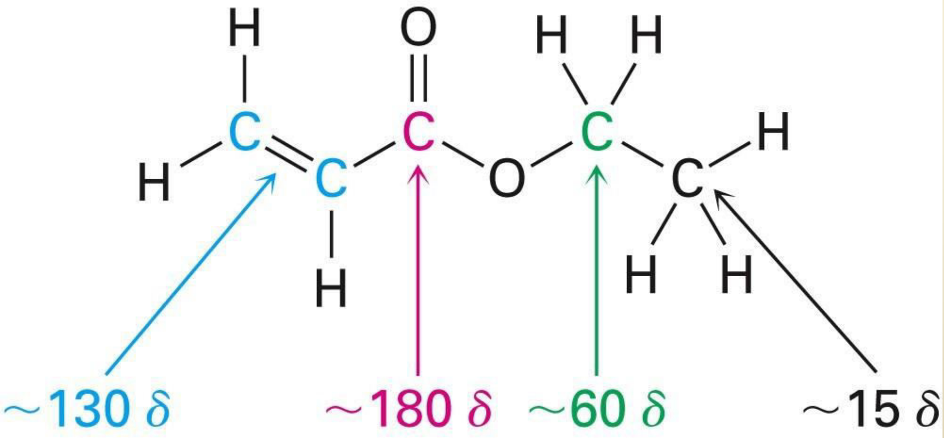
- Identify the distinct carbons in the molecule, and note whether each is alkyl, vinylic, aromatic, or in a carbonyl group.then predict the value with the help of correlation chart.

Example

Predicting Chemical Shifts in ^{13}C NMR Spectra

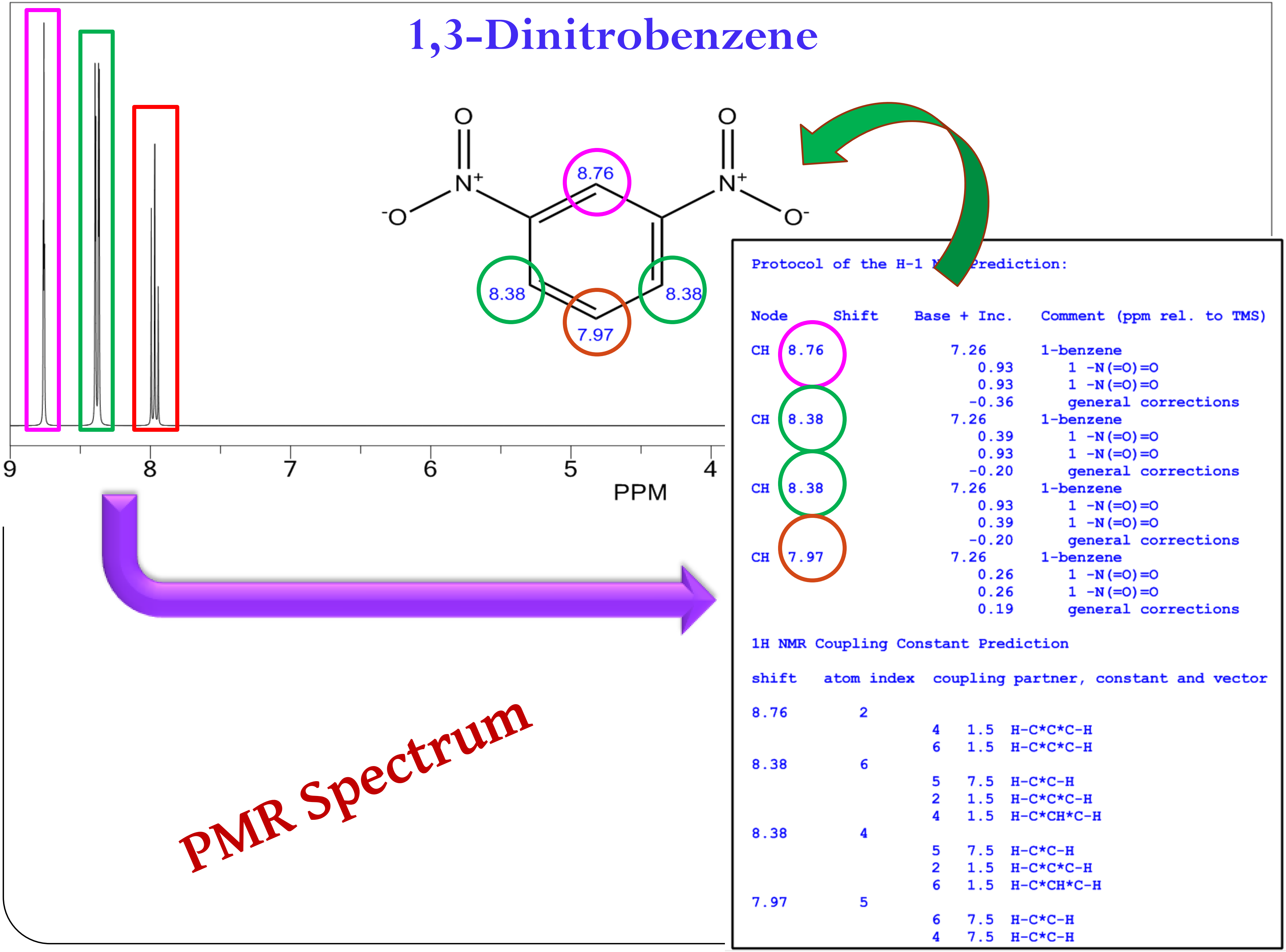
Solution

- Ethyl acrylate has five distinct carbons: two different C=C, one C=O, one C(O)-C, and one alkyl C. From Correlation chart the likely absorptions are



Interpreting Some NMR Spectra

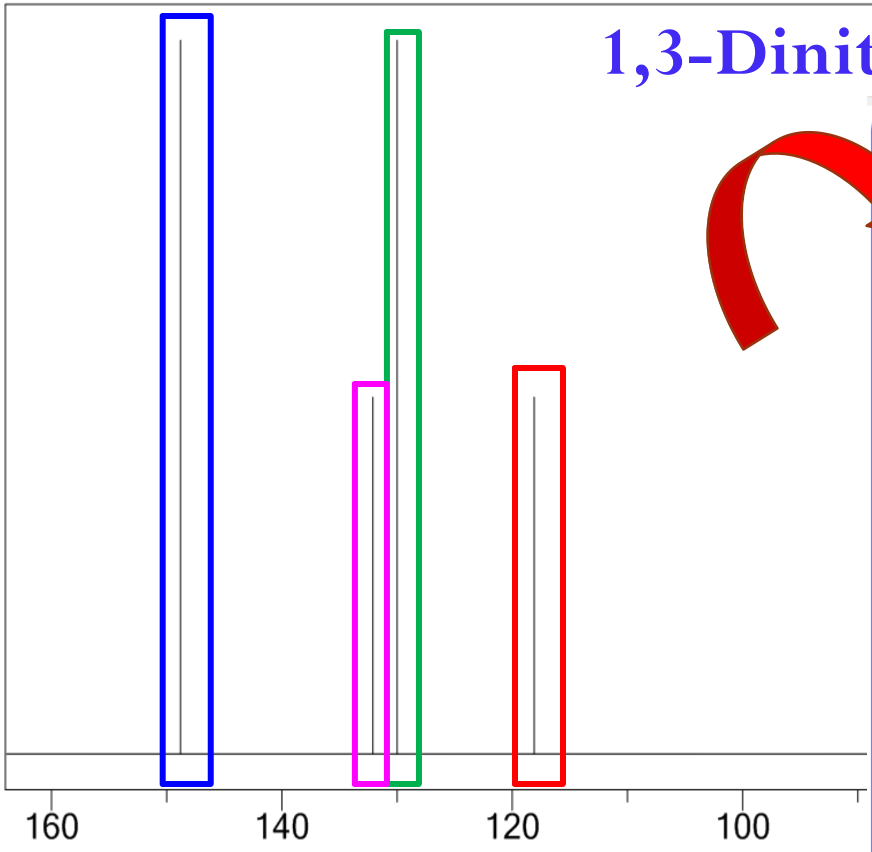
1,3-Dinitrobenzene

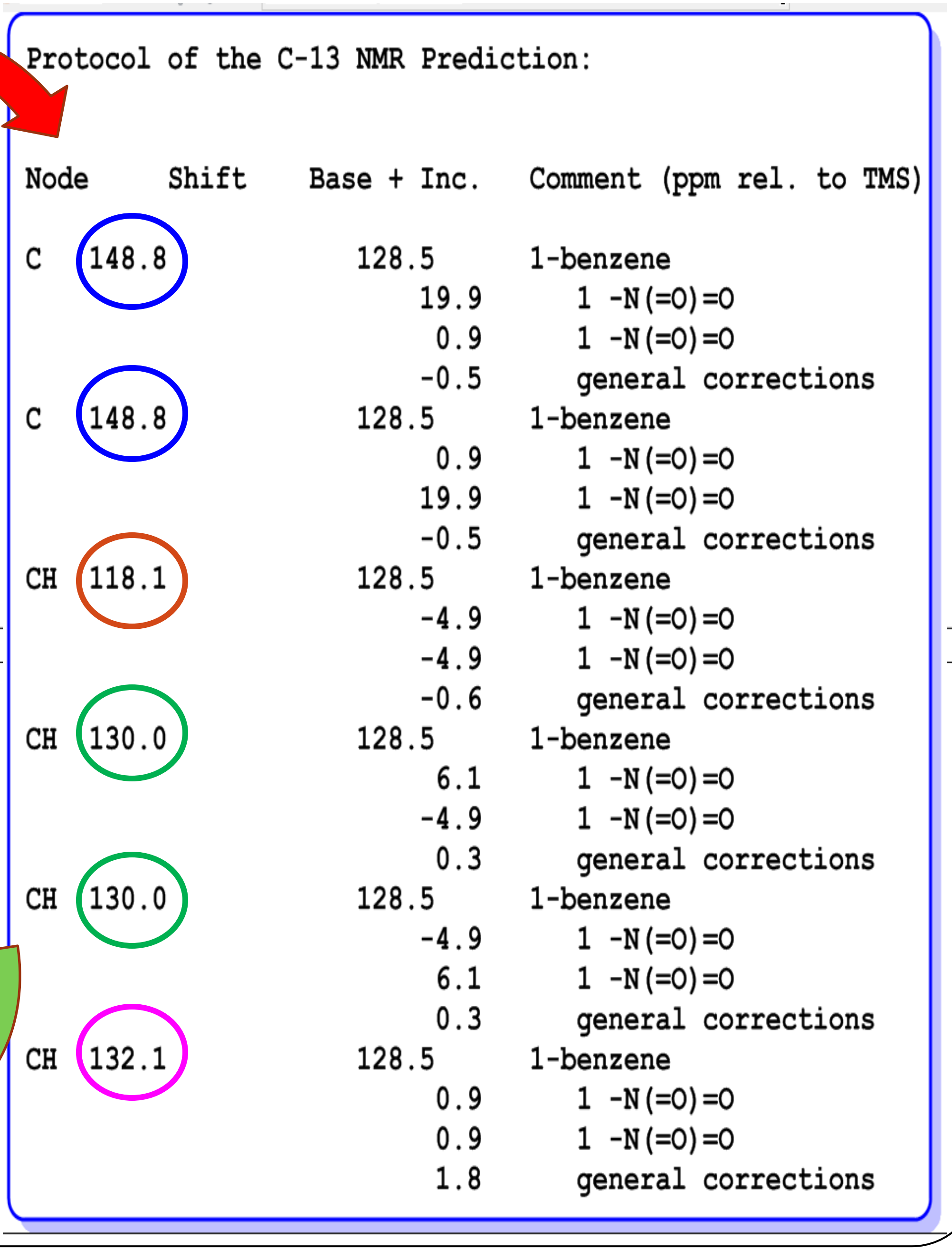


```
Protocol of the H-1 N[illegible] Prediction:

Node      Shift     Base + Inc.    Comment (ppm rel. to TMS)

CH   8.76              7.26        1-benzene
                          0.93        1 -N(=O)=O
                          0.93        1 -N(=O)=O
                         -0.36        general corrections
CH   8.38              7.26        1-benzene
                          0.39        1 -N(=O)=O
                          0.93        1 -N(=O)=O
                         -0.20        general corrections
CH   8.38              7.26        1-benzene
                          0.93        1 -N(=O)=O
                          0.39        1 -N(=O)=O
                         -0.20        general corrections
CH   7.97              7.26        1-benzene
                          0.26        1 -N(=O)=O
                          0.26        1 -N(=O)=O
                          0.19        general corrections

1H NMR Coupling Constant Prediction

shift    atom index  coupling partner, constant and vector

8.76          2
                     4    1.5   H-C*C*C-H
                     6    1.5   H-C*C*C-H
8.38          6
                     5    7.5   H-C*C-H
                     2    1.5   H-C*C*C-H
                     4    1.5   H-C*CH*C-H
8.38          4
                     5    7.5   H-C*C-H
                     2    1.5   H-C*C*C-H
                     6    1.5   H-C*CH*C-H
7.97          5
                     6    7.5   H-C*C-H
                     4    7.5   H-C*C-H
```

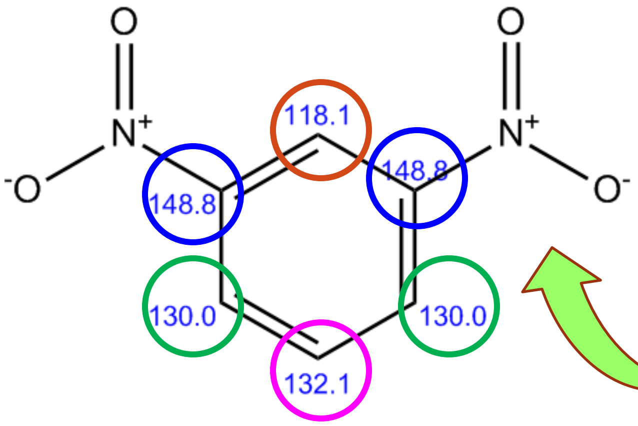
PMR Spectrum

1,3-Dinitrobenzene



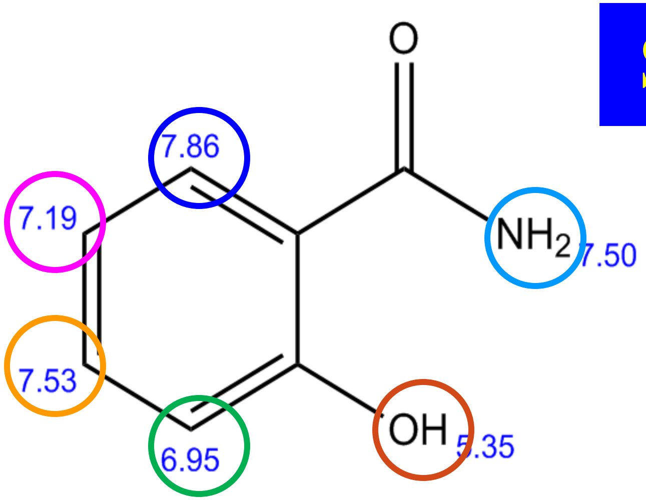


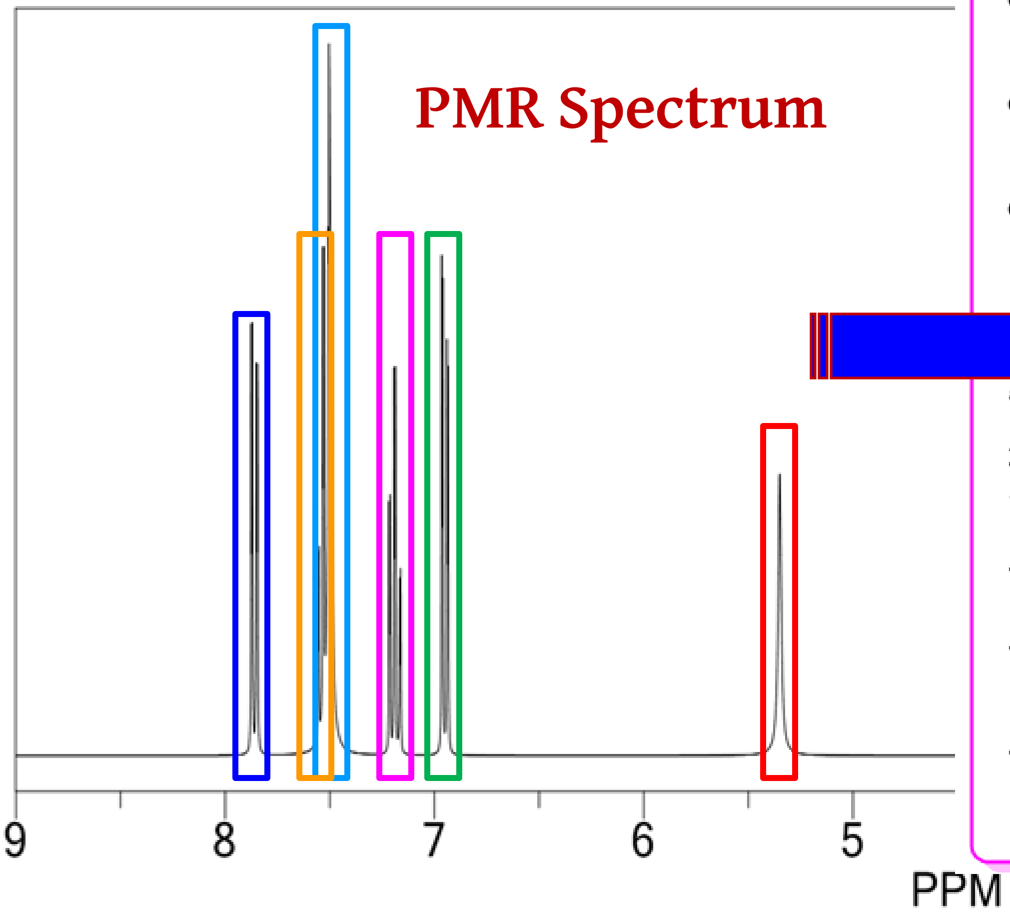
```
Protocol of the C-13 NMR Prediction:

Node      Shift      Base + Inc.    Comment (ppm rel. to TMS)

C       148.8           128.5       1-benzene
                         19.9         1 -N(=O)=O
                          0.9         1 -N(=O)=O
                         -0.5         general corrections
C       148.8           128.5       1-benzene
                          0.9         1 -N(=O)=O
                         19.9         1 -N(=O)=O
                         -0.5         general corrections
CH      118.1           128.5       1-benzene
                         -4.9         1 -N(=O)=O
                         -4.9         1 -N(=O)=O
                         -0.6         general corrections
CH      130.0           128.5       1-benzene
                          6.1         1 -N(=O)=O
                         -4.9         1 -N(=O)=O
                          0.3         general corrections
CH      130.0           128.5       1-benzene
                         -4.9         1 -N(=O)=O
                          6.1         1 -N(=O)=O
                          0.3         general corrections
CH      132.1           128.5       1-benzene
                          0.9         1 -N(=O)=O
                          0.9         1 -N(=O)=O
                          1.8         general corrections
```



CMR Spectrum

Salicylamide

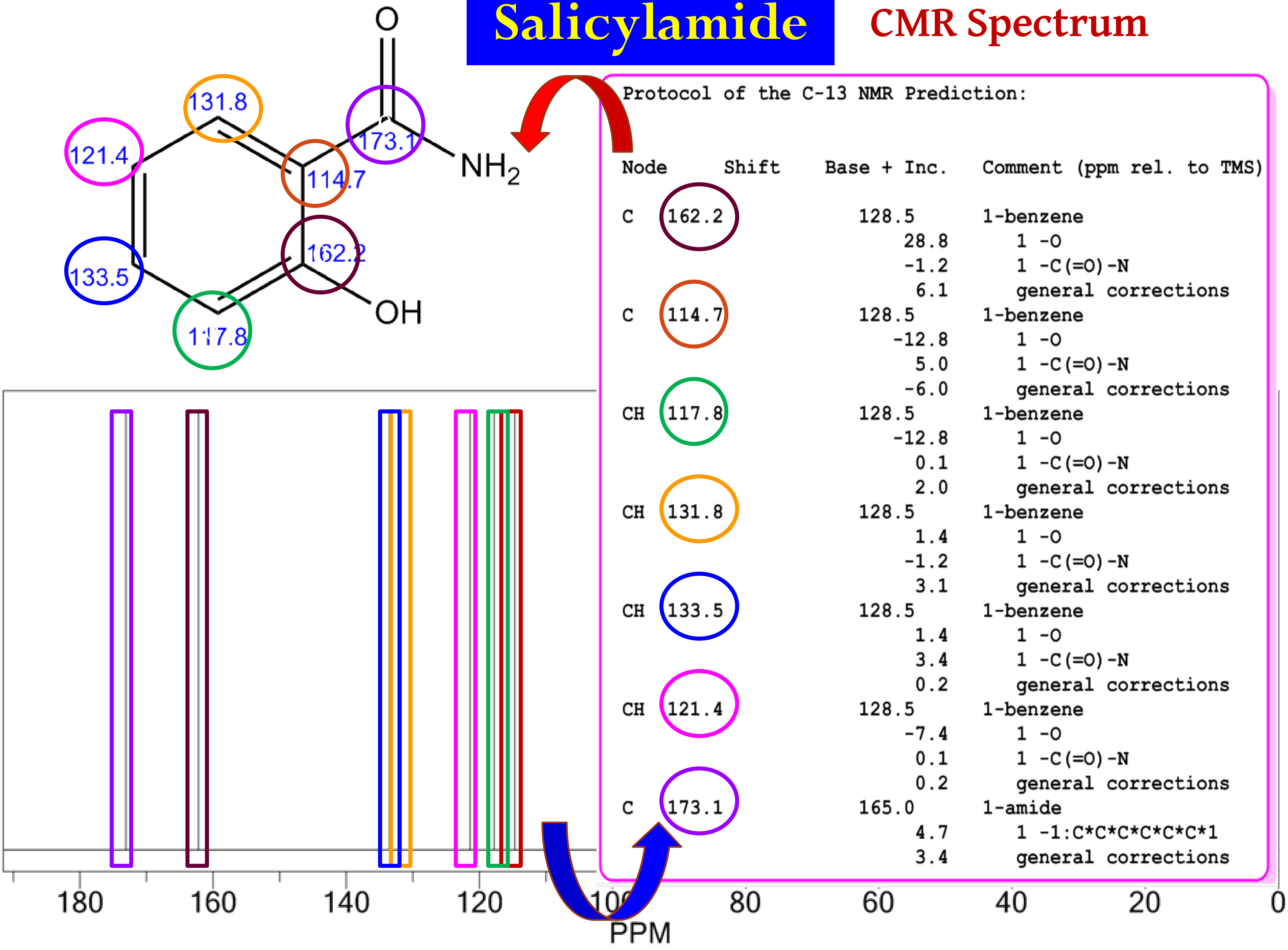



PMR Spectrum

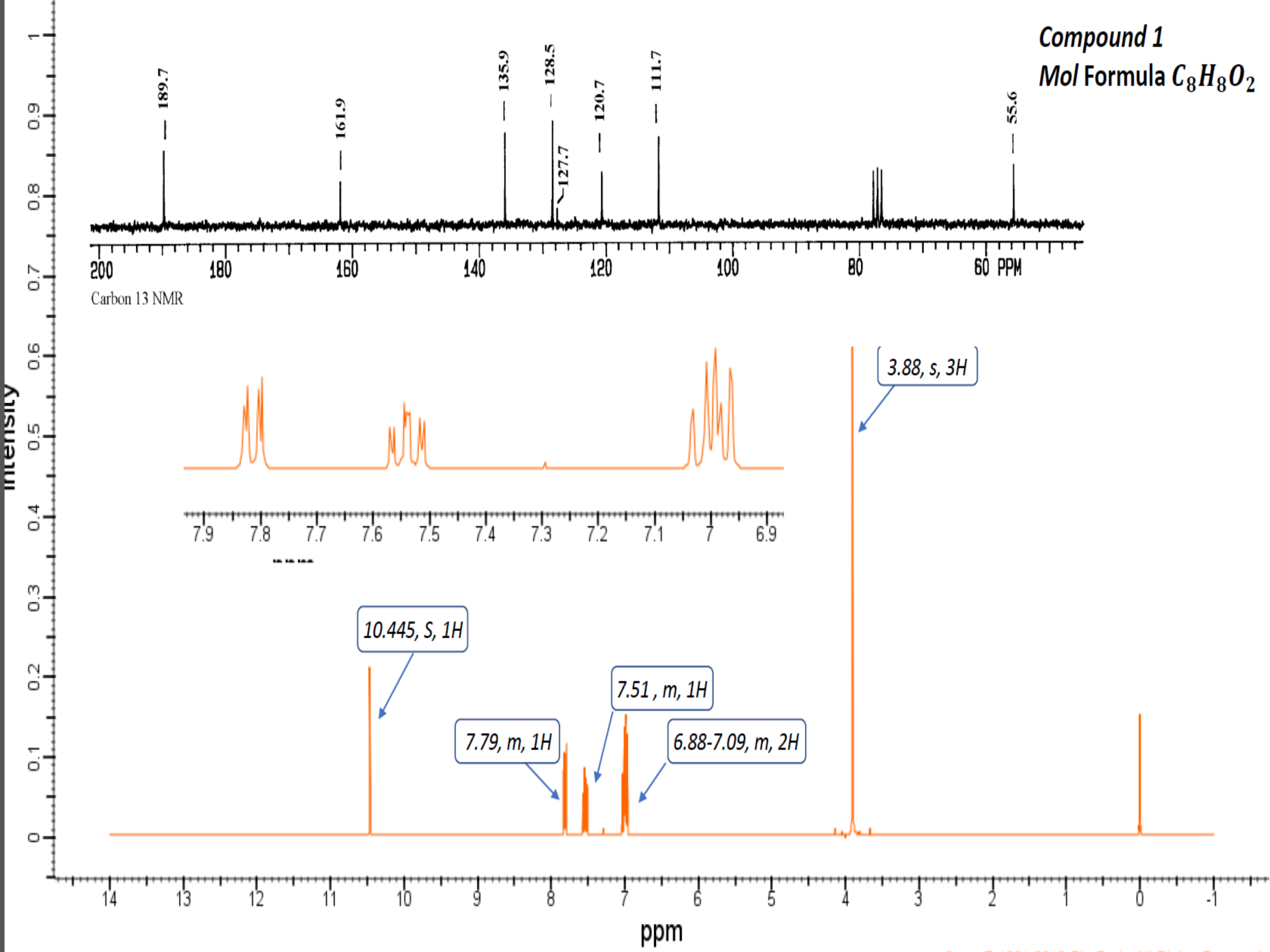
```
Protocol of the H-1 NMR Prediction:

Node     Shift    Base + Inc.   Comment (ppm rel. to TMS)

OH       5.35         5.00      aromatic C-OH
                      0.35         general corrections
NH2      7.50         6.00      prim. amide
                      1.50         general corrections
CH       6.95         7.26      1-benzene
                     -0.53         1 -O
                      0.18         1 -C(=O)N
                      0.04         general corrections
CH       7.86         7.26      1-benzene
                     -0.17         1 -O
                      0.69         1 -C(=O)N
                      0.08         general corrections
CH       7.53         7.26      1-benzene
                     -0.17         1 -O
                      0.25         1 -C(=O)N
                      0.19         general corrections
CH       7.19         7.26      1-benzene
                     -0.44         1 -O
                      0.18         1 -C(=O)N
                      0.19         general corrections

          Coupling Constant Prediction

shift   atom index  coupling partner, constant and vector

5.35        4
7.50       10
6.95        5
                      6   7.5  H-C*C-H
                      7   1.5  H-C*CH*C-H
7.86        8
                      7   7.5  H-C*C-H
                      6   1.5  H-C*CH*C-H
7.53        6
                      5   7.5  H-C*C-H
                      7   7.5  H-C*C-H
                      8   1.5  H-C*CH*C-H
7.19        7
                      8   7.5  H-C*C-H
                      6   7.5  H-C*C-H
                      5   1.5  H-C*CH*C-H
```

Salicylamide

CMR Spectrum



```
Protocol of the C-13 NMR Prediction:

Node      Shift     Base + Inc.   Comment (ppm rel. to TMS)

C         162.2        128.5      1-benzene
                        28.8        1 -O
                        -1.2        1 -C(=O)-N
                         6.1        general corrections
C         114.7        128.5      1-benzene
                       -12.8        1 -O
                         5.0        1 -C(=O)-N
                        -6.0        general corrections
CH        117.8        128.5      1-benzene
                       -12.8        1 -O
                         0.1        1 -C(=O)-N
                         2.0        general corrections
CH        131.8        128.5      1-benzene
                         1.4        1 -O
                        -1.2        1 -C(=O)-N
                         3.1        general corrections
CH        133.5        128.5      1-benzene
                         1.4        1 -O
                         3.4        1 -C(=O)-N
                         0.2        general corrections
CH        121.4        128.5      1-benzene
                        -7.4        1 -O
                         0.1        1 -C(=O)-N
                         0.2        general corrections
C         173.1        165.0      1-amide
                         4.7        1 -1:C*C*C*C*C*1
                         3.4        general corrections
```

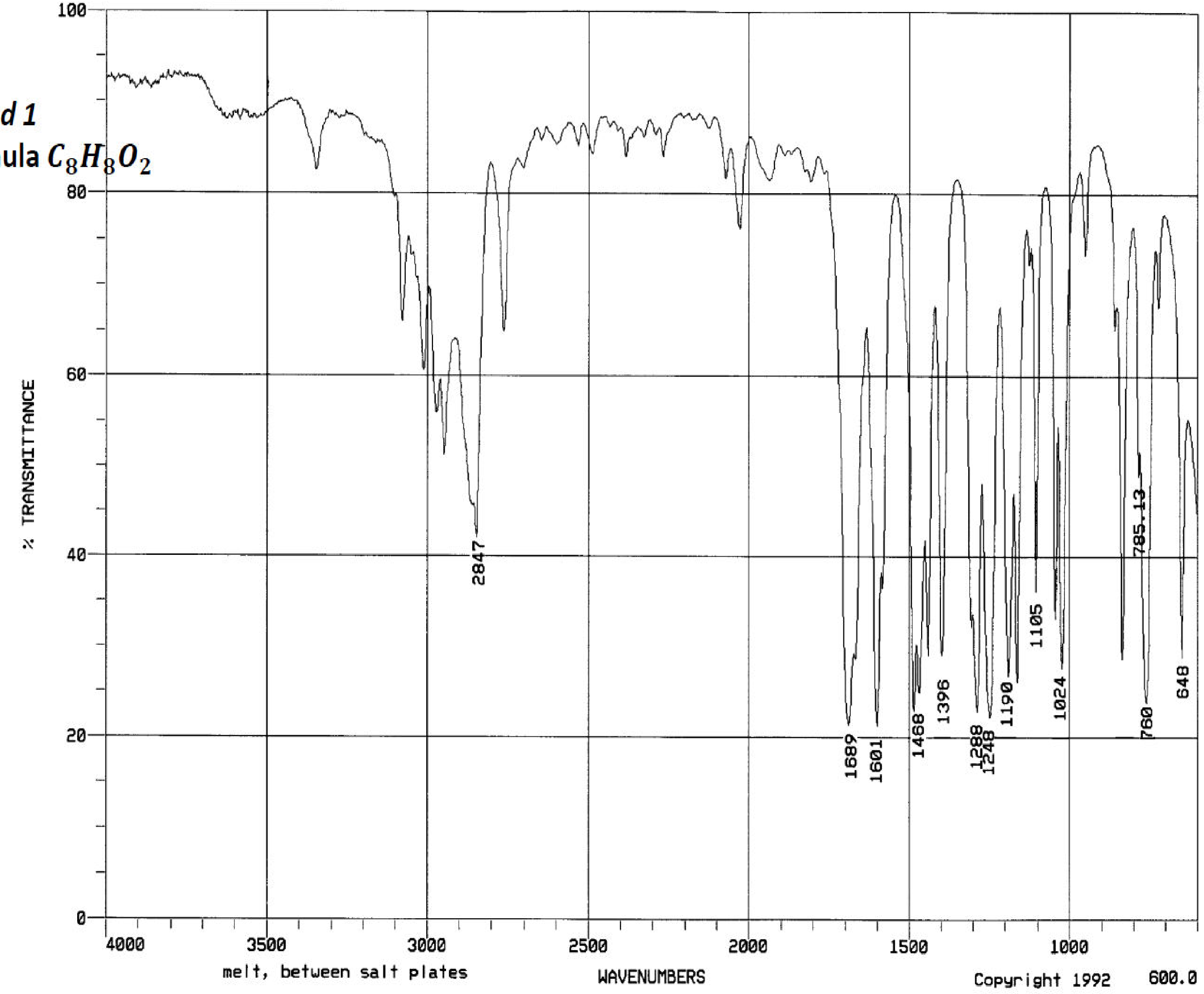


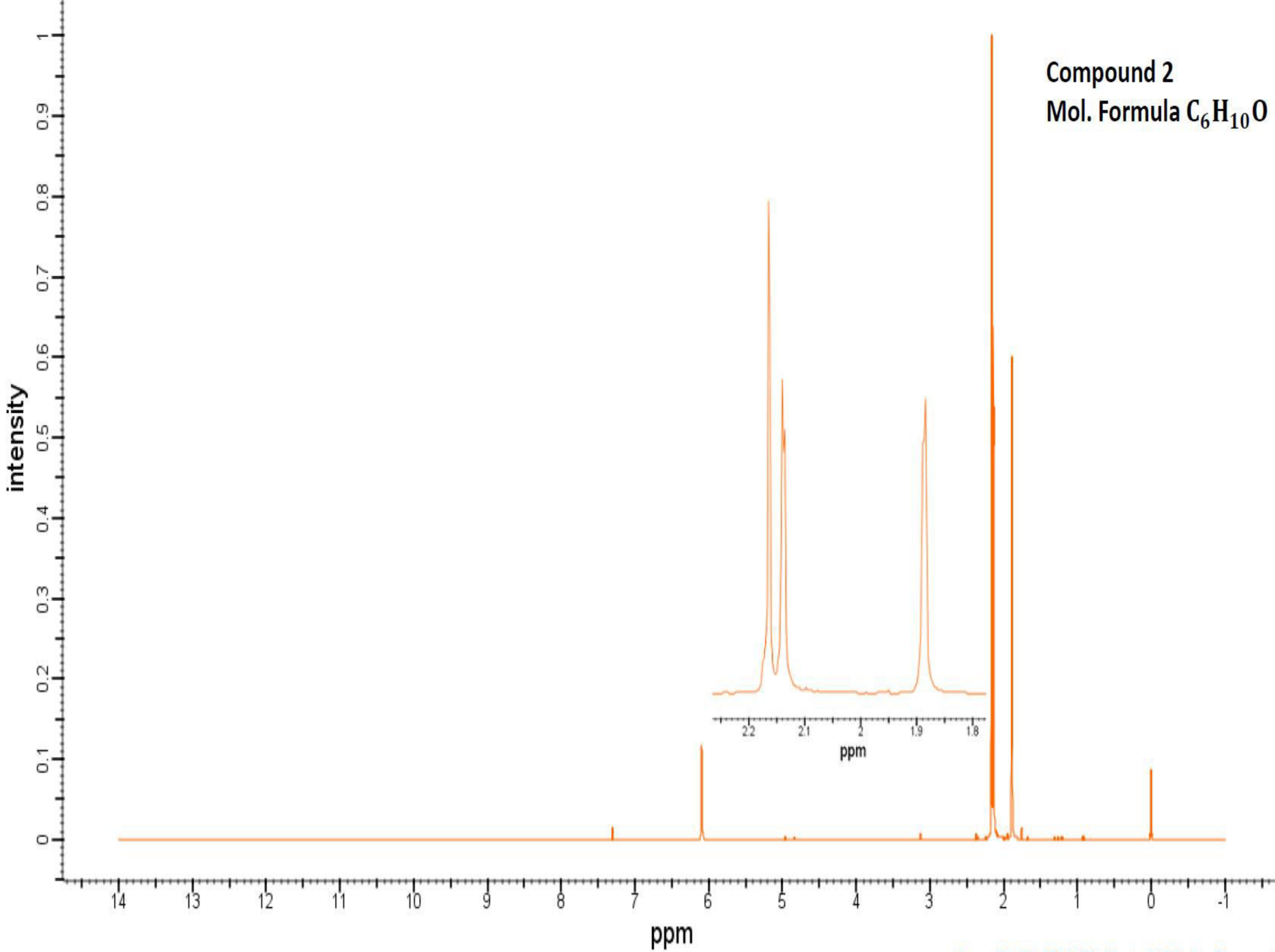
Compound 1

***Mol* Formula $C_8H_8O_2$**

Carbon 13 NMR

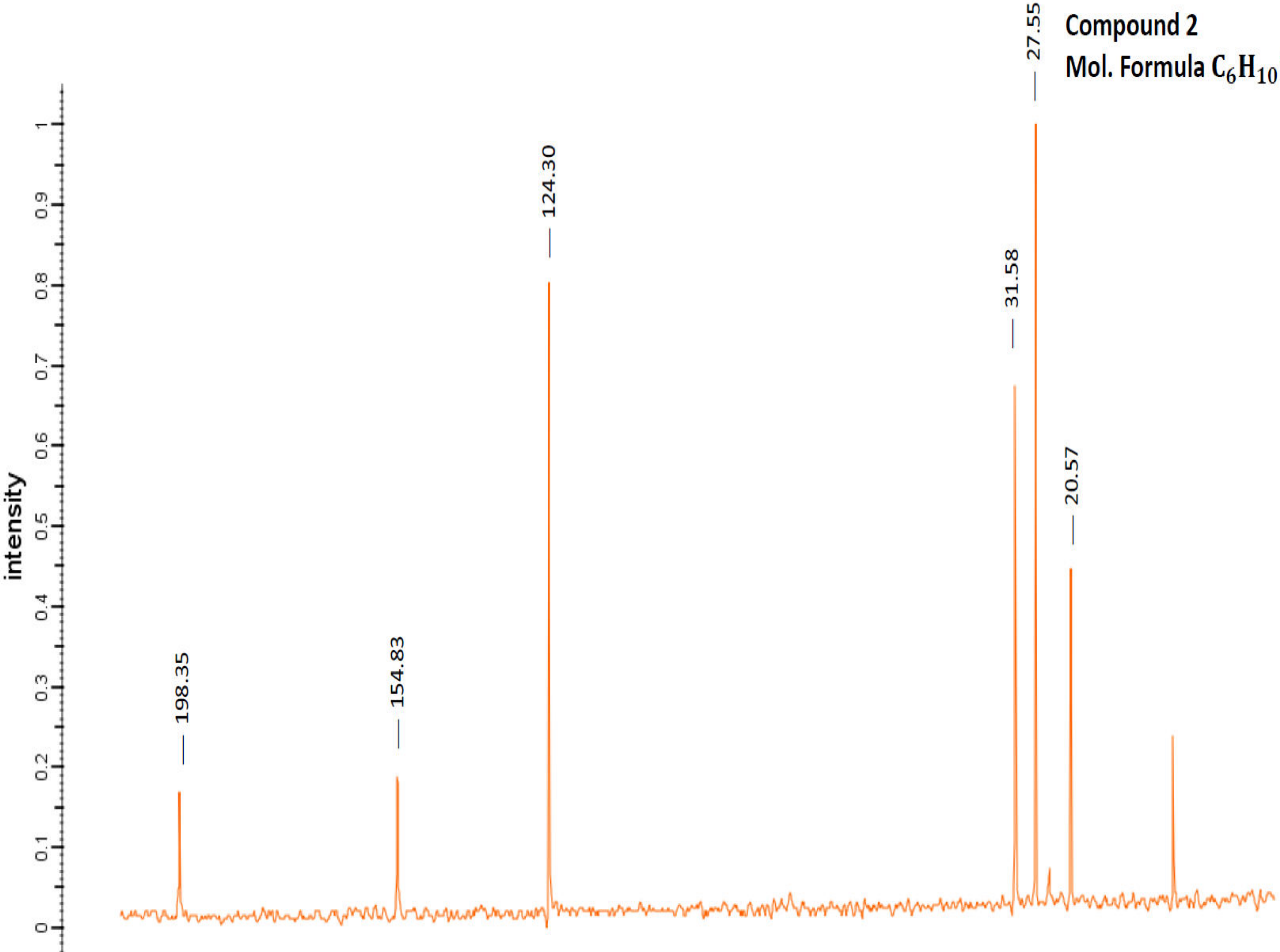
Compound 1
Mol **Formula** $C_8H_8O_2$





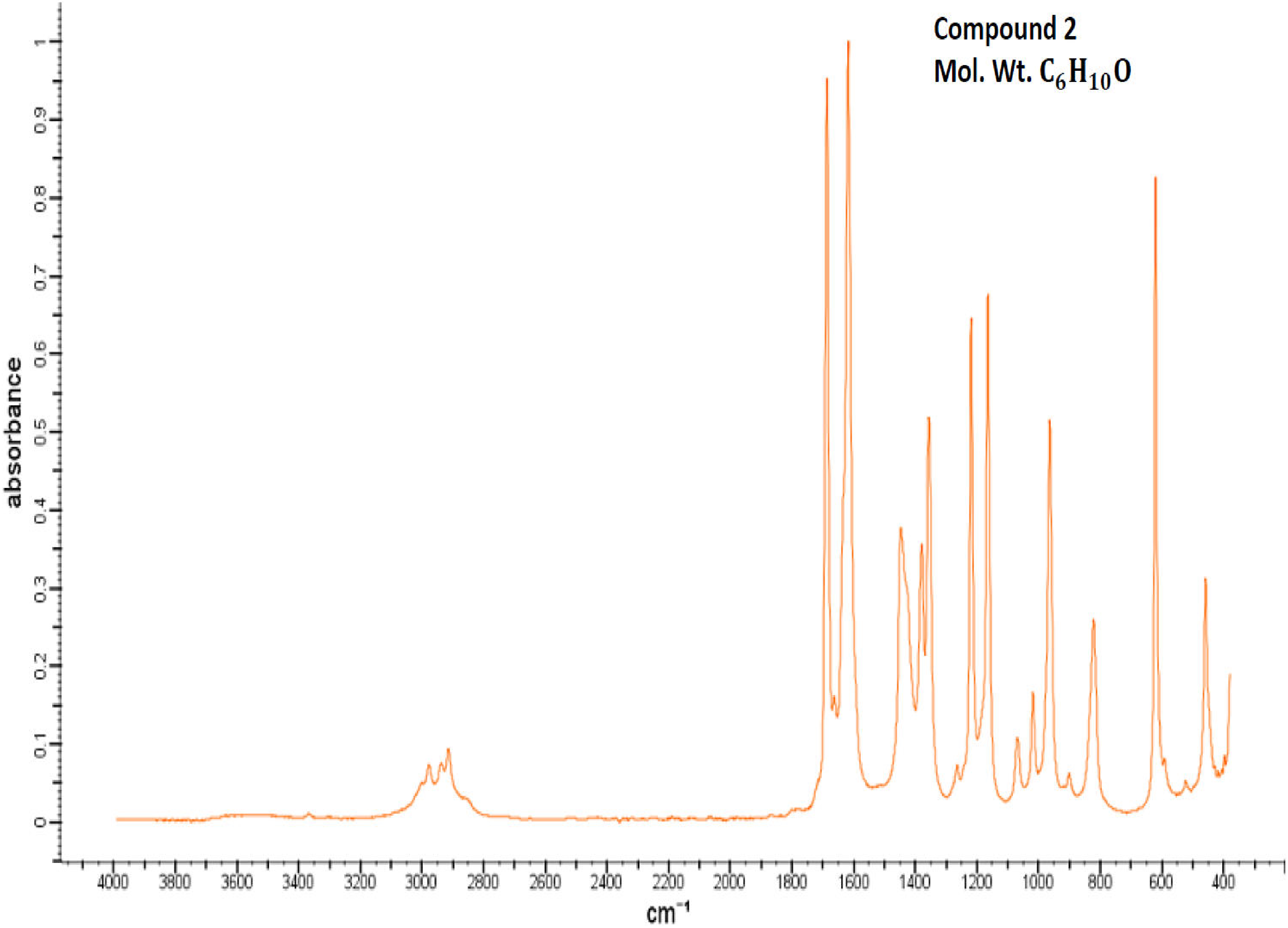
Compound 2

Mol. Formula $C_6H_{10}O$



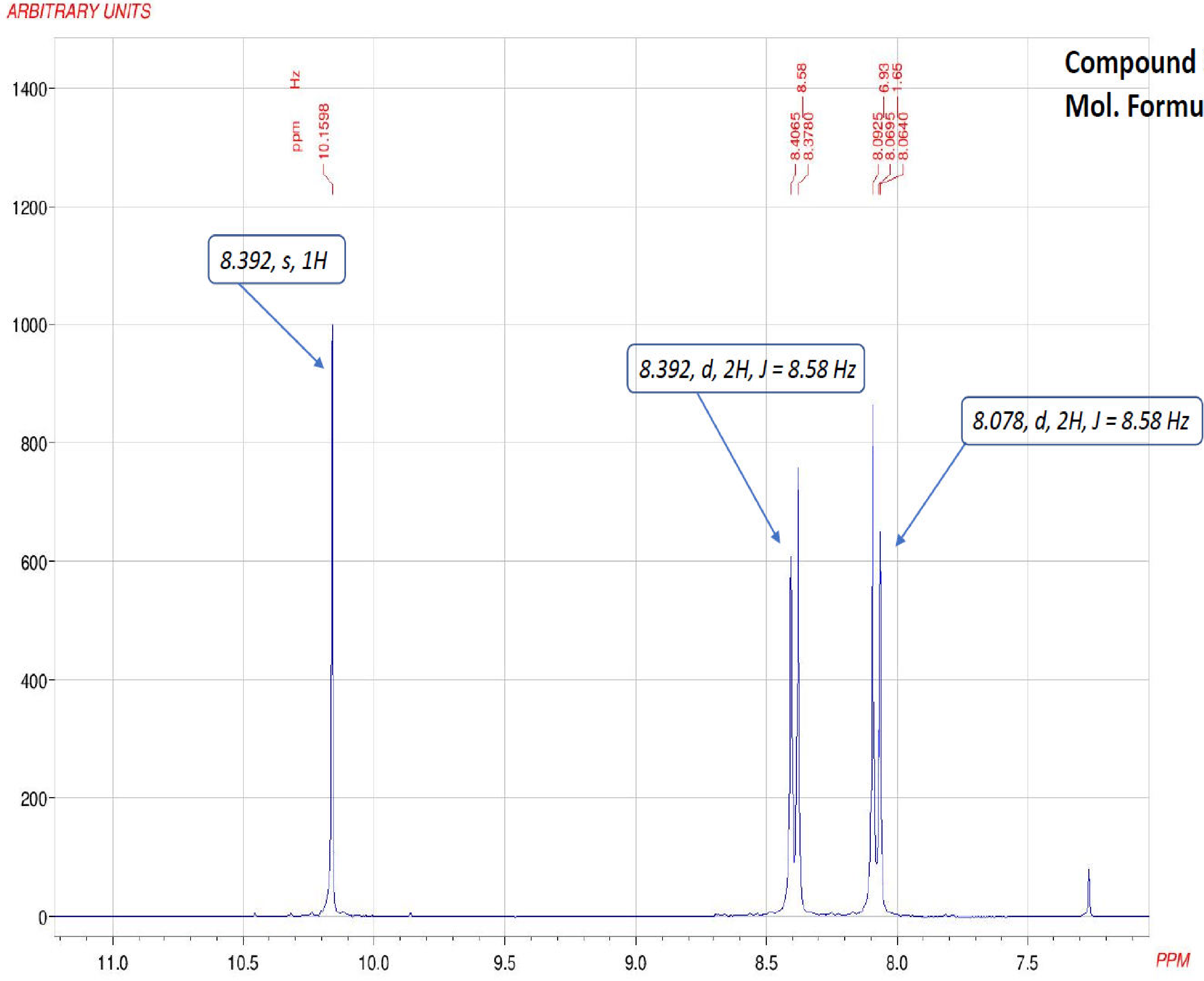
Compound 2

Mol. Formula $C_6H_{10}O$


Compound 2
Mol. Wt. $C_6H_{10}O$
absorbance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
cm⁻¹

Compound 3

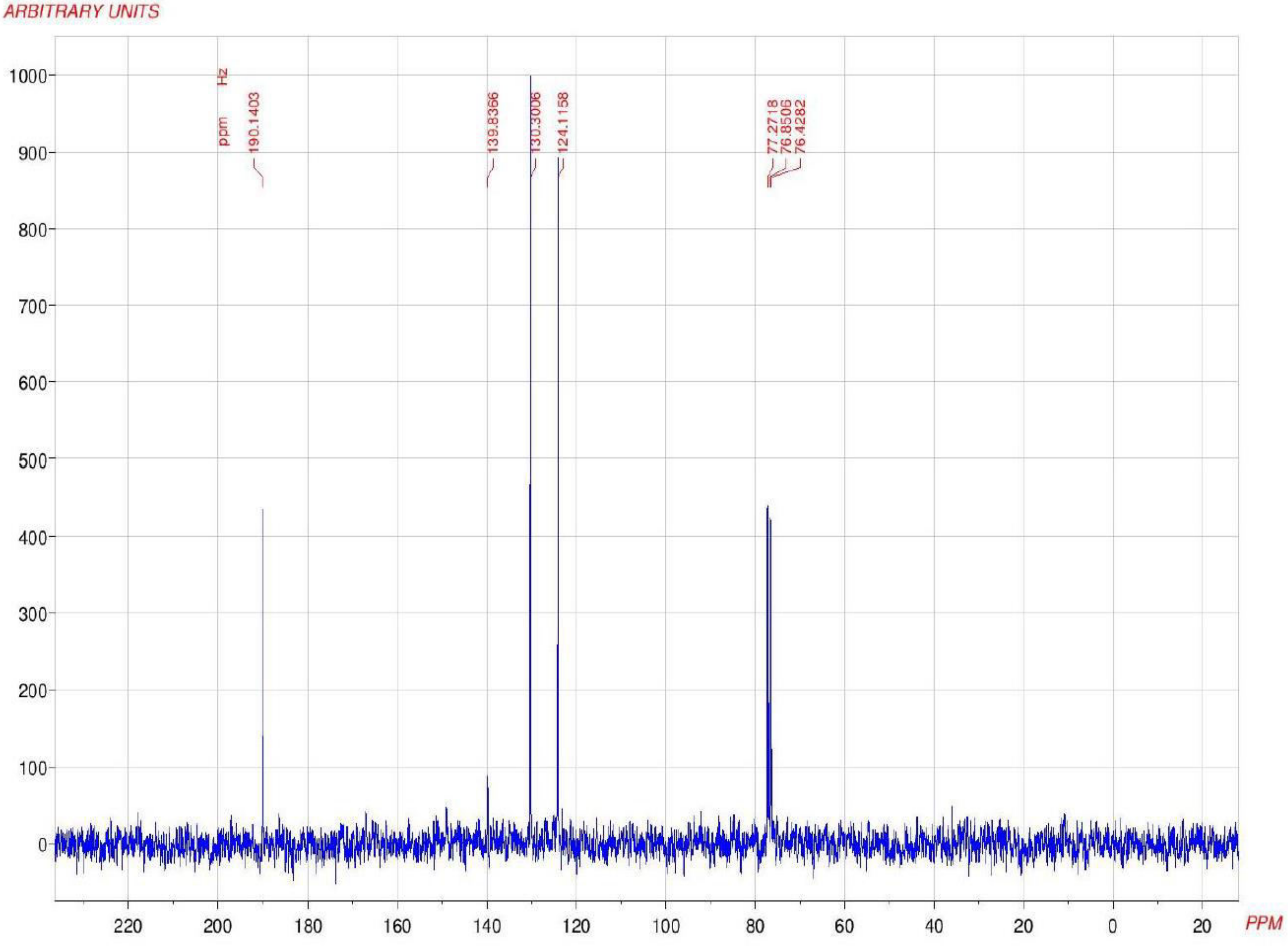
Mol. Formula $C_7H_5O_3N$



8.392, s, 1H

8.392, d, 2H, J = 8.58 Hz

8.078, d, 2H, J = 8.58 Hz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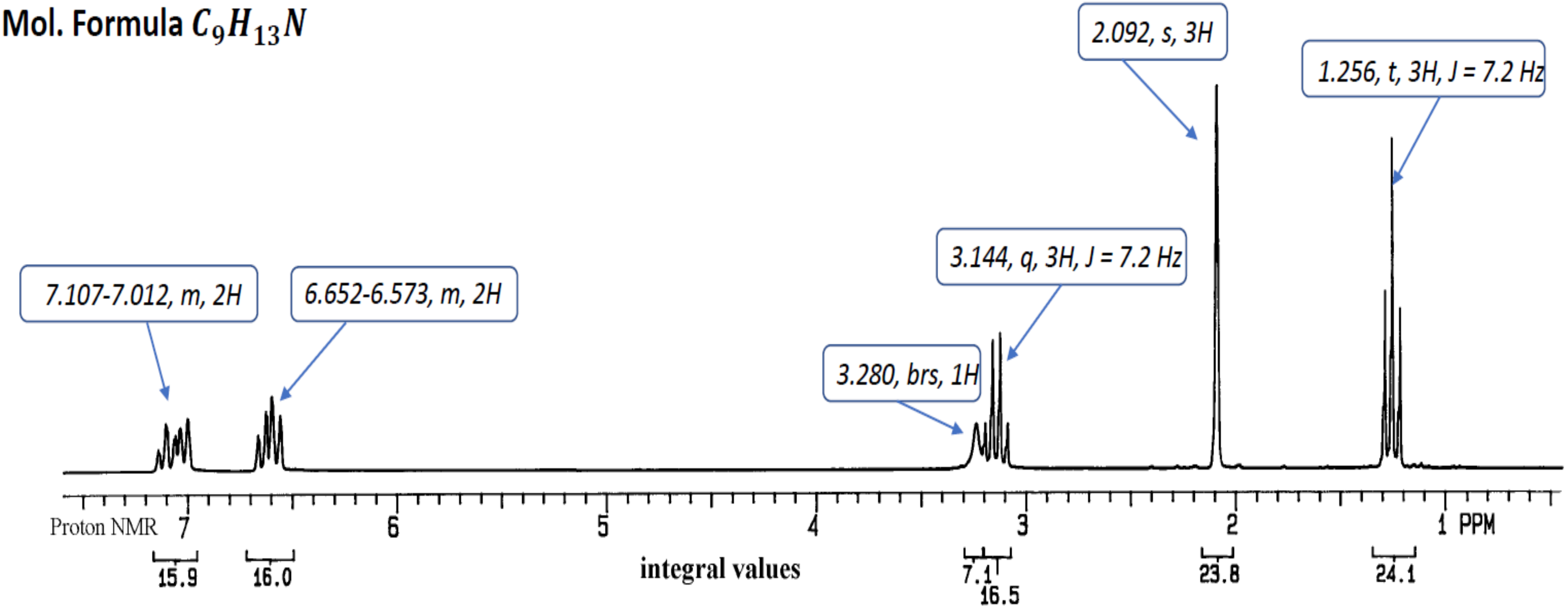
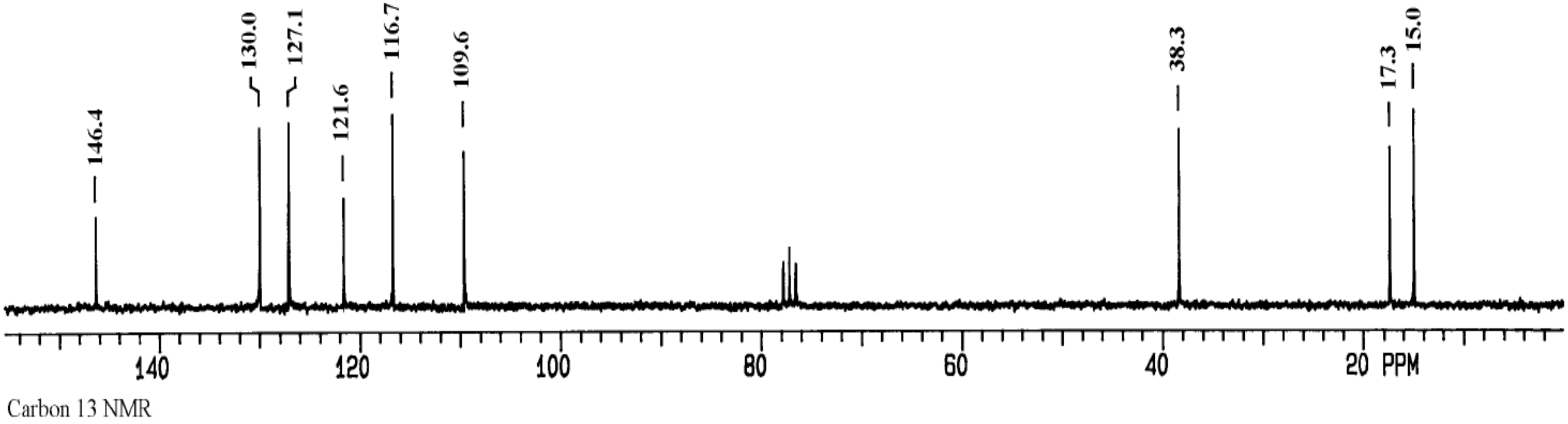
124.1158
77.2718
76.8506
76.4282
220
200
180
160
140
120
100
80
60
40
20
0
20
PPM

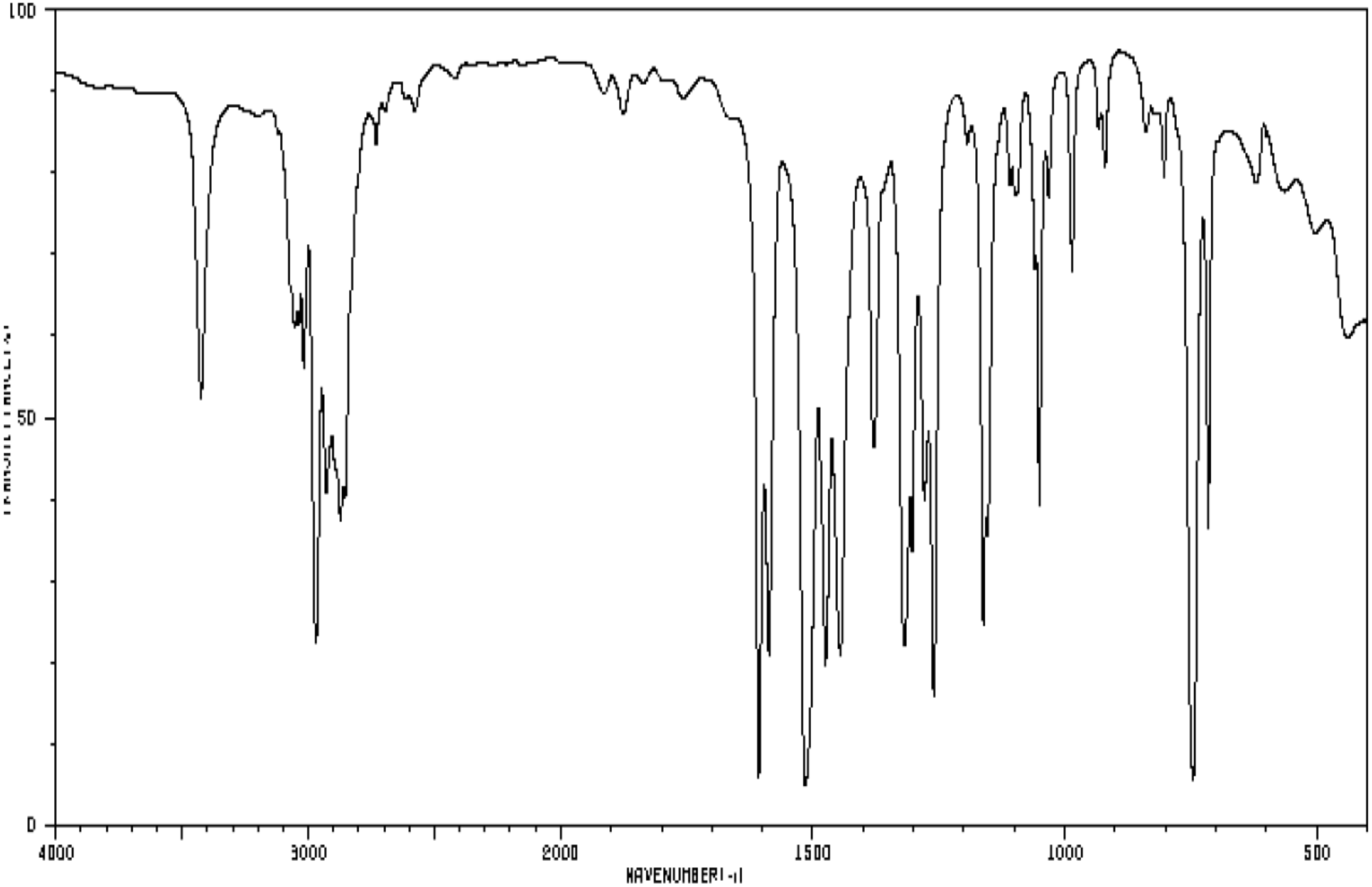
Compound 4

Mol. Formula $C_9H_{13}N$



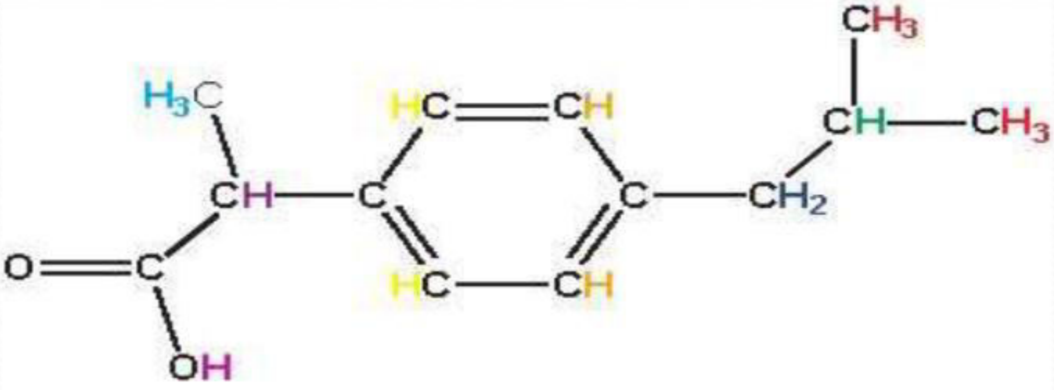


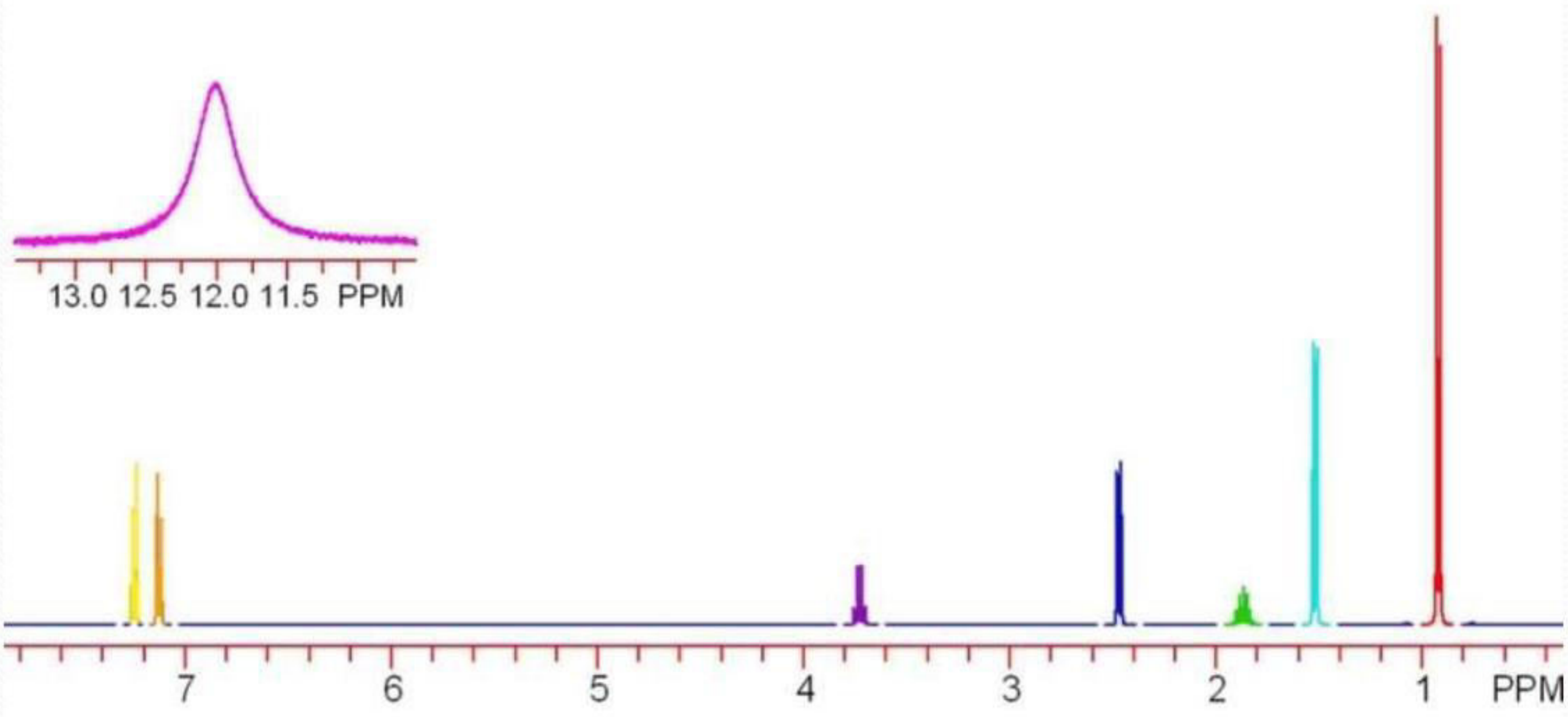
Compound 4
Mol. Formula $C_9H_{13}N$



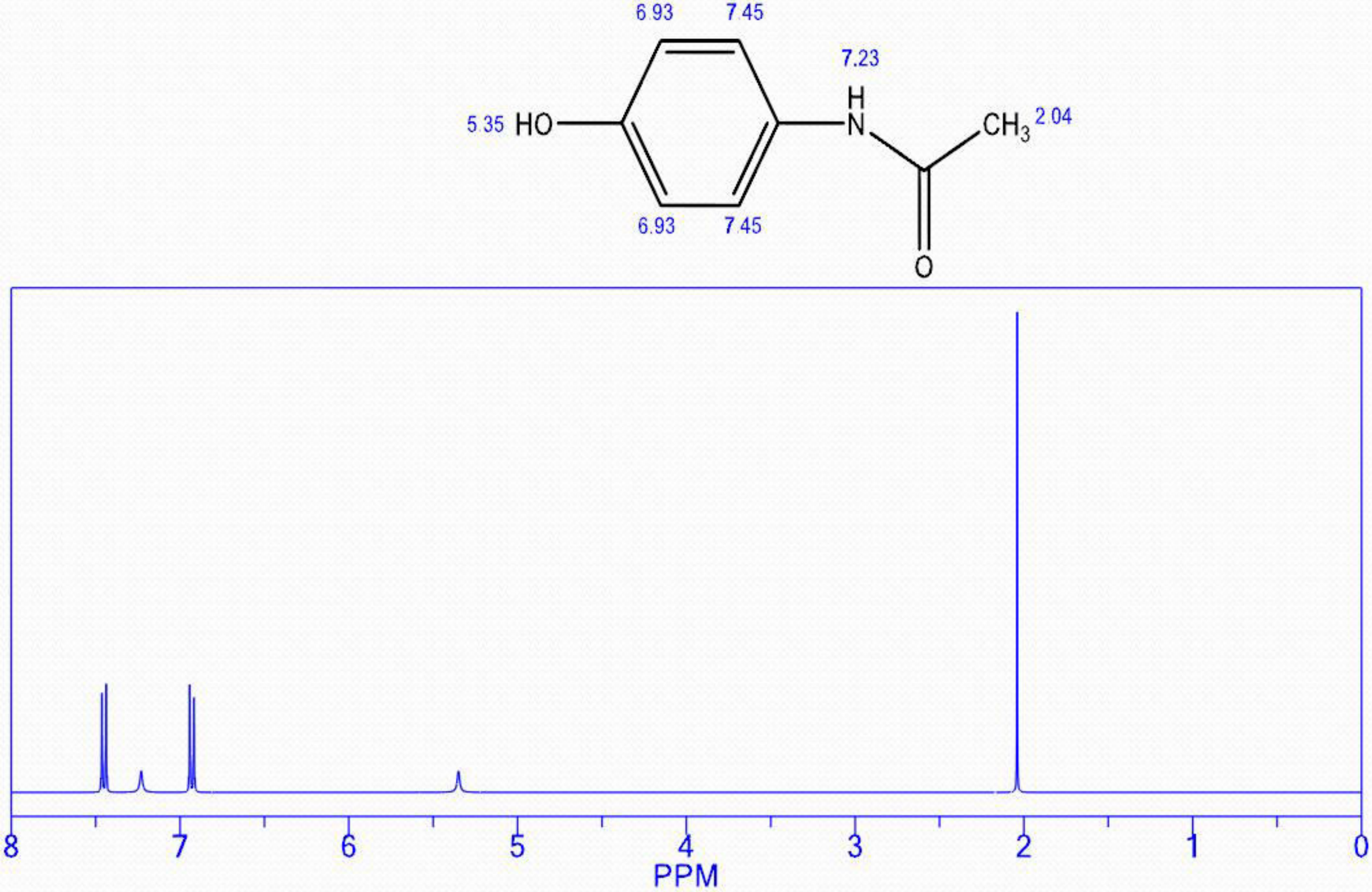
3426	60	2866	38	1319	21	1097	74	746	6
3054	58	1607	5	1303	32	1060	66	716	35
3037	58	1587	20	1279	38	1051	37	629	77
3018	63	1614	4	1260	16	1033	74	620	77
2970	21	1475	18	1162	23	986	66	564	74
2929	39	1445	20	1154	34	920	77	502	70
2872	36	1379	44	1109	74	803	77	439	67

Ibuprofen

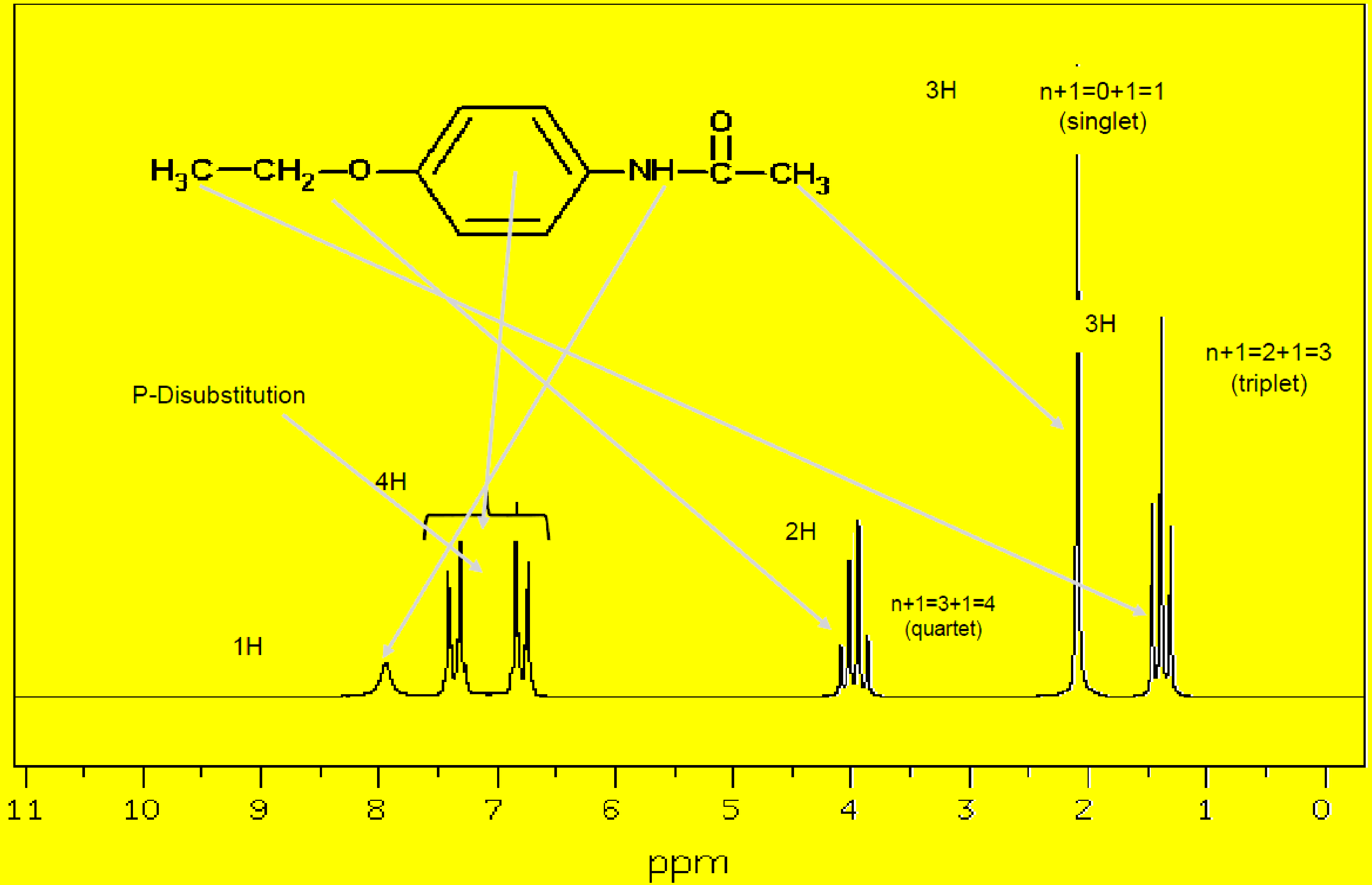

CH3
H3C
HC
CH
CH
CH—CH3
CH—C
C
C—CH2
O=C
HC
CH
OH


13.0 12.5 12.0 11.5 PPM
7
6
5
4
3
2
1
PPM

Paracetamol



Phenacetin ($C_{10}H_{13}NO_2$)

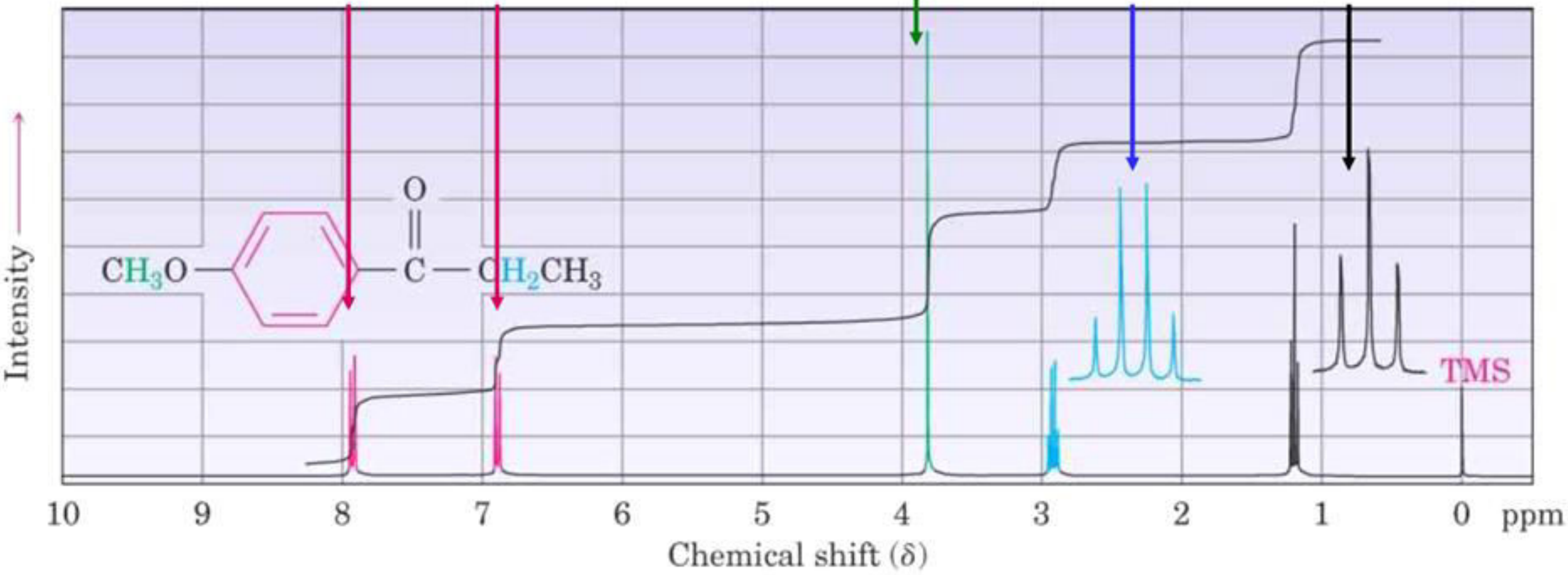


- ***Example**: para*-methoxypropiophenone

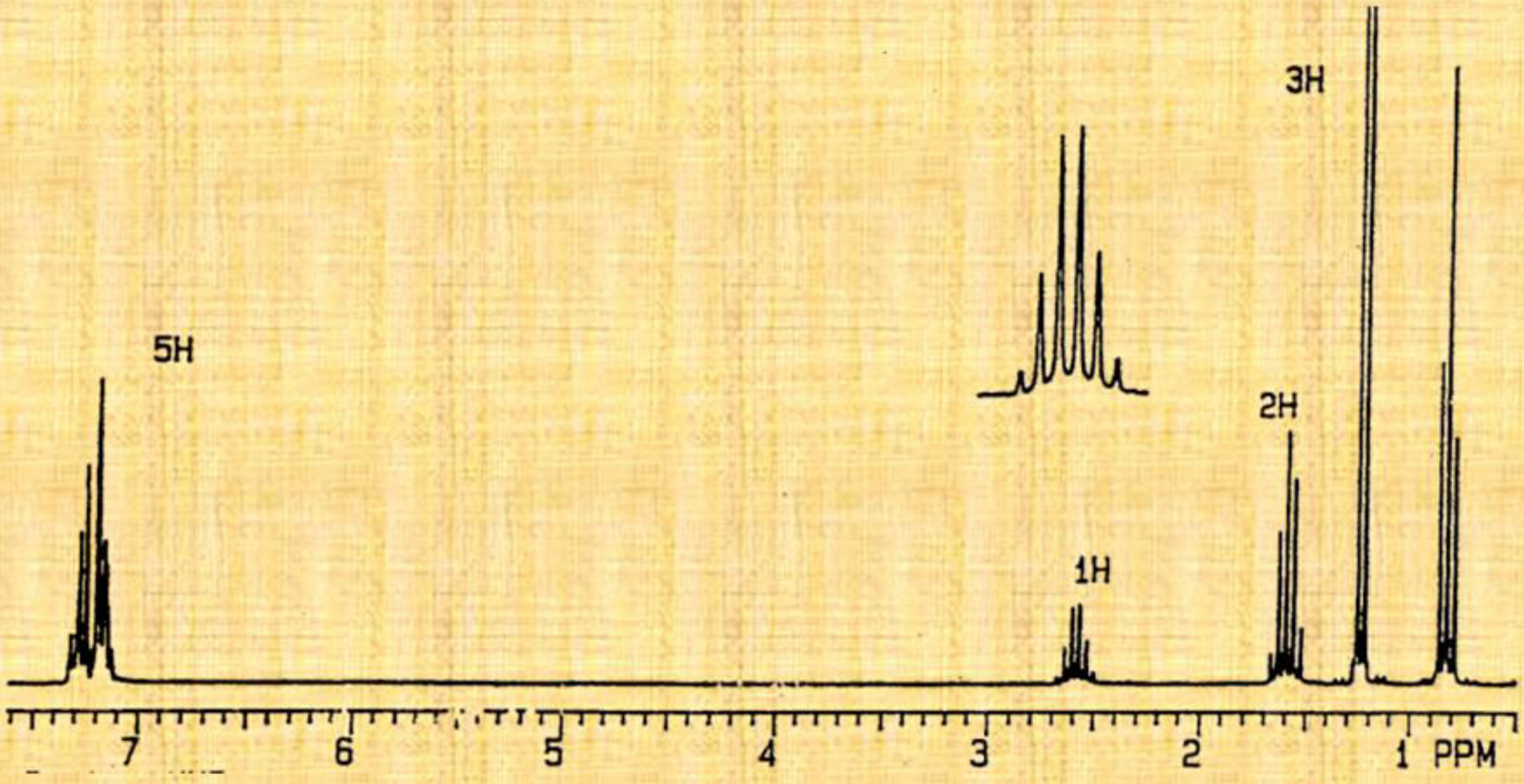
The -OCH_3 protons are unsplit (n = 0): a singlet

Each of two types of equivalent Ar-H protons is split by its neighbor (n = 1): a doublet

The 2 equivalent O=CCH_2 protons are split by 3 –CH_3 protons (n = 3): a quartet and vice-versa, a triplet

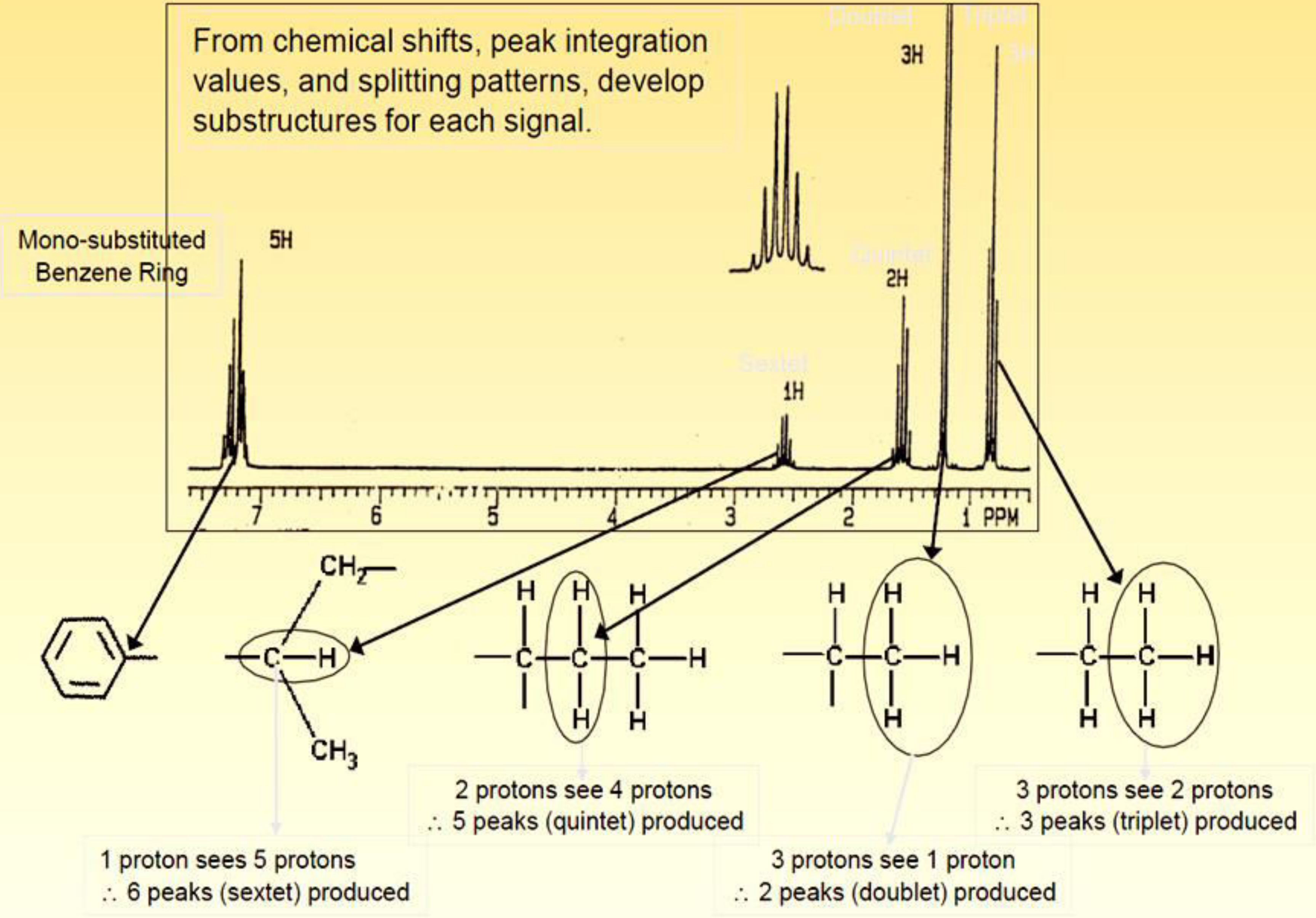


Four slides demonstrating a process for interpreting an NMR Spectra



← Chemical Shift (δ) in PPM

Note: Magnetic Field (H_o) increases →



From chemical shifts, peak integration values, and splitting patterns, develop substructures for each signal.

Mono-substituted Benzene Ring

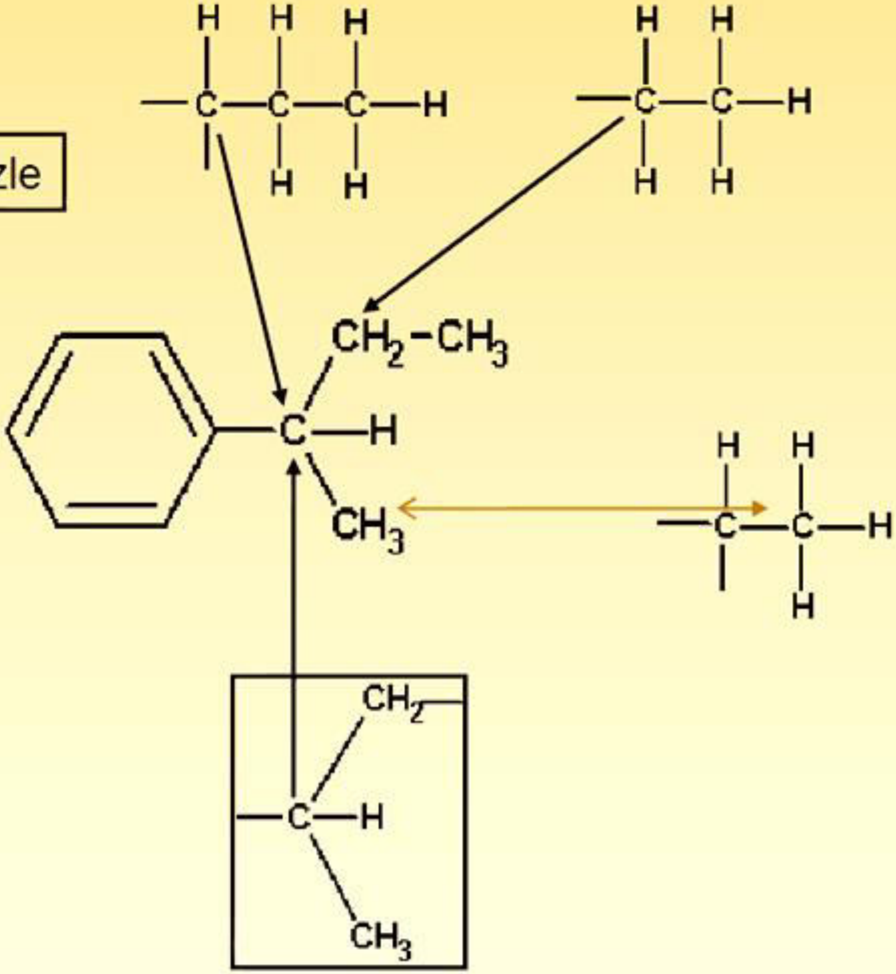
1 proton sees 5 protons
∴ 6 peaks (sextet) produced

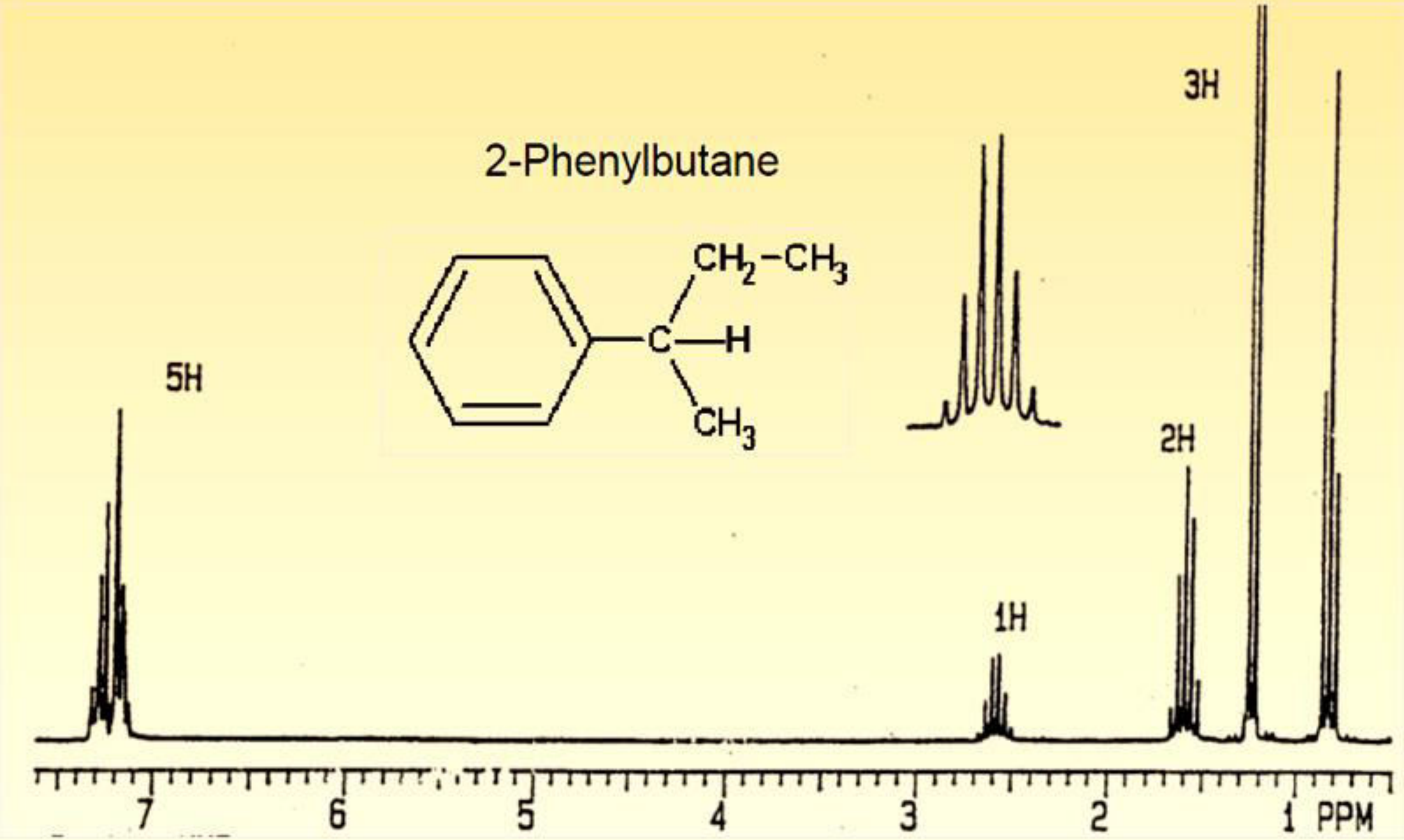
2 protons see 4 protons
∴ 5 peaks (quintet) produced

3 protons see 1 proton
∴ 2 peaks (doublet) produced

3 protons see 2 protons
∴ 3 peaks (triplet) produced

Solve the Puzzle





2-Phenylbutane

THANK YOU