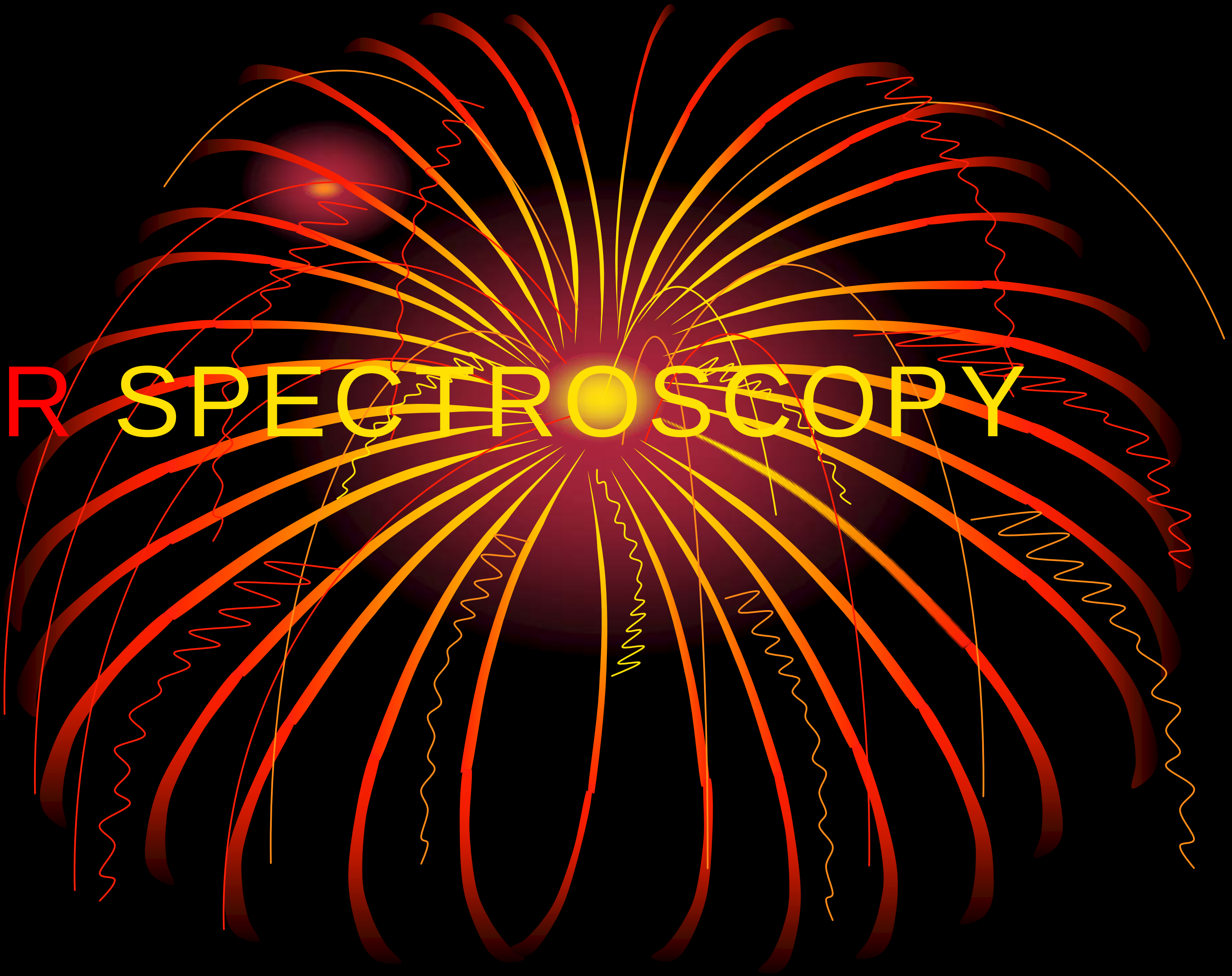
NMR SPECTROSCOPY



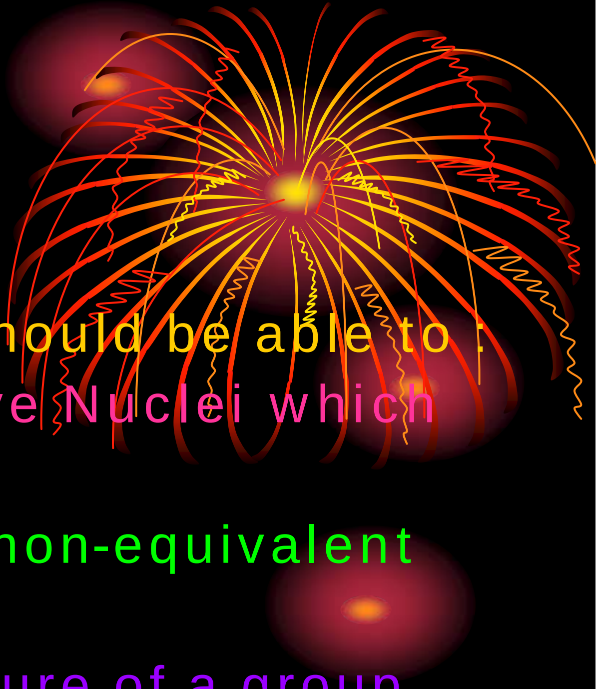
DR. M. KANJIA

Introduction To Practical High Resolution Nuclear Magnetic Resonance (N M R) spectroscopy

- Level 1 Stage Foundation
- Aims :
- To learn the basic Principles of simple NMR spectroscopy.
- To understand the features of simple NMR spectra.
- To recognise, Relate and Understand the Importance aspect of :-

  - - Chemical shift and reference
  - - Integration and
  - - Coupling constant

OBJECTIVES :

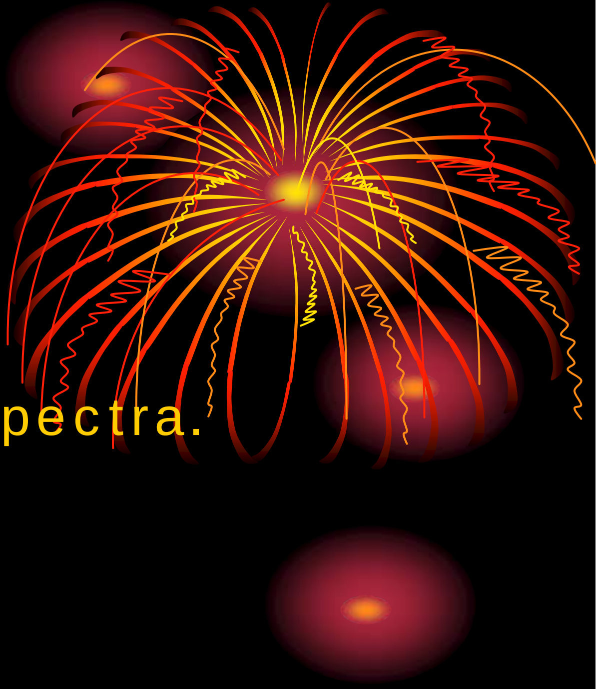


- On completing Level One Students should be able to :
- 1. Identify and Recognize the spin active Nuclei which
- give rise to NMR Signals.
- 2. Distinguish between equivalent and non-equivalent
- atoms and groups.
- 3. Predict and deduce a possible structure of a group
- and compound from NMR data.
- 4. Assign and Use chemical shifts in solving structural
- information.
- 5. Measure and use of integration in solving problems of
- structural information.
- 6. Calculate and use of coupling constants in solving
- structural information.

Level : One Part : One

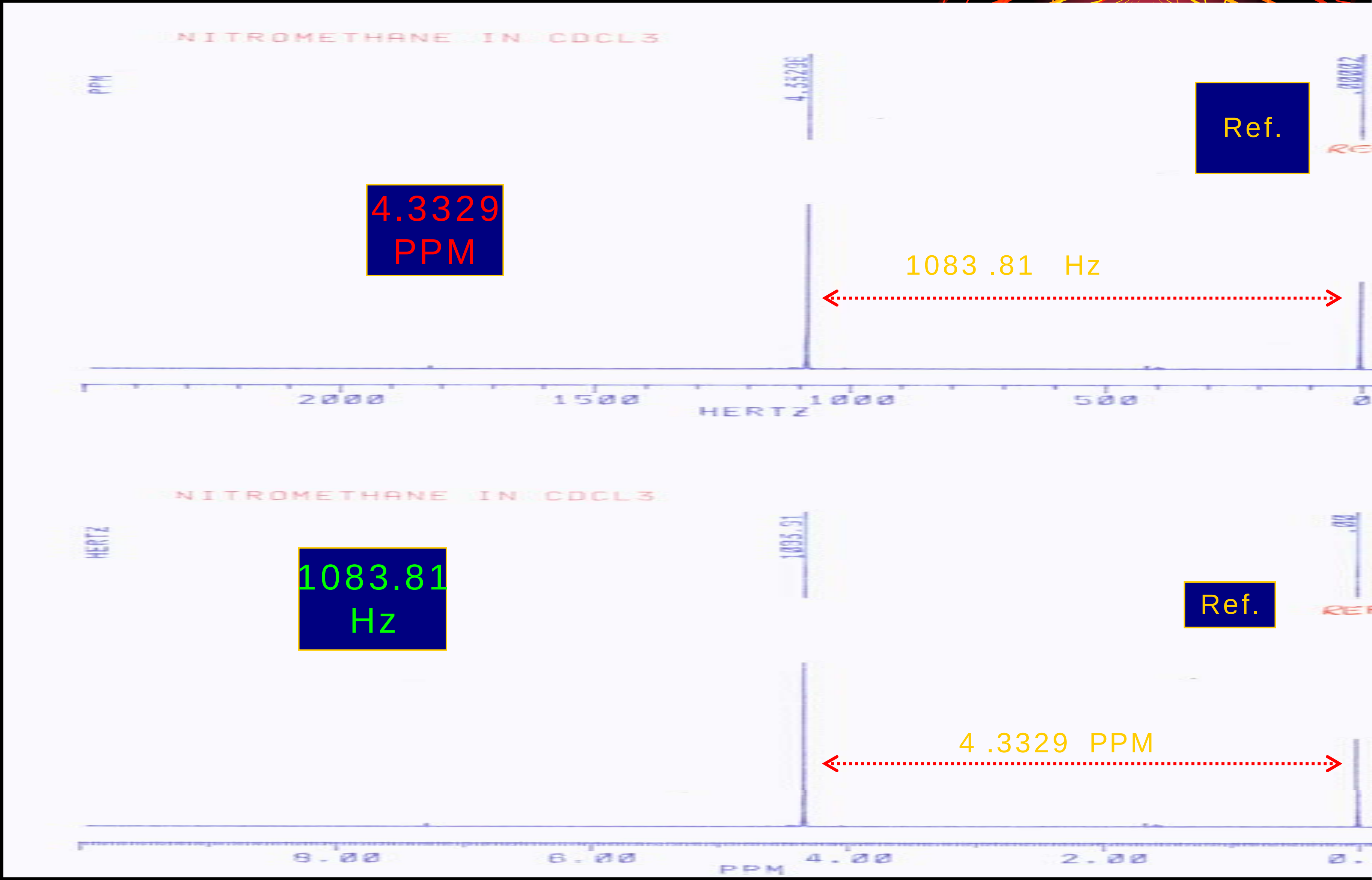
- Introduction to Practical NMR Spectroscopy.
- Introduction and Study of Simple NMR Spectra.

Introduction To Practical High Resolution N M R spectroscopy.
Level : One Stage : Foundation



- Let us look at the following ^1H NMR Spectra.
- 1. CH_3NO_2 Nitromethane
- 2. CH_2Cl_2 Dichloromethane
- 3. $CHCl_3$ Trichloromethane (Chloroform)
- 4. CH_3OH Methanol (Methyl alcohol)
- Read and record the position of each NMR
- Peak in Hz and PPM from the NMR spectra.

Nitromethane in $CDCl_3$



4.3329 PPM

Ref.

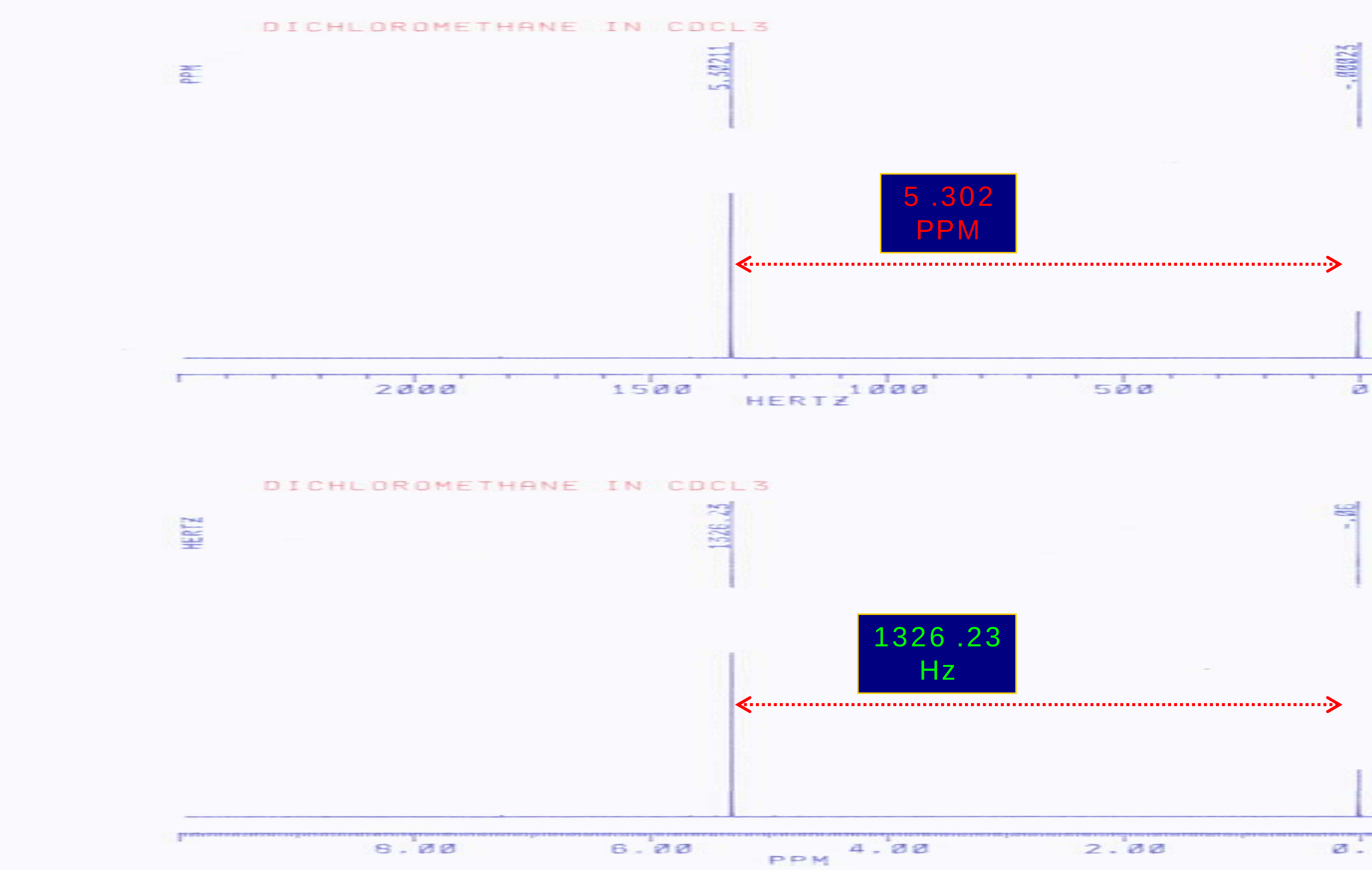
1083 .81 Hz

1083.81 Hz

Ref.

4 .3329 PPM

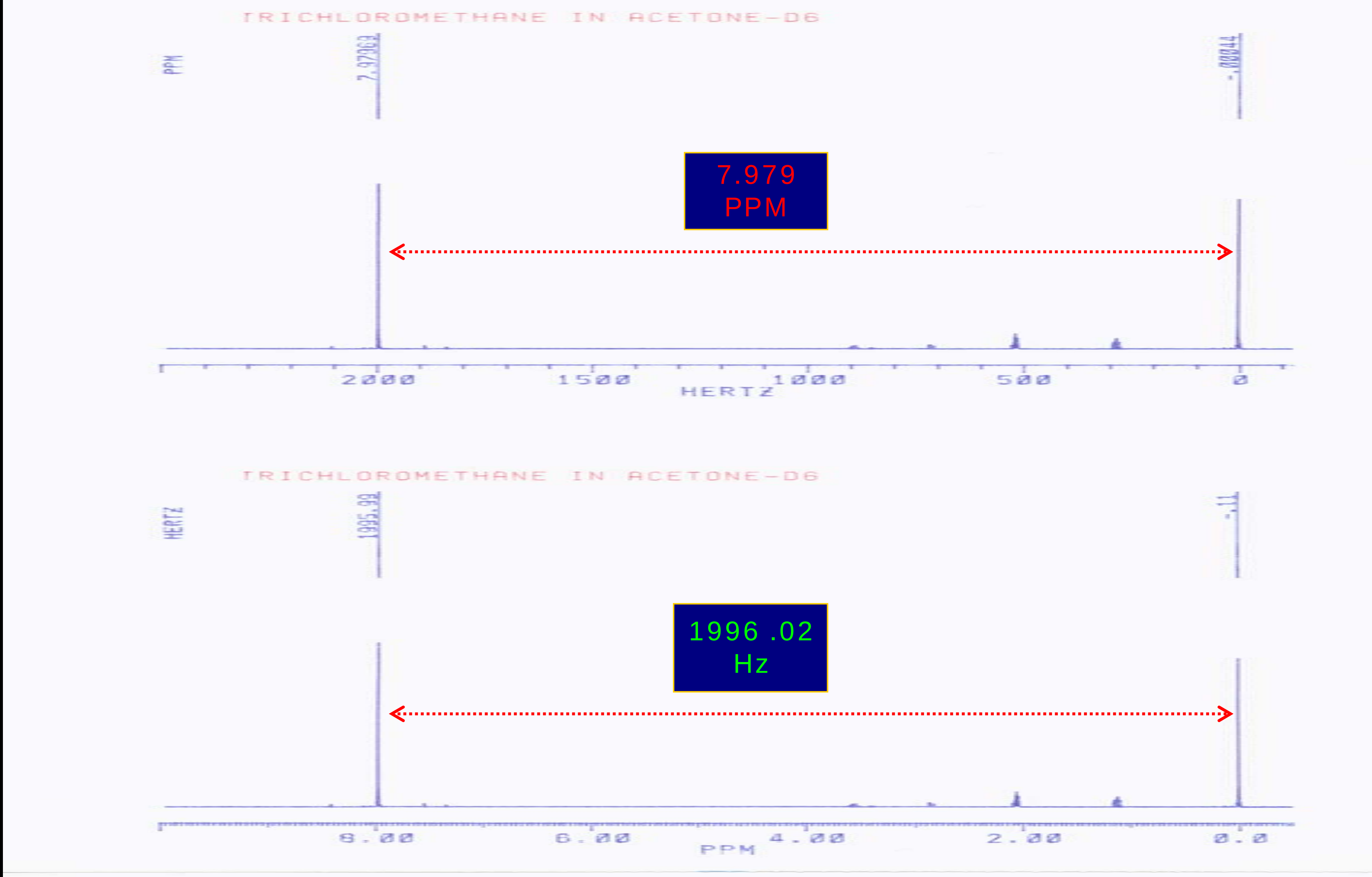
Dichloromethane in $CDCl_3$



5 .302 PPM

1326 .23 Hz

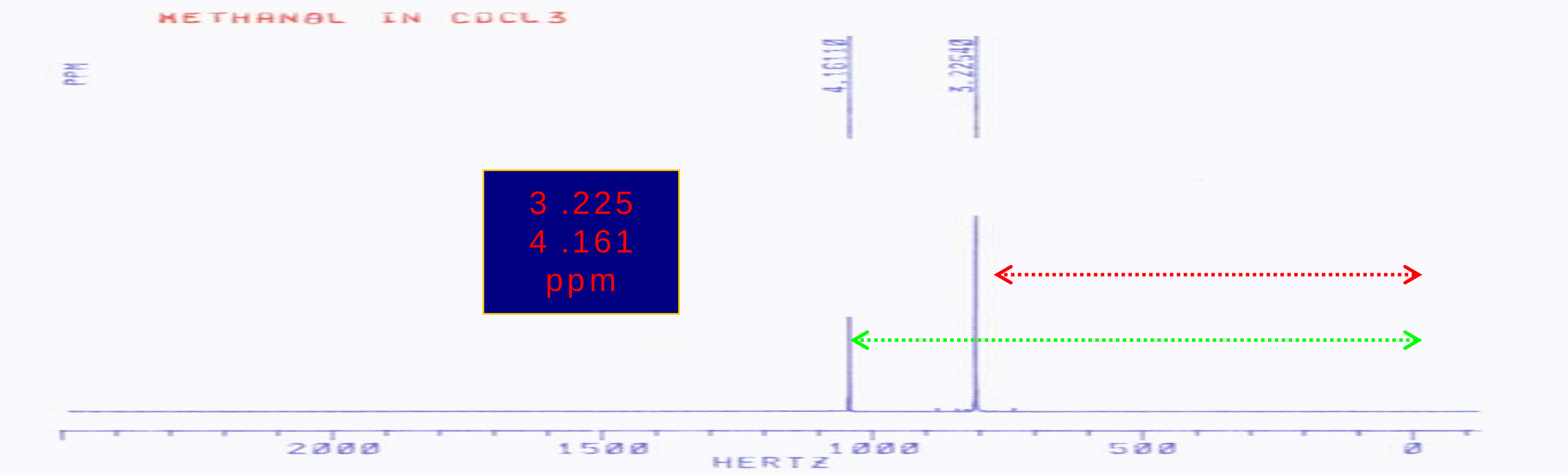
Trichloromethane in Acetone-D6



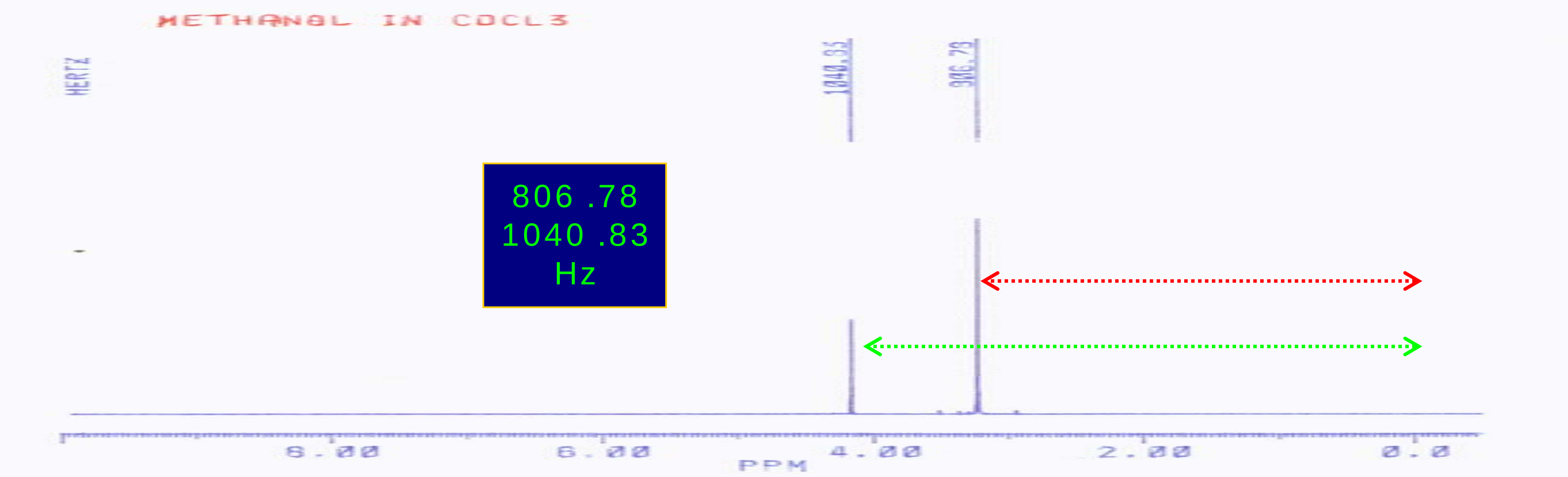
7.979
PPM

1996 .02
Hz

Methanol in $CDCl_3$

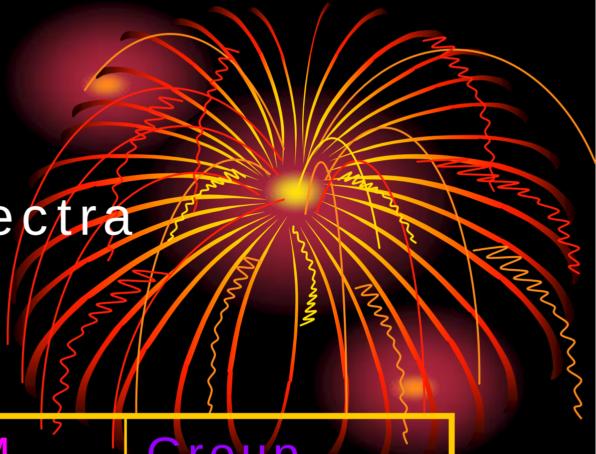


3.225
4.161
ppm



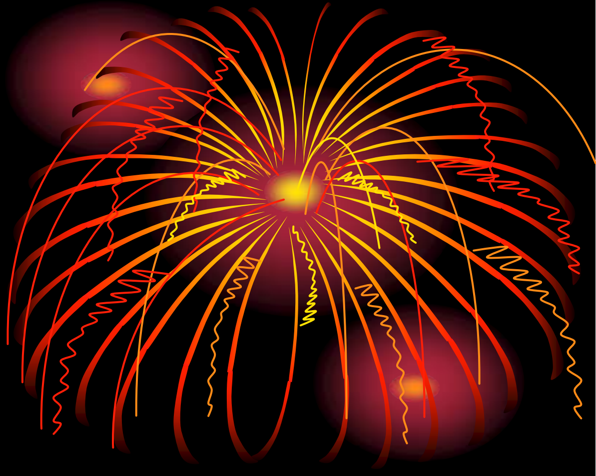
806.78
1040.83
Hz

Analysis and assignment of ^{1}H NMR Spectra



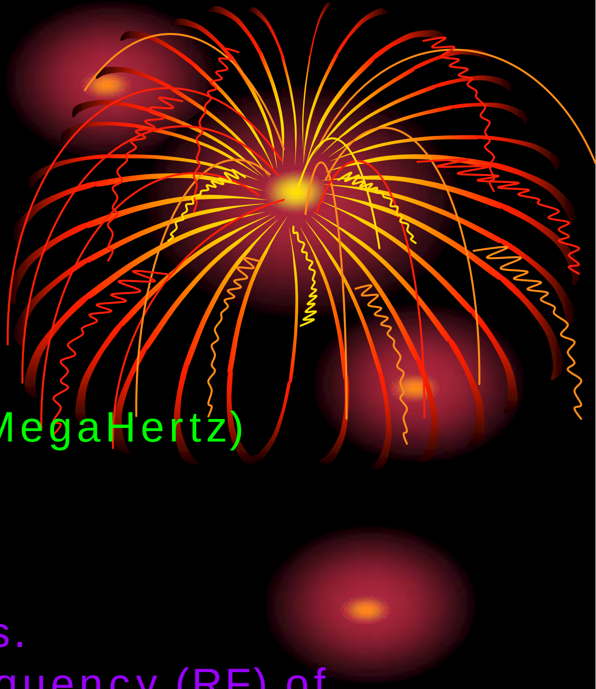
	Compound	Hz	PPM	Group
1	CH_3NO_2	1083.81	4.333	CH_3
2	CH_2Cl_2	1326.23	5.302	CH_2
3	$CHCl_3$	1996.02	7.979	CH
4	CH_3OH	806.78 1040.83	3.225 4.161	CH_3 & OH

Conclusion Notes



- 1. Hydrogen atoms attached to the elements, such as
- C (Carbon), N (Nitrogen) or O (Oxygen) will absorb
- in ^{1}H NMR Spectrum.

- 2. The absorption positions (Chemical Shifts) for each
- group is different hence this can be used in identifying
- and assigning the nature of the group and its likely
- neighbouring element or group.



Conclusion Notes

- 3. What is Hz (Hertz) ?
- Hz is a unit for Frequency.
- One cycle per second is One Herts. (1x 10^6 = 1MegaHertz)
- 4. What is PPM ?
- PPM means Parts Per Million. It is dimensionless.
- CH3 in CH3NO2 absorbs at 1083.81 Hz at radio frequency (RF) of 250.13 MHz hence
- 1083.81 Hz 4.333
- -------------------------- = ------------- = 4.333 PPM
- 250.13 x 10^6 Hz 10^6

--CH_3	2.062	PPM	In CH_3CHCl_2
--NCH_3	4.333	PPM	In CH_3NO_2
--OCH_3	3.225	PPM	In CH_3OH
--OH	4.161	PPM	In CH_3OH

How many peaks (Absorption) would you expect to see in a 1H NMR spectrum of Propan-2-one ?

$CH_3\text{-}CO\text{-}CH_3$

- Select the correct statement
- 1. Doublet (Two Peaks)
- 2. Complex (Many Peaks)
- 3. Singlet (One Peak)

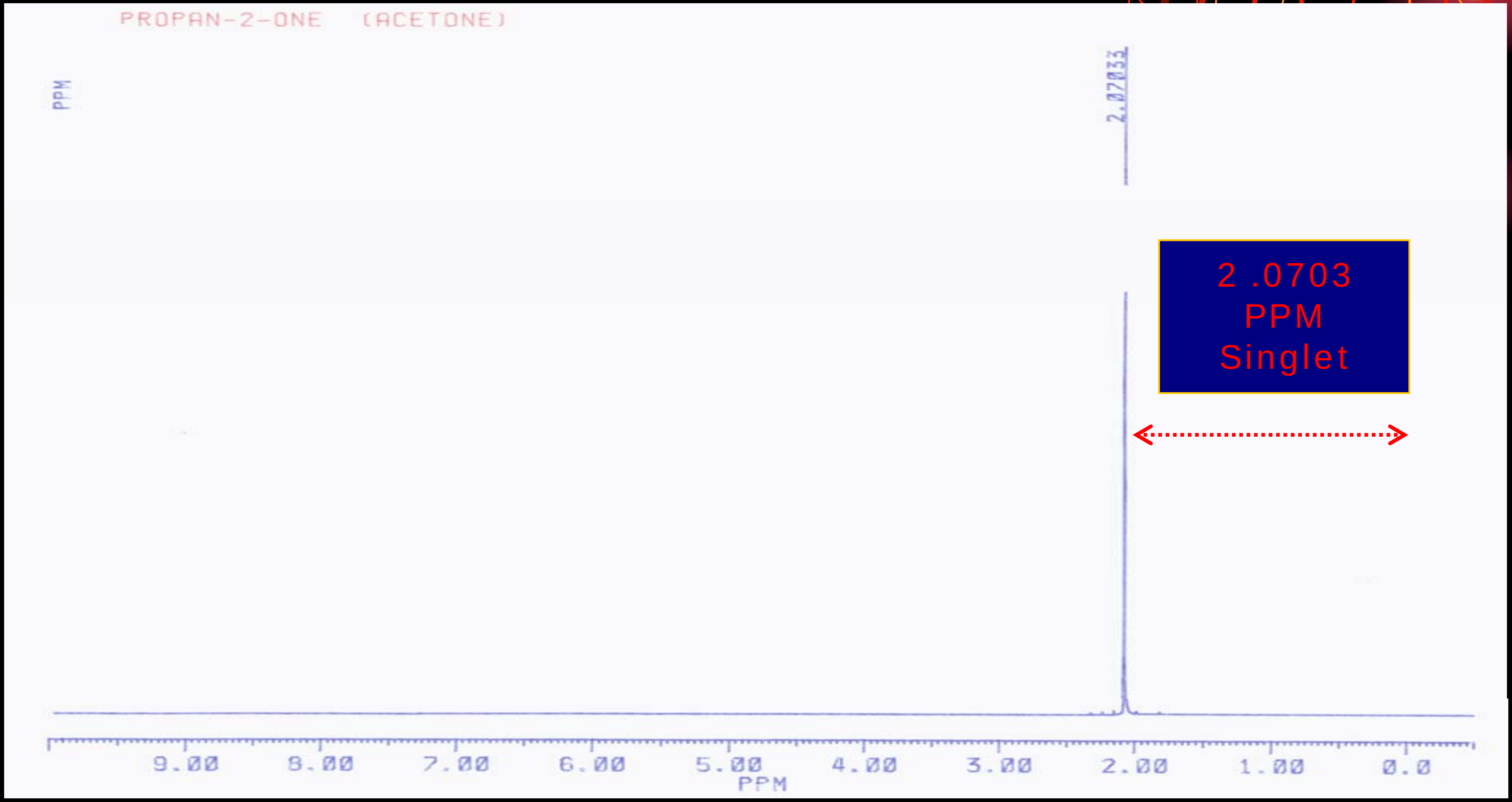
How many peaks (Absorption) would you expect to see in a ^{1}H NMR spectrum of Propan-2-one ?

CH_3-CO- CH_3

- Select the correct statement
- 1. Doublet (Two Peaks)
- 2. Complex (Many Peaks)
- 3. ✓ Singlet (One Peak)
- 4. Answer is No. 3 Singlet

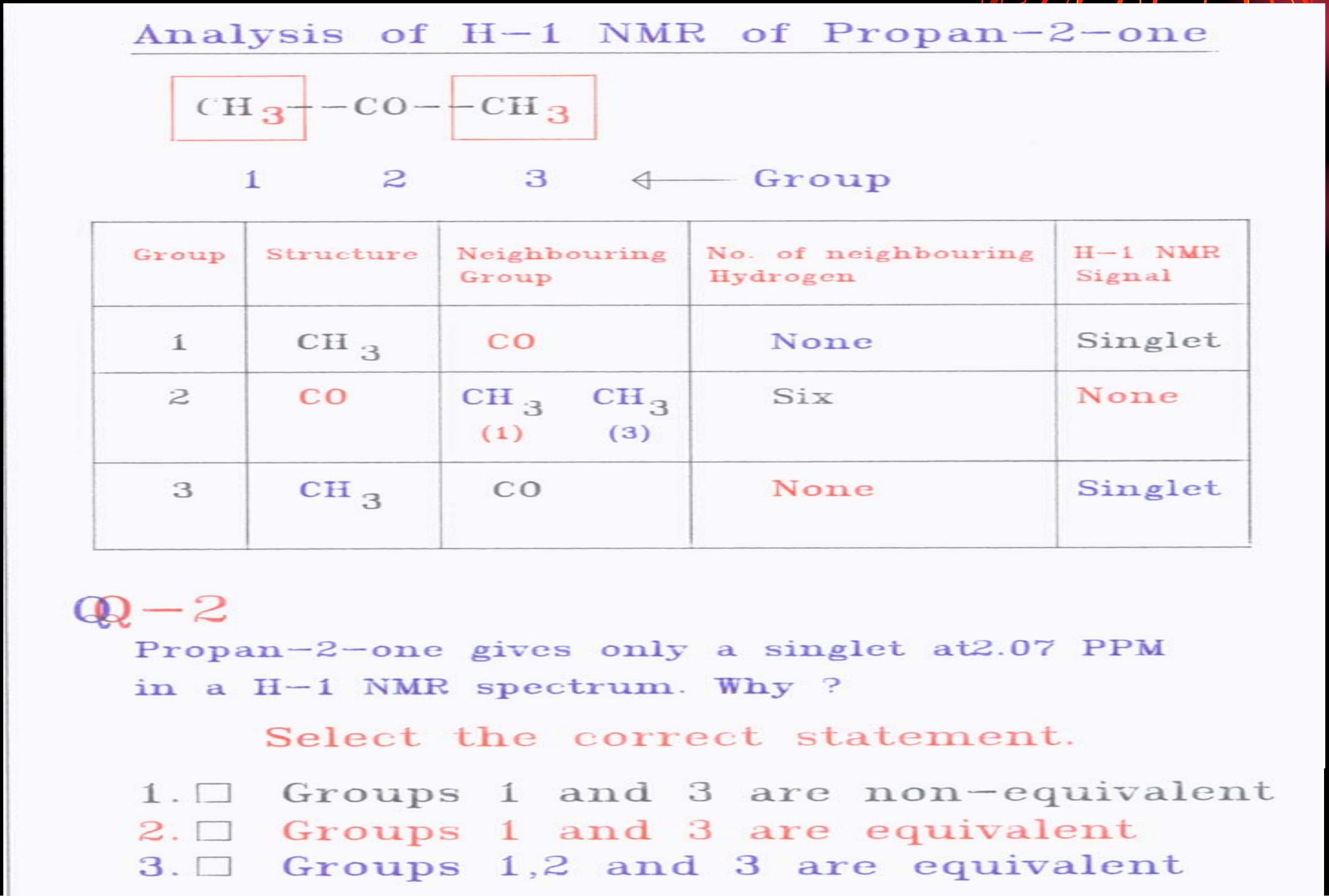
^{1}H NMR Spectrum Of Propan-2-one in Acetone-D6

CH_3-CO-CH_3



2 .0703
PPM
Singlet

Analysis of ^{1}H NMR of Propan-2-one CH_3—CO—CH_3



Analysis of H−1 NMR of Propan−2−one

$\boxed{CH_3}$ — CO — $\boxed{CH_3}$

1 2 3 ← Group

Group	Structure	Neighbouring Group	No. of neighbouring Hydrogen	H−1 NMR Signal
1	CH_3	CO	None	Singlet
2	CO	CH_3 (1) CH_3 (3)	Six	None
3	CH_3	CO	None	Singlet

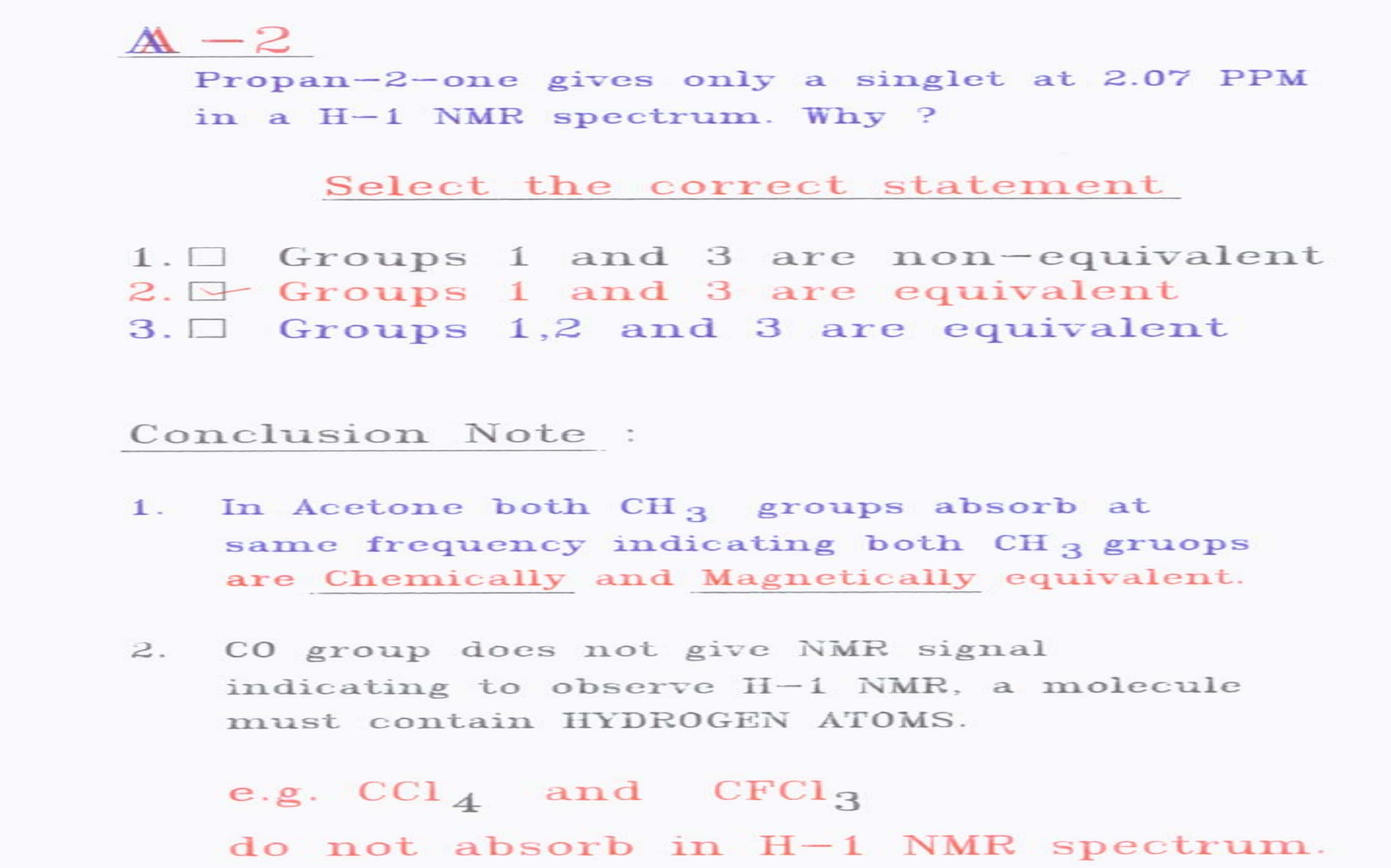
Q−2

Propan−2−one gives only a singlet at2.07 PPM in a H−1 NMR spectrum. Why ?

Select the correct statement.

1. ☐ Groups 1 and 3 are non−equivalent
2. ☐ Groups 1 and 3 are equivalent
3. ☐ Groups 1,2 and 3 are equivalent

Analysis of ^{1}H NMR of Propan-2-one $CH_3—CO—CH_3$



A – 2

Propan–2–one gives only a singlet at 2.07 PPM in a H–1 NMR spectrum. Why ?

Select the correct statement

1. ☐ Groups 1 and 3 are non–equivalent
2. ☑ Groups 1 and 3 are equivalent
3. ☐ Groups 1,2 and 3 are equivalent

Conclusion Note :

1. In Acetone both CH_3 groups absorb at same frequency indicating both CH_3 gruops are Chemically and Magnetically equivalent.

2. CO group does not give NMR signal indicating to observe H–1 NMR, a molecule must contain HYDROGEN ATOMS.

e.g. CCl_4 and $CFCl_3$

do not absorb in H–1 NMR spectrum.

	No. of Peaks	Terminology	Intensity Ratio
n=0	One Peak	Singlet	1
n=1	Two Peaks	Doublet	1 1
n=2	Three Peaks	Triplet	1 2 1
n=3	Four Peaks	Quartet	1 3 3 1
n=4	Five Peaks	Quintet	1 4 6 4 1
n=5	Six Peaks	Sextet	1 5 10 10 5 1
n=6	Seven Peaks	Septet	1 6 15 20 15 6 1
n=7	Eight Peaks	Octet	1 7 21 35 35 21 7 1

Pascal 's Triangle

The relative intensities of multiplet are given by the coefficients of the binomial expansion.

1 : n/1 (n = 0), 1 : n/1 (n = 1), 1 : n/1 : n(n-1) / 2 x 1 (n=2), and so on.

Read the intensity ratio directly from Pascal Triangle.

Level : One Part : Two

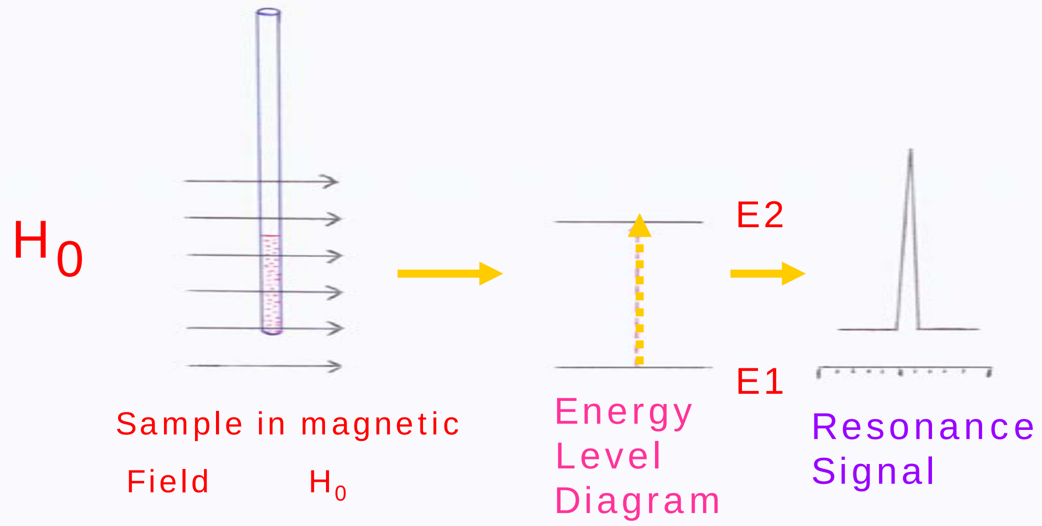
- Introduction to Practical High Resolution NMR Spectroscopy.

Topics :

- 1. What is NMR ?
- 2. Choice of Solvents.
- 3. Sample preparation.
- 4. Referencing of NMR Spectra.
- 5. NMR Parameters.
  - (a) Chemical Shifts
  - (b) Integration
  - (c) Spin-Spin Interactions or Coupling Constants.
- 6. Interpretation of NMR Spectra.

When certain Nuclei are placed in a strong magnetic field, ^{1}H, ^{13}C, ^{19}F, ^{14}N, ^{15}N, ^{10}B, ^{11}B, & ^{31}P These nuclei can absorb electromagnetic radiation in the Radiofrequency (R.F.) range.

The absorption of energy can be detected, amplified and recorded as NMR signal. This phenomenon is known as NMR spectroscopy.



H_0

Sample in magnetic Field H_0

E2

E1

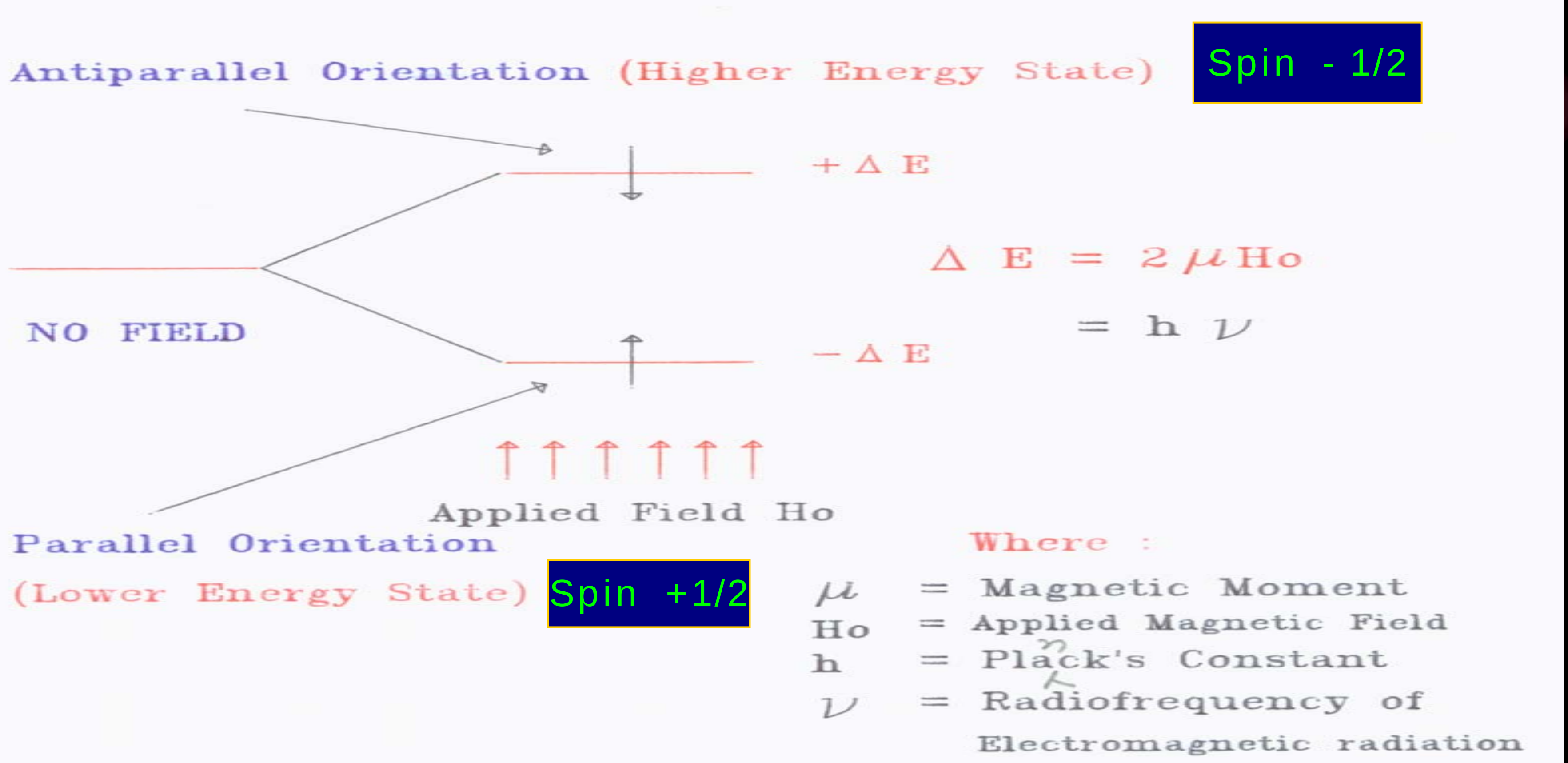
Energy Level Diagram

Resonance Signal

Radio Frequency spectrum

3.10^{6} 3.10^{8} 3.10^{10} 3.10^{12} 3.10^{14} 3.10^{16} R.F.

NMR | Microwave | Infrared | Ultraviolet

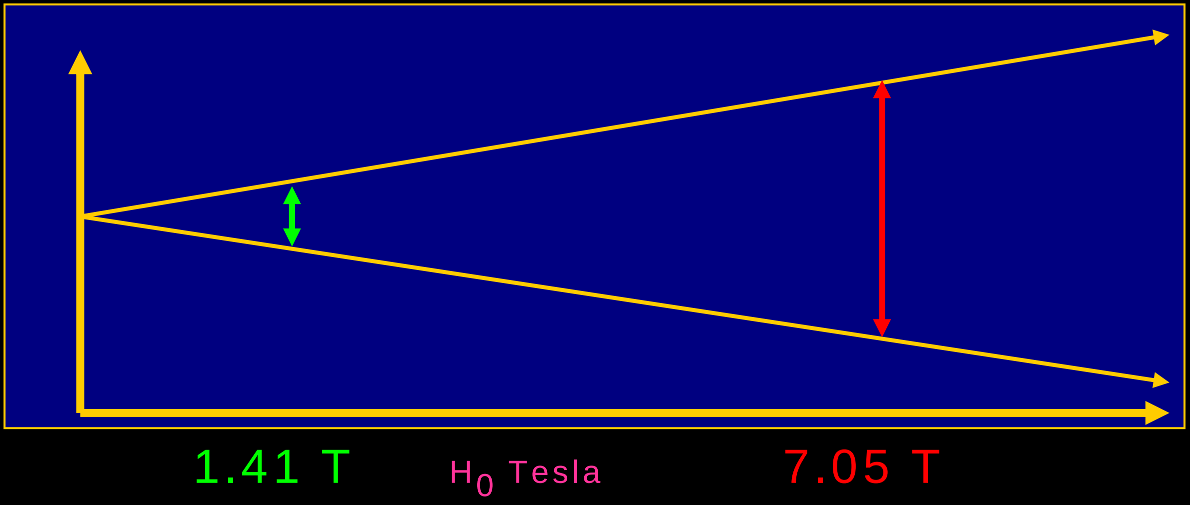


$$\Delta E = 2\mu Ho$$
$$= h\nu$$

Where :

μ = Magnetic Moment
Ho = Applied Magnetic Field
h = Planck's Constant
ν = Radiofrequency of Electromagnetic radiation

- For ^{1}H ^{13}C ^{19}F ^{15}N & ^{31}P nuclei only two orientations are allowed under applied magnetic field spins are aligned parallel
- (in line with applied field) and anti parallel (opposite with applied field)
- The energy difference ΔE between allowed spin states increases linearly with applied field (H_0) strength.
- ^{1}H @ 7.05 T the energy difference = 0.120 J/mol = 0..286 Cal/mol
- Which corresponds to electromagnetic radiation of 300 MHz
- (300 000 000 Hz = 300 x 10^{6} Hz) .
- For ^{13}C = 0.030 J/mol = 0.00715 Cal/mol corresponds to RF of 75 MHz.

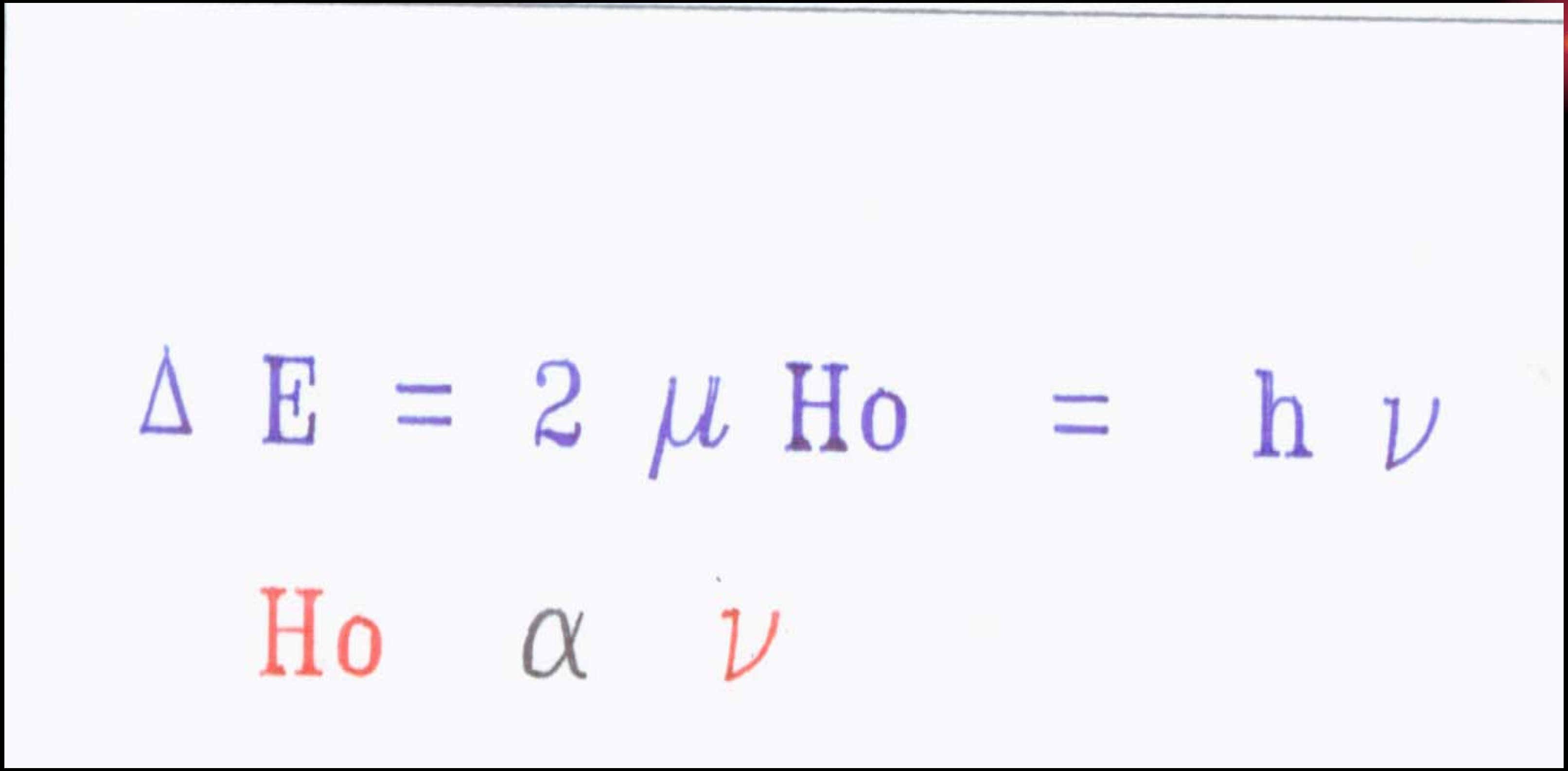


Δ E =0.0239 J/mol

Δ E = 0.120 J/mol

Applied field is directly proportional to radiofrequency.

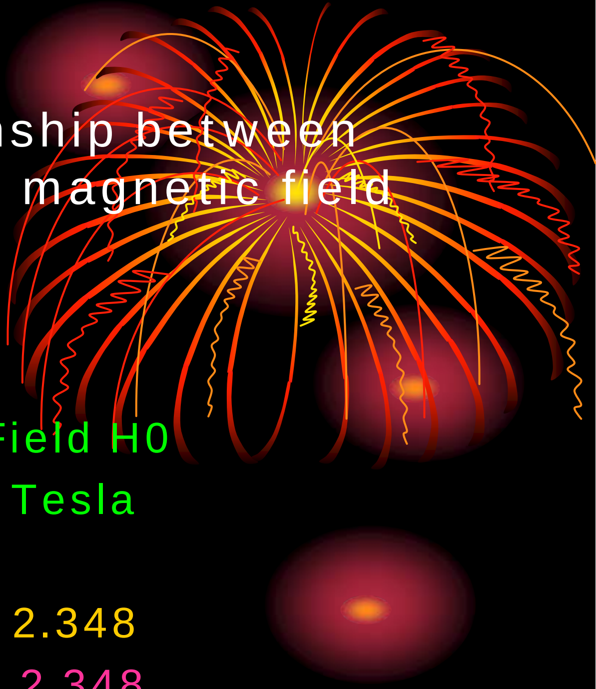
H_0 = Magnetic Field
U = Magnetic moment
v = Radiofrequency
h = Planck's constant



$$\Delta E = 2 \mu H_o = h \nu$$

$$H_o \; \alpha \; \nu$$

Typical conditions which satisfy the relationship between radiofrequencies for different nuclei at fixed magnetic field strength are given in the below table.



Nucleus	Spin No. I	% Natural Abundance	Frequency MHz	Field H0 Tesla
^{1}H	1/2	99.98	100.00	2.348
^{10}B	3	19.00	10.74	2.348
^{11}B	3/2	81.00	32.07	2.348
^{13}C	1/2	1.10	25.14	2.348
^{14}N	1	99.60	7.22	2.348
^{15}N	1/2	0.40	10.13	2.348
^{19}F	1/2	100.00	94.05	2.348
^{29}Si	1/2	4.70	19.86	2.348
^{31}P	1/2	100.00	40.45	2.348
^{12}C	0 (zero)	98.80	NO NMR SIGNAL	
^{16}O	0 (zero)	99.80	NO NMR SIGNAL	

Condition for NMR Signals

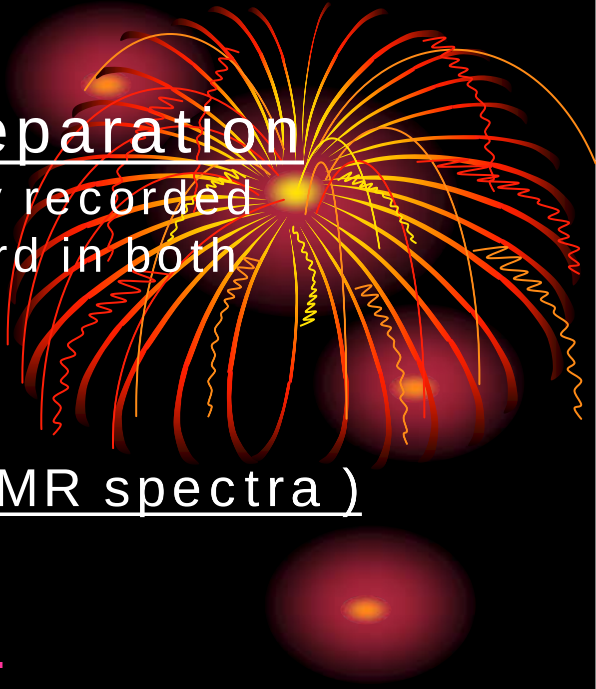
- 1. All the nuclei with odd mass number.

- 2. All the nuclei with even mass number
- and odd number of protons & neutrons.

- 3. Those nuclei which have a non zero
- magnetic moment (u) and spin angular moment (I)
- produce NMR signals.

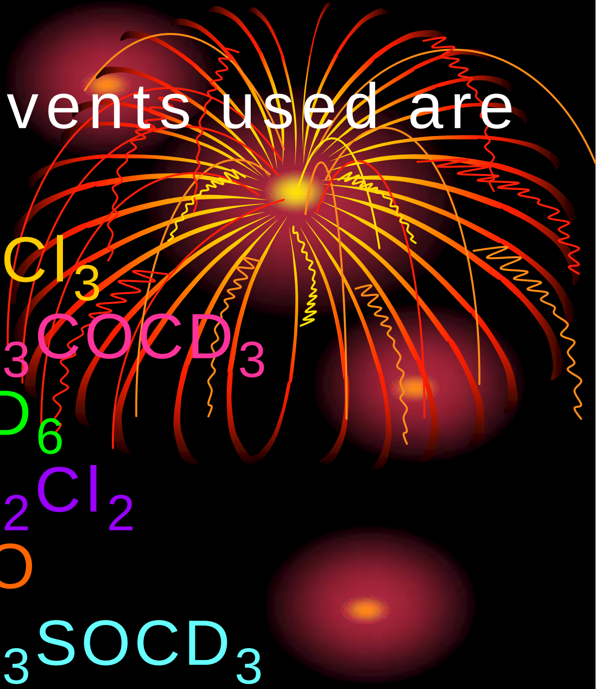
Choice of solvent and Sample preparation

The high resolution NMR spectra are usually recorded in Liquid Phase though it is possible to record in both Gaseous and Solid phases.



CHOICE OF SOLVENT (Liquid phase NMR spectra)

- The choice of solvent depends on :-
- 1. Solubility of the interested compound.
- 2. Physical properties of solvent.
- 3. Produce no NMR signal.
- 4. Interfering signals from solvent.
- 5. For Variable temperature work m.p. (melting point) and
- b.p. (boiling point).
- 6. Locking frequency from solvent. Usually Deuterium
- lock is used.

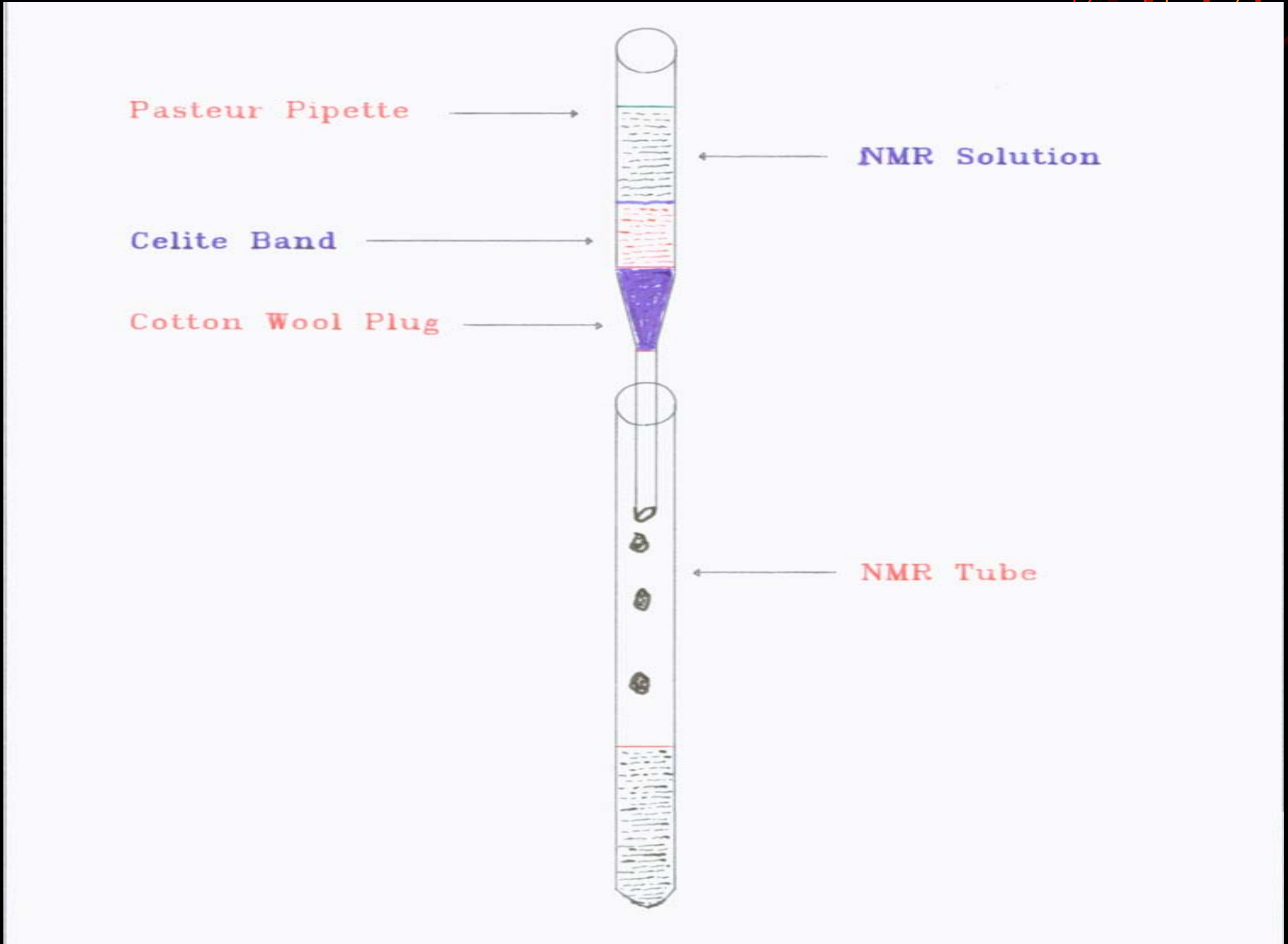


- The most common Deuterated solvents used are

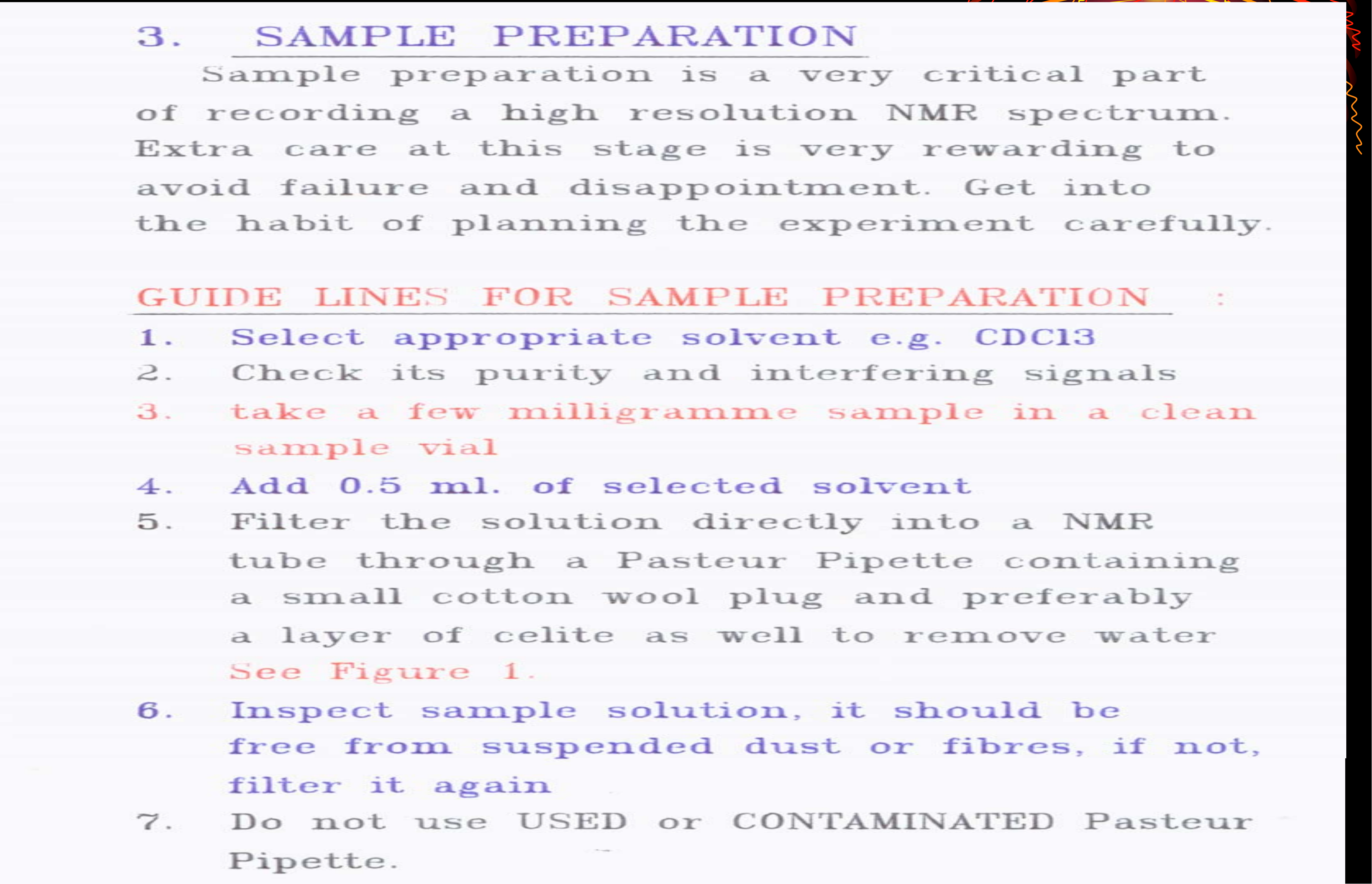
1.	Deuterochloroform	$CDCl_3$
2.	Deuteroacetone	CD_3COCD_3
3.	Deuterobenzene	C_6D_6
4.	Deuterodichloromethane	CD_2Cl_2
5.	Deuterated water	D_2O
6.	Deuterodimethysulphoxide	CD_3SOCD_3

Note :- The hydrogen atoms are replaced with deuterium so that no signal from solvent and also used for locking the lock frequency.

Sample Preparation



Sample Preparation for NMR spectrum (Liquid Phase)



3. SAMPLE PREPARATION

Sample preparation is a very critical part of recording a high resolution NMR spectrum. Extra care at this stage is very rewarding to avoid failure and disappointment. Get into the habit of planning the experiment carefully.

GUIDE LINES FOR SAMPLE PREPARATION :

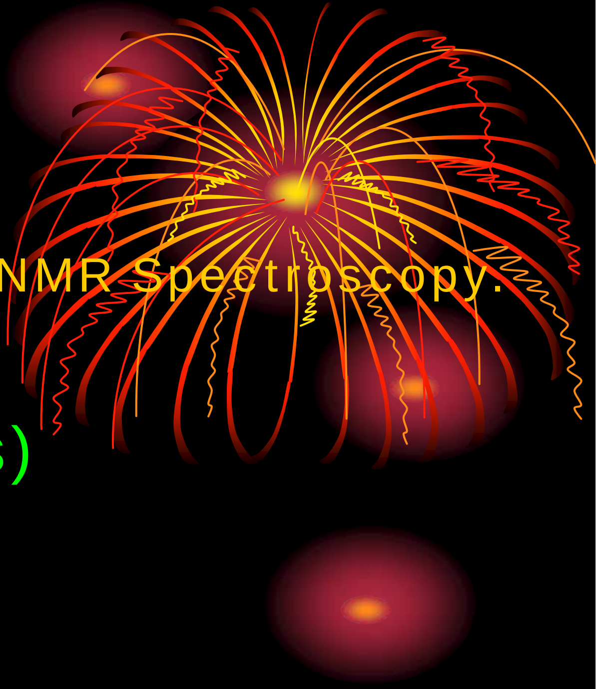
1. Select appropriate solvent e.g. CDCl3
2. Check its purity and interfering signals
3. take a few milligramme sample in a clean sample vial
4. Add 0.5 ml. of selected solvent
5. Filter the solution directly into a NMR tube through a Pasteur Pipette containing a small cotton wool plug and preferably a layer of celite as well to remove water See Figure 1.
6. Inspect sample solution, it should be free from suspended dust or fibres, if not, filter it again
7. Do not use USED or CONTAMINATED Pasteur Pipette.

Referencing of NMR Spectra

- The reference compound should have only one absorption peak for the interested compound.
- It should also be :-
  - 1. Chemically Stable.
  - 2. Chemically Inert.
  - 3. Soluble in most common solvents.

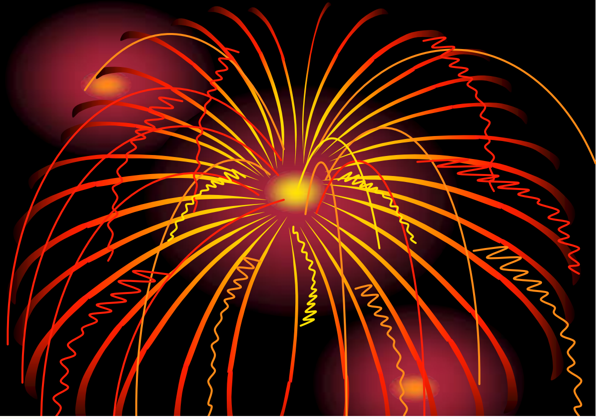
NMR OF	Reference Compounds	
^{1}H	TMS	(TetraMethylSilane)
	TSP-D4	(3-TrimethySilyl-2,2,3,3-tetra DeuteroPropionic acid Sodium salt.)
^{13}C	TMS, $CDCl_3$	
^{14}N	NH_4NO_3	Acidified Saturated Solution
^{15}N	NH_2CHO	90% Formamide
	CD_3NO_2	Deuteronitromethane
^{19}F	TFA	TriFluoroAcetic Acid
	$CFCl_3$	Freon 1,1
^{31}P	H_3PO_4	85% Phosphoric Acid

NMR PARAMETERS

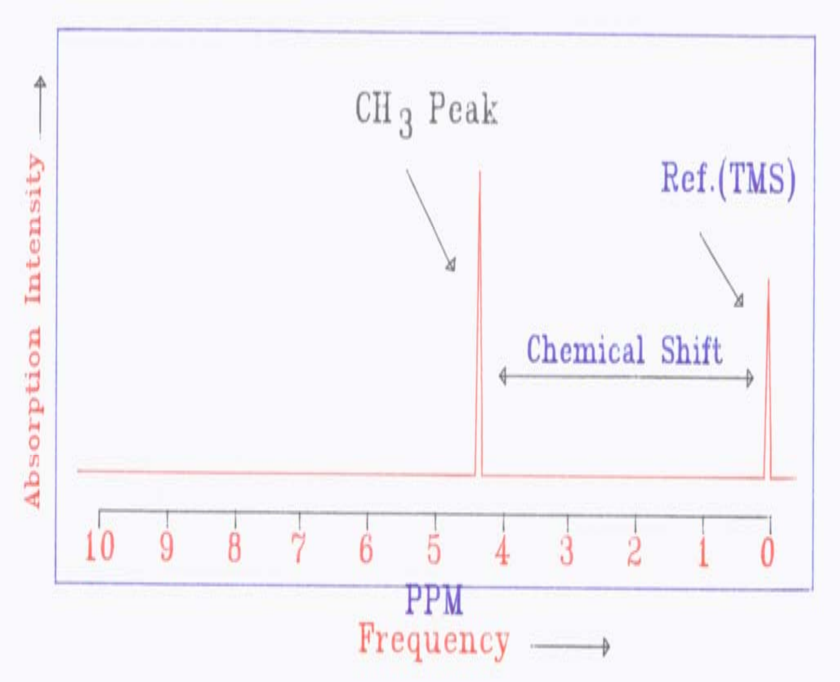


- There are Four very important Parameters in NMR Spectroscopy.
- 1. Chemical Shifts
- 2. Integration (Area Under Peaks)
- 3. Coupling Constants
- 4. Relaxation Processes

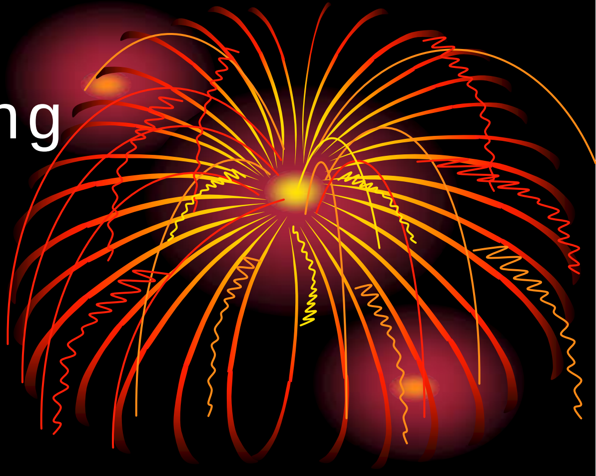
Chemical Shifts



- Let us look at the ^{1}H NMR
- Spectrum of Nitromethane
- CH_3NO_2
- It is plot of absorption intensity
- Against frequency.
- There are two peaks (absorptions), one labelled reference peak (TMS) 0.0 PPM
- And another CH_3 peak 4.333 PPM
- The distance between reference peak and interested peak in NMR Spectrum is known as chemical shift.
- Chemical Shift = $d_{sample} - d_{ref}$



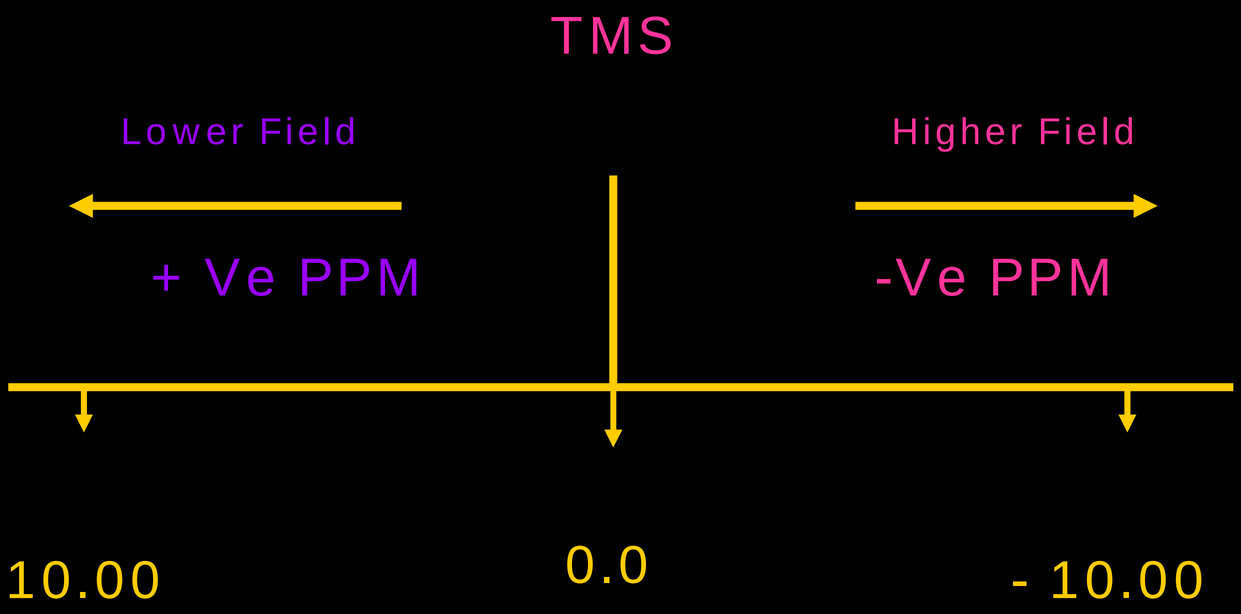
What is widely used for referencing ^{1}H NMR Spectra ?



- Choose one of the following.
- 1. Ammonium nitrate
- 2. Trifluoroacetic acid
- 3. Tetramethylsilane
- Answer is
- Tetramethylsilane (TMS)

The TMS absorption is assigned ZERO PPM or ZERO HERTZ in ^1H NMR Spectra as a Reference point.

Typical ^1H NMR Spectrum



TMS

Lower Field

Higher Field

+ Ve PPM

-Ve PPM

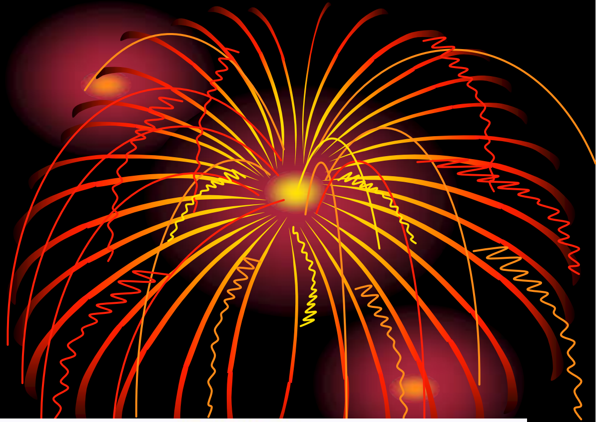
10.00

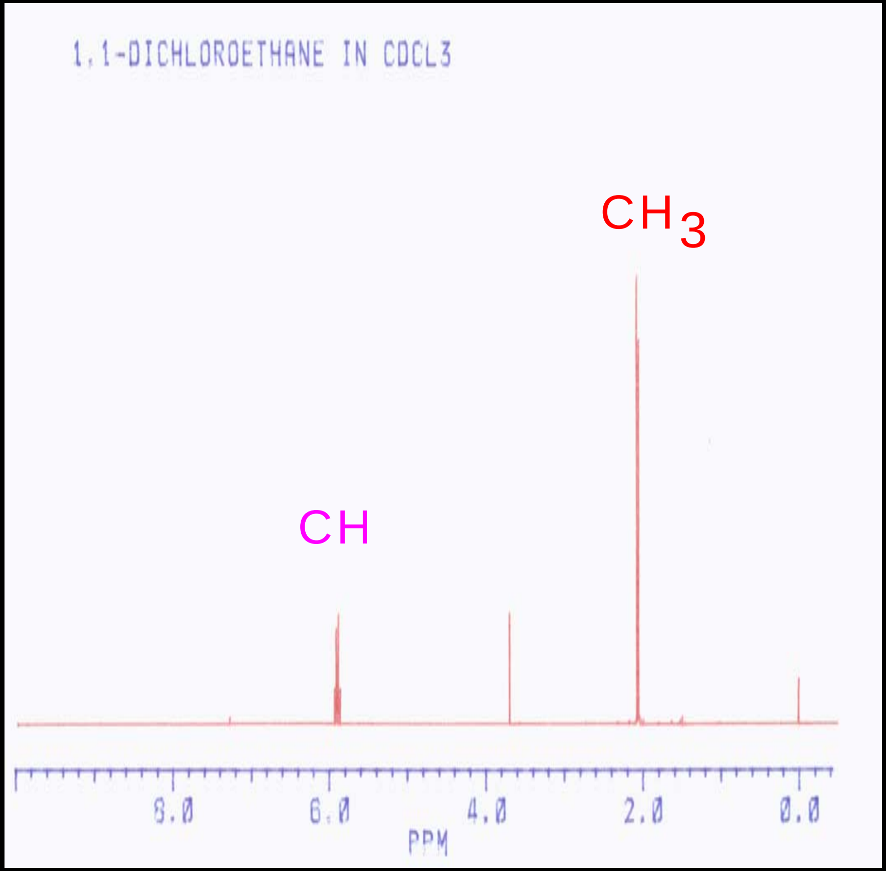
0.0

- 10.00

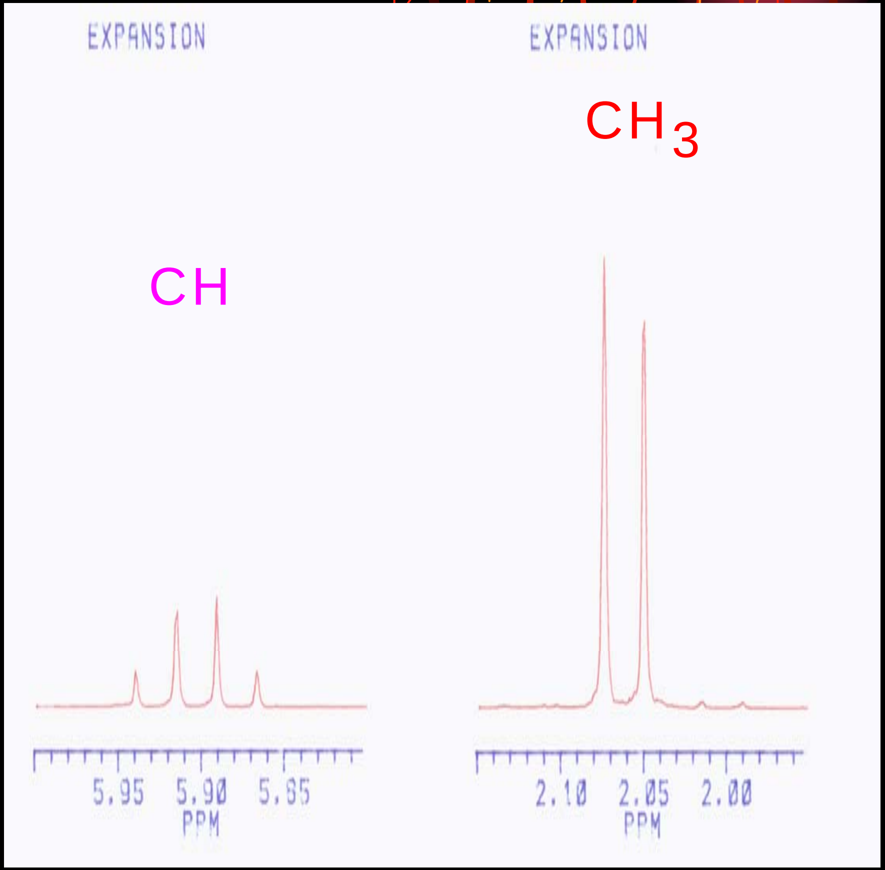
Analysis of 1,1-Dichloroethane
^{1}H NMR Spectrum

CH_3- $CHCl_2$

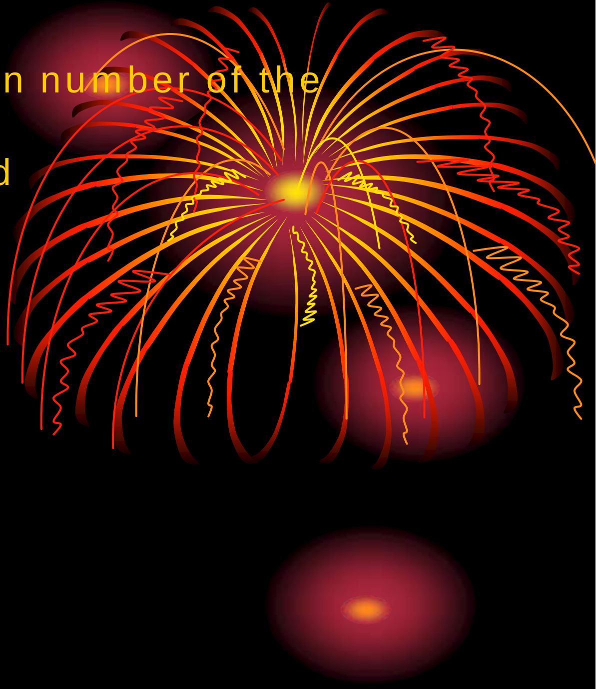




Normal NMR Spectrum
0.0 to 10.00 PPM Range



Expansion of two area 2.00 & 5.90 PPM



- n = No. of neighbours of spin active nucleus and I = spin number of the
- Spin active nucleus.

E. g. CH_3-$CHCl_2$ CH_3 has only one neighbour n = 1 and

- CH has three neighbours n = 3

Spin number (I) for ^1H = 1/2 (Half)

- No. Of Peaks for CH3 = 2nI +1 (n=1 & I = 1/2)

= 2 x 1 x 1/2 +1

= 1 + 1

= 2 (Doublet)

- No of Peaks for CH = 2nI +1 (n=3 & I =1/2)

= 2 x 3 x 1/2 + 1

= 3 + 1

= 4 (Quartet)

- From Pascal's triangle the intensity ratio of doublet should be 1 : 1 and for quartet should be 1 : 3 : 3 : 1

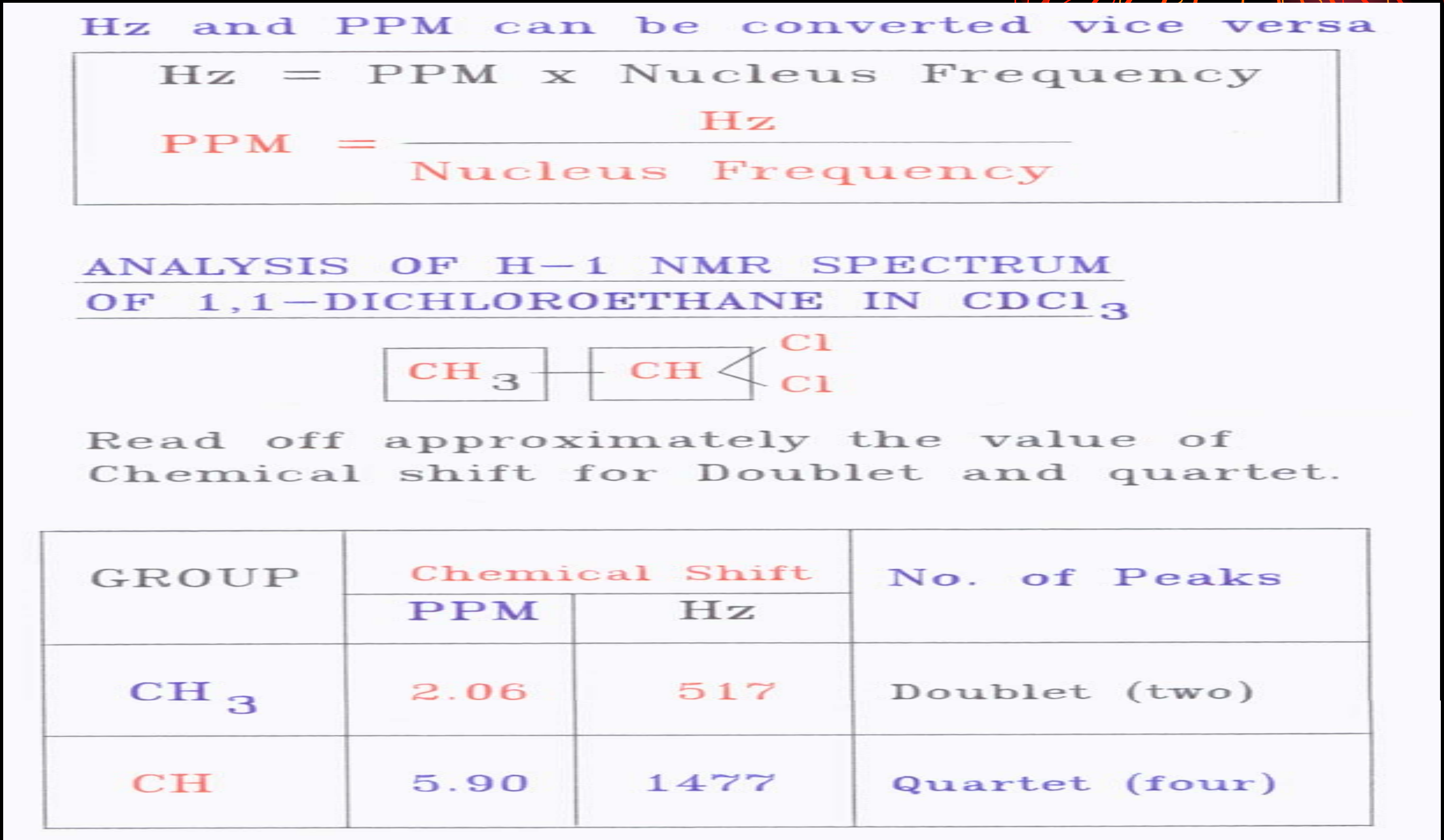
- In reality the same thing is observed in the NMR spectrum.

Note:- No of peaks = 2nI + 1 For any Nuclei

In short No. of Peaks ^1H NMR = n + 1

Analysis of 1H NMR of 1,1-Dichloroethane

$CH_3—CHCl_2$



Hz and PPM can be converted vice versa

$$Hz = PPM \times Nucleus\ Frequency$$

$$PPM = \frac{Hz}{Nucleus\ Frequency}$$

ANALYSIS OF H–1 NMR SPECTRUM OF 1,1–DICHLOROETHANE IN $CDCl_3$

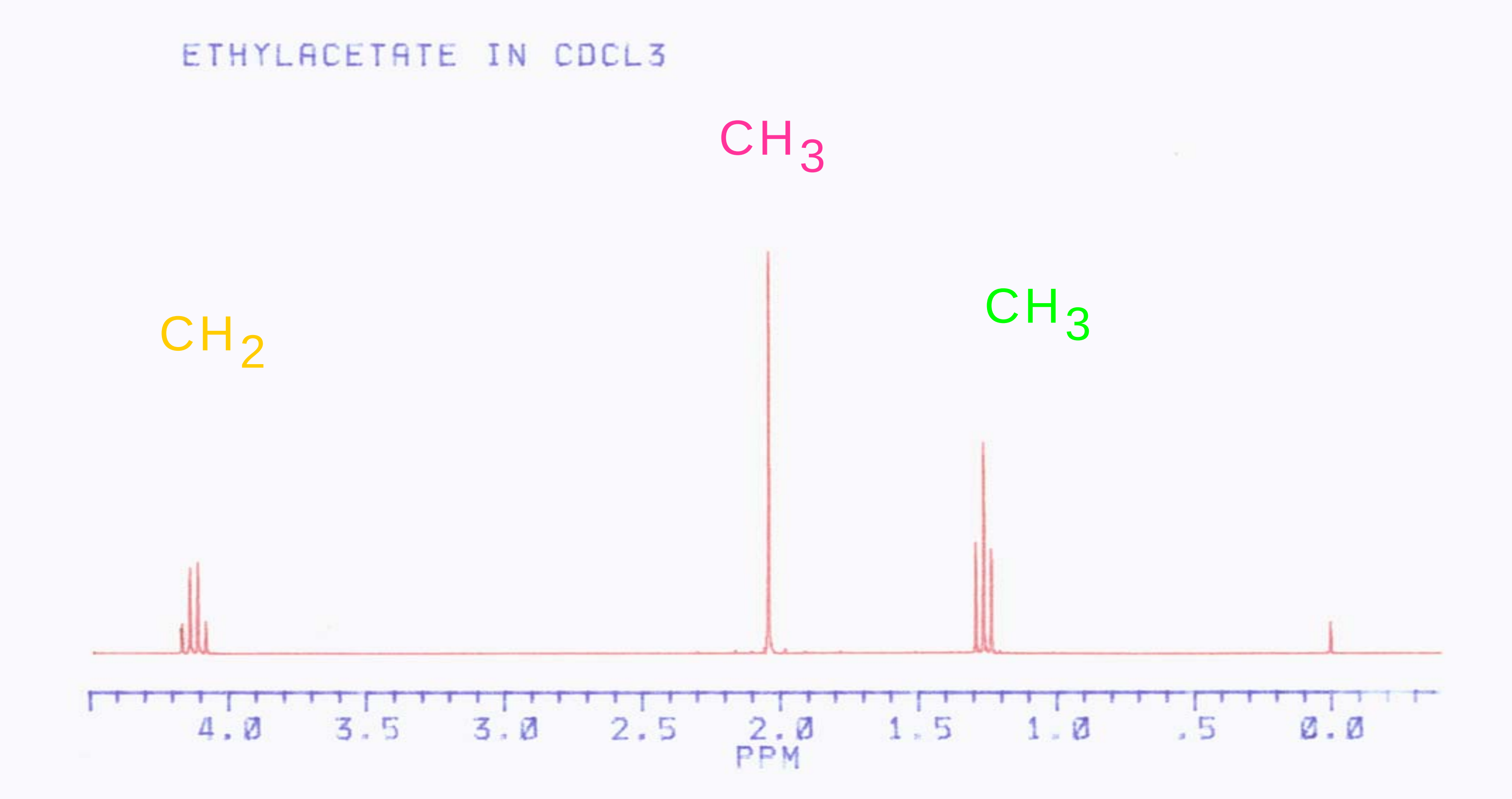
$CH_3 — CH<^{Cl}_{Cl}$

Read off approximately the value of Chemical shift for Doublet and quartet.

GROUP	Chemical Shift		No. of Peaks
	PPM	Hz	
CH_3	2.06	517	Doublet (two)
CH	5.90	1477	Quartet (four)

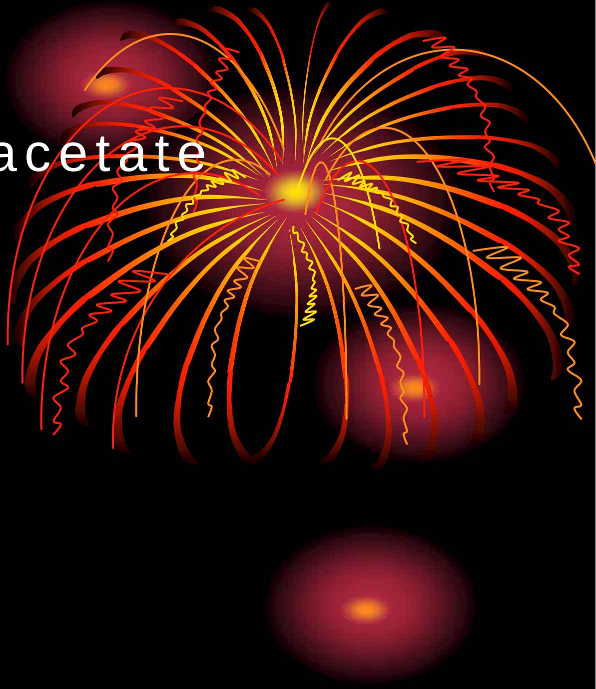
Analyse the ^{1}H NMR spectrum of Ethyl acetate

CH_3 CO OCH_2 CH_3



Analyse the ^{1}H NMR spectrum of Ethyl acetate

$CH_3\ CO\ OCH_2\ CH_3$

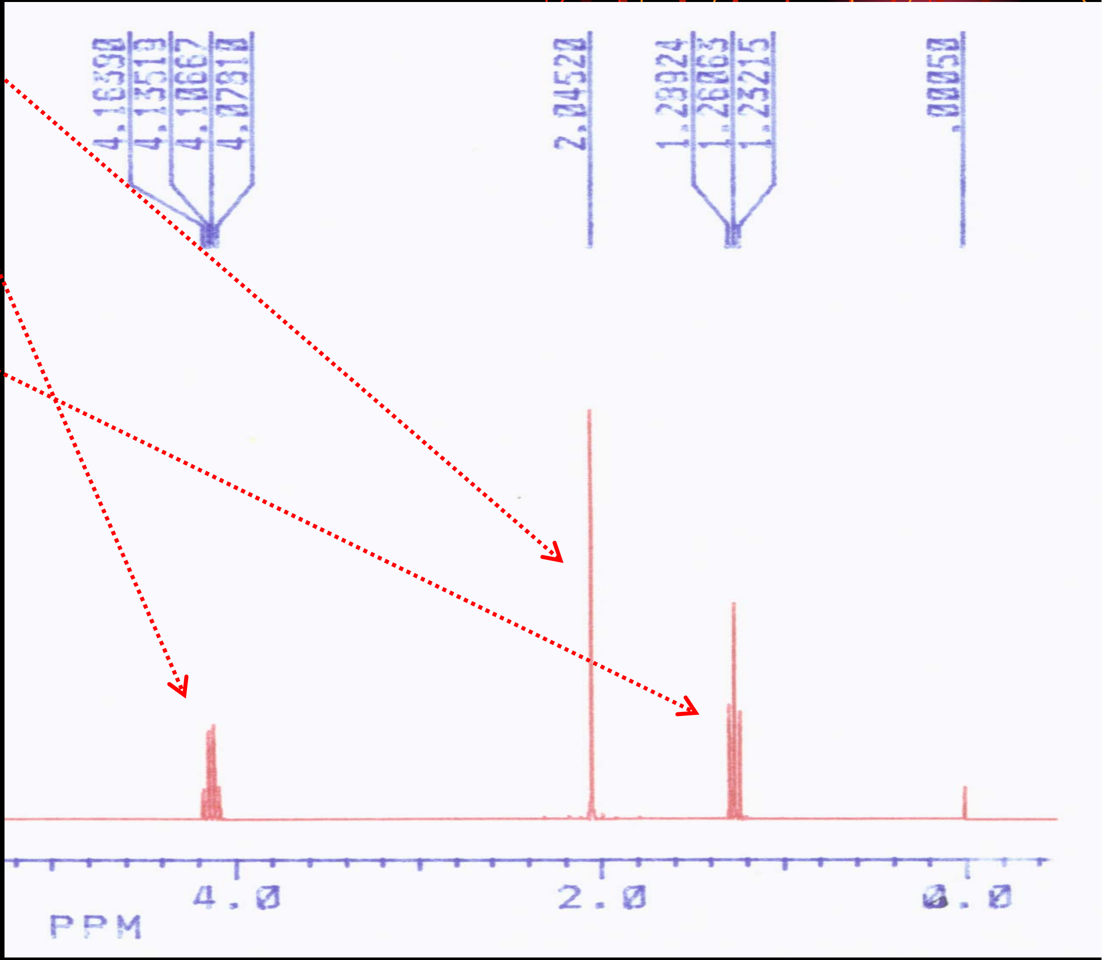


- CH3 has zero neighbour n = 0
- No of Peaks = n + 1
- = 0 + 1
- = 1 (Singlet)
- CH2 has Three neighbours n = 3
- No. of Peaks = n + 1 = 3 + 1 = 4 (Quartet)
- CH3 has Two neighbours n = 2
- No. of Peaks = n + 1 = 2 + 1 = 3 (Triplet)
- Note :- CO and O groups do not give any peak because
- They do not contain H element.

Analyse the ^{1}H NMR spectrum of Ethyl acetate

CH_3 CO OCH_2 CH_3

- CH3 Singlet @ 2.05 PPM
- CH2 Quartet @ 4.12 PPM
- CH3 Triplet @ 1.26 PPM
- CO no NMR signal
- O no NMR signal



Analyse the ^{1}H NMR spectrum of Ethyl acetate

CH_3 CO OCH_2 CH_3

- Use of integration in solving problems of structural information.
-
- There are two ways used in measuring integration of NMR Spectrum. E.g. 1H NMR of Ethyl acetate
- 1. Manual Measurement
- 2. Electronic (computer) Measurement

- In manual measurement the height of the different Peaks Areas are measured using ruler and then all the Areas are divided by the smallest area to get the relative areas of the peaks (groups).

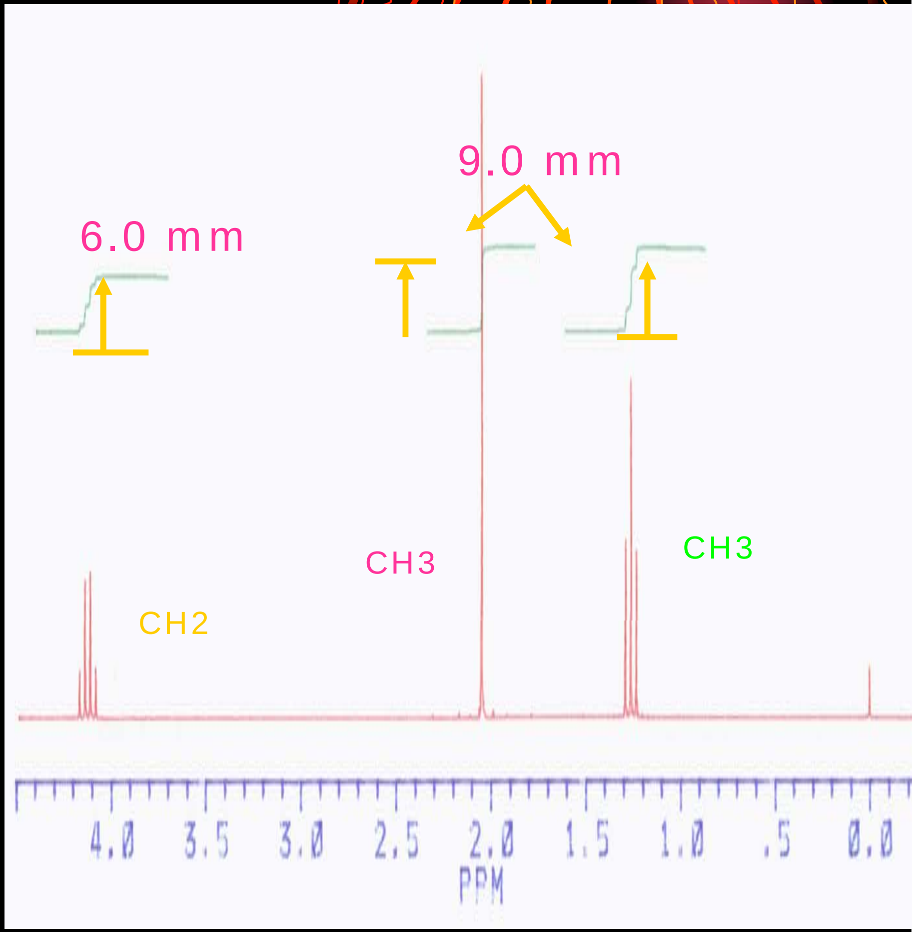
- This is an approximation process hence the ratio is calculated and rounded to the whole number.

Analyse the ^{1}H NMR spectrum of Ethyl acetate

CH_3 CO OCH_2 CH_3 Manual Measurement

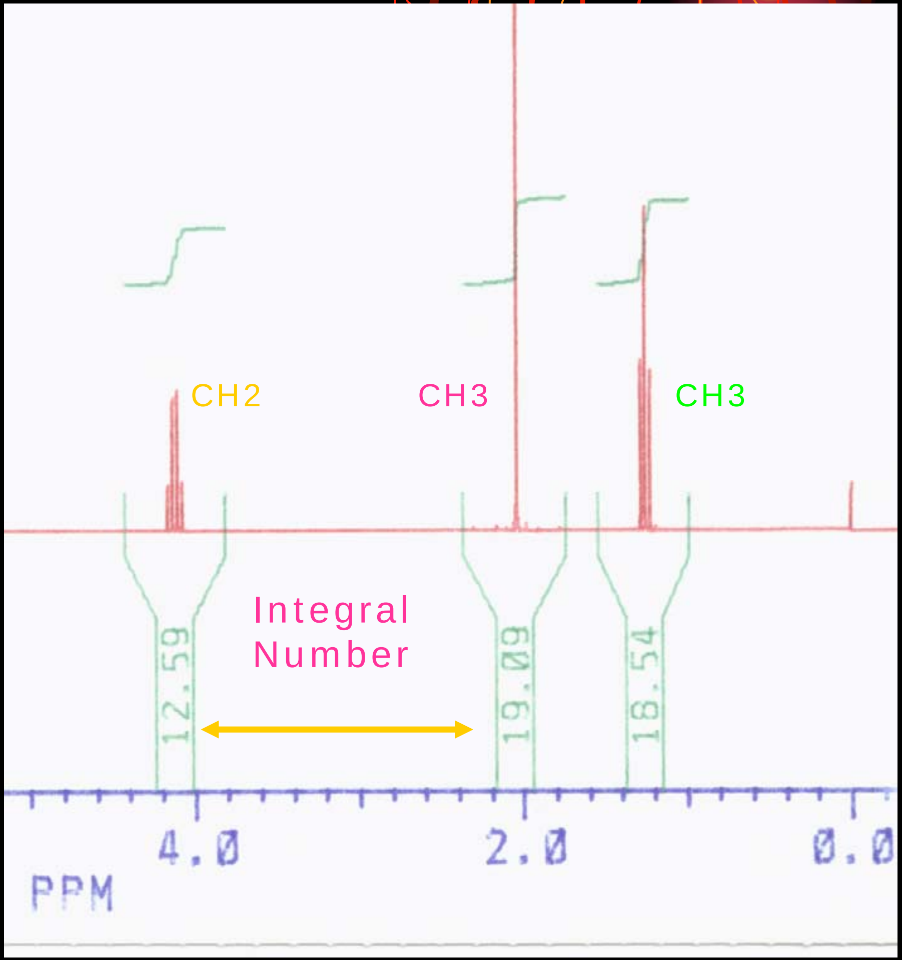
- Integration Analysis
- CH_3 CO O CH_2 CH_3

Height In mm	9.0	6.0	9.0
Integration ratio	1.5	1.0	1.5
Multiply By 2	3.0	2.0	3.0
Area Indicates	3 H	2 H	3 H

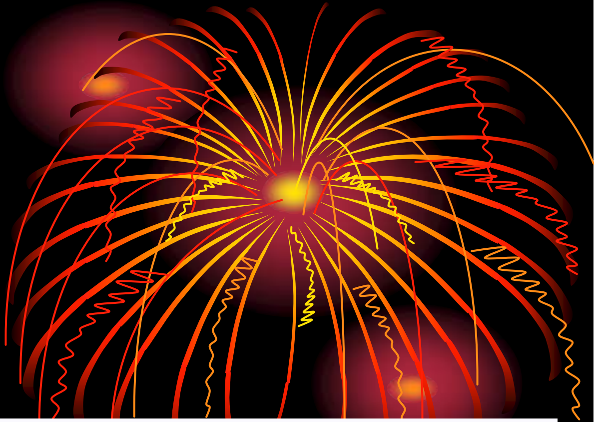


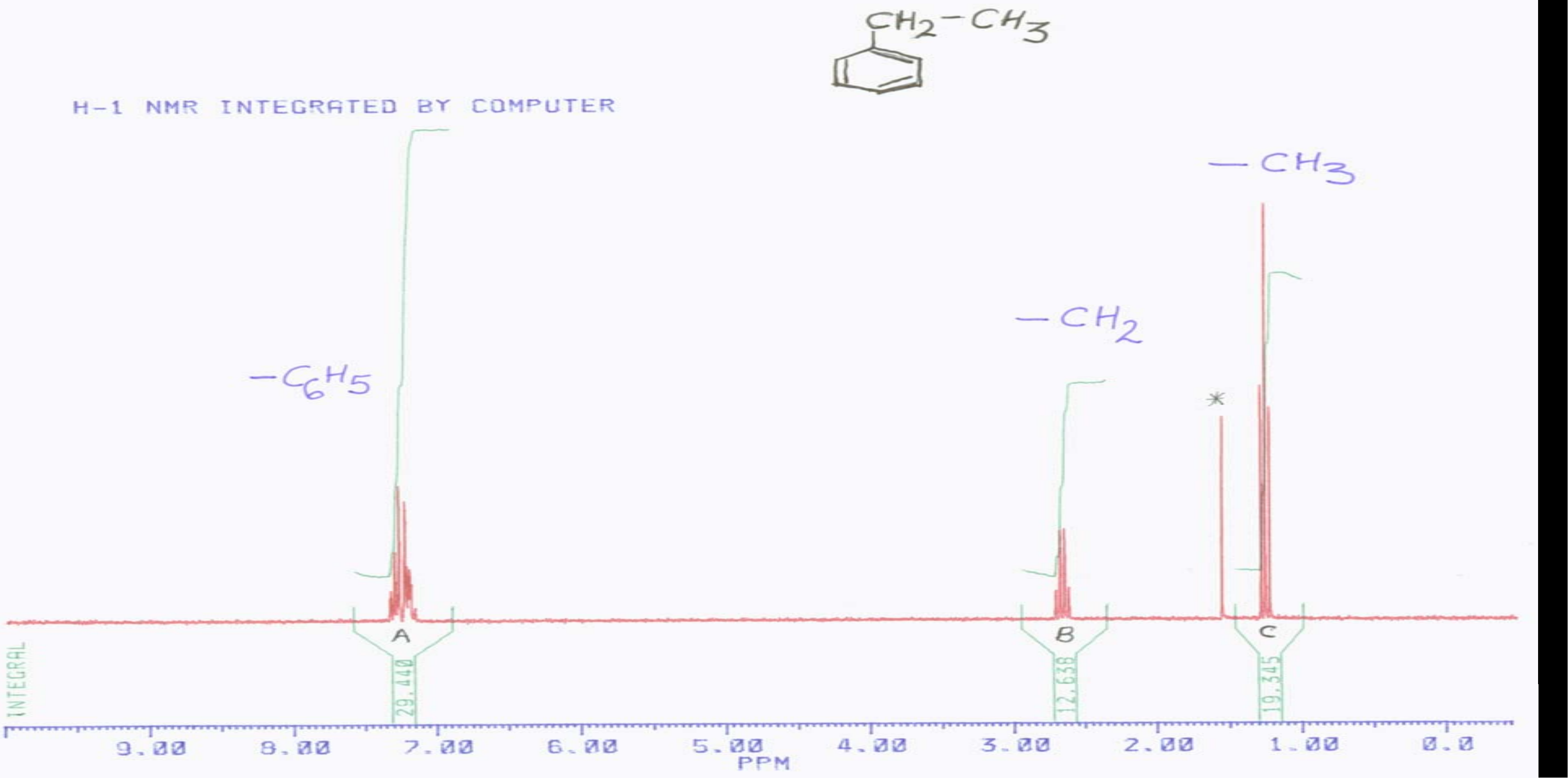
Integration Analysis of Ethyl Acetate Electronic measurement

- CH_3 CO O CH_2 CH_3
- ↓ ↓ ↓
- Integral 19.09 12.59 18.54
- Number
- Integral 1.52 1.00 1.47
- Ratio
- Multiply 3.04 2.00 2.94
- By 2
- Rounding 3.00 2.00 3.00
- The number
- Area 3 H 2 H 3 H
- Indicates



	C_6H_5	CH_2	CH_3
Integral	29.440	12.638	19.345
Ratio	2.33	1.00	1.53
Times 2	4.66	2.00	3.06
Rounded	5.00	2.00	3.00
	5 H	2 H	3 H





Conclusion Notes on Integration In NMR Spectroscopy

1. The area under the absorption peak is directly proportional to the number of spin Active nuclei. (e.g. ^{1}H , ^{13}C , ^{19}F , ^{31}P) responsible for the absorption signals in the NMR Spectrum.

2. To integrate the NMR spectrum there must be at least two peaks in the NMR that excluding reference peak. (TMS).

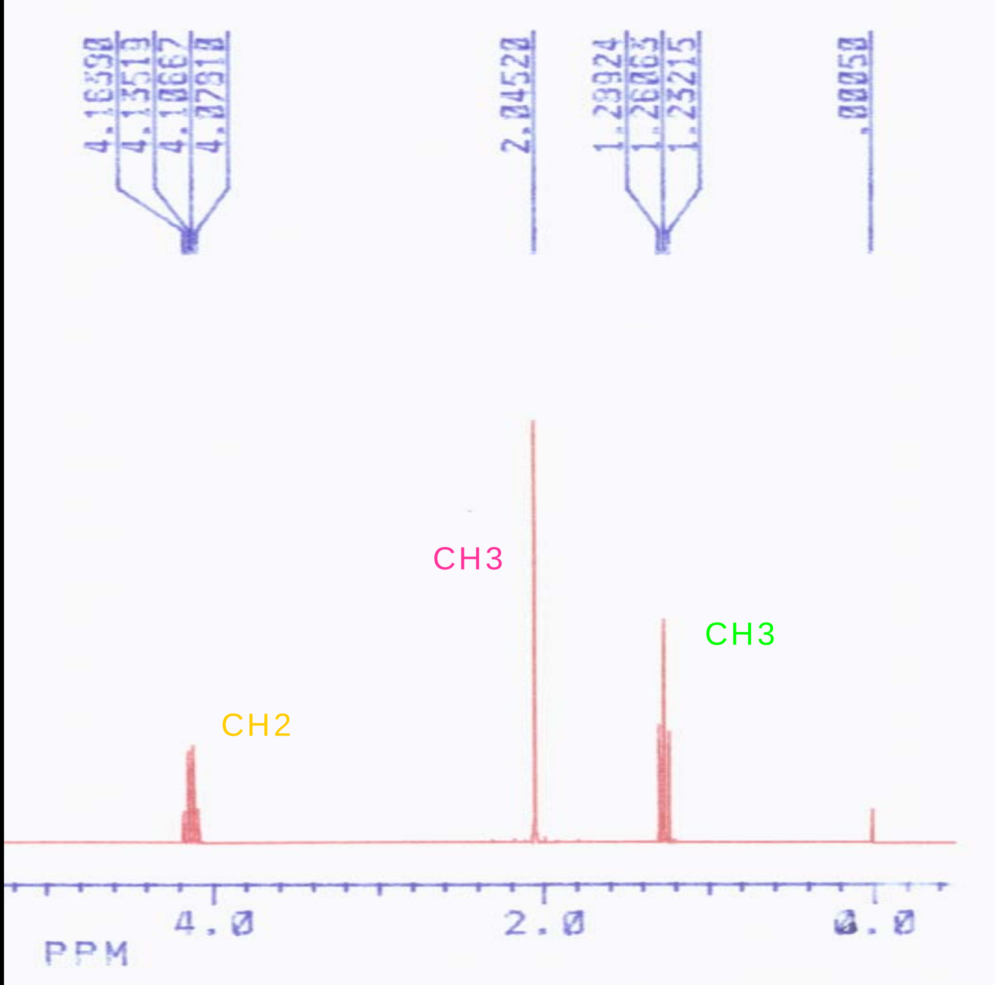
   e. g. ^{1}H NMR spectra of Acetone CH_3 CO CH_3 gives only singlet hence integration has no meaning but Ethyl Acetate CH_3 CO O CH_2 CH_3 there are three signals which can be integrated to measure its relative ratio of the peak areas of spin active nuclei. (^{1}H)

3. Integration is an approximation measurement and it is expressed as a Whole Number Ratio.

   e.g. for Ethyl Acetate 3 : 2 : 3 for ^{1}H NMR Spectrum.

Coupling Constant or Spin Spin Interactions Analysis of Ethyl Acetate CH_3 CO O CH_2 CH_3

- CH3 Singlet @ 2.05 PPM
- CH2 Quartet @ 4.12 PPM
- CH3 Triplet @ 1.26 PPM
-
- TMS Ref. @ 0 .00 PPM
-
- CO no NMR signal
- O no NMR signal

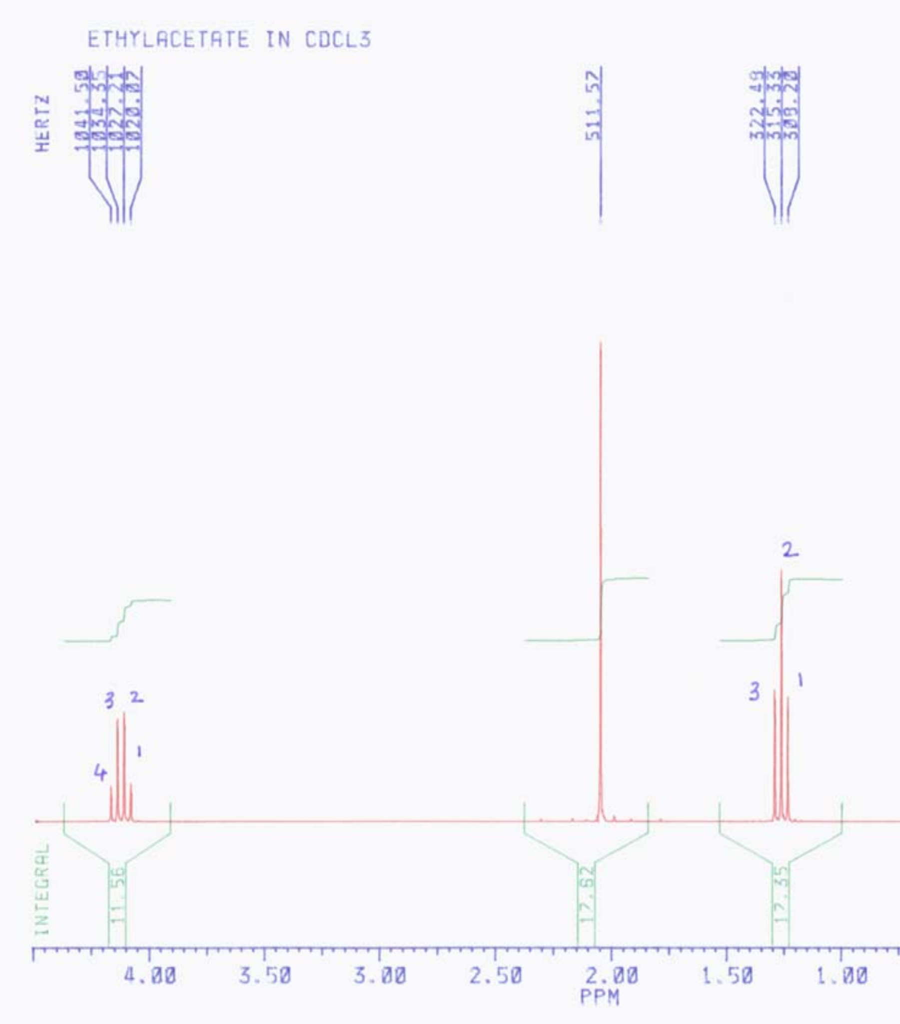


Ethyl Acetate	CH_3	CO	O	CH_2	CH_3
Group No.	1	2	3	4	5

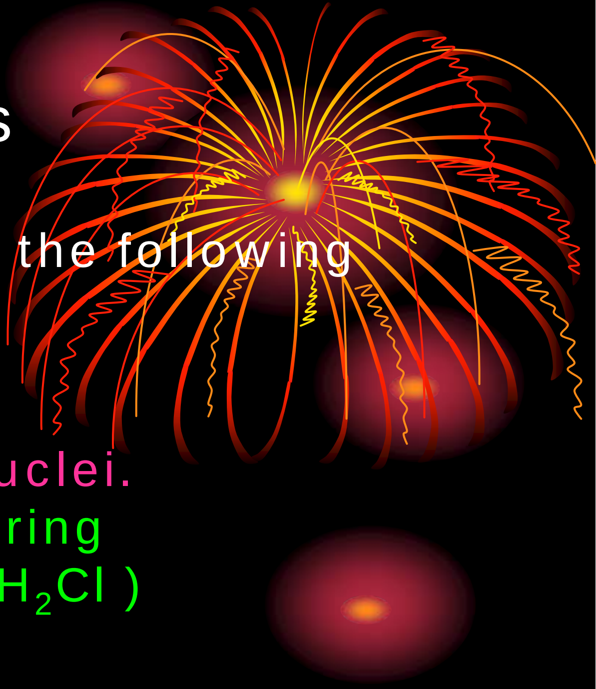
Group No.	Chemical Shift ppm	Signal Structure
1	2 .05	Singlet
2	no signal	
3	no signal	
4	4 .12	Quartet
5	1 .26	Triplet

Why groups 4 & 5 split into Quartet & Triplet ?

This is due to Spin Spin Interactions between groups 4 & 5.



Analysis of Spin Spin interactions



The spin spin interactions can be predicted using the following equation :-

Number of Interactions = 2nI + 1

Where n = Number of neighbouring spin active nuclei.
I = Spin quantum number of the neighbouring spin active nuclei (^1H & ^{19}F in $CH_2F\ CH_2Cl$)

Analysis of Ethyl Acetate 1H NMR spectrum

CH_3--- CO— O--- CH_2–- CH_3

Groups	1	2	3	4	5	
n =	o	3	2	3	2	(both sides neighbours)

I = ½ only ^1H nucleus

Number of interactions = number of peaks = 2nI + 1

For Group 1 (CH3) No. of peaks = 2 x 0 x ½ + 1
= 0 + 1
= 1 (Singlet)

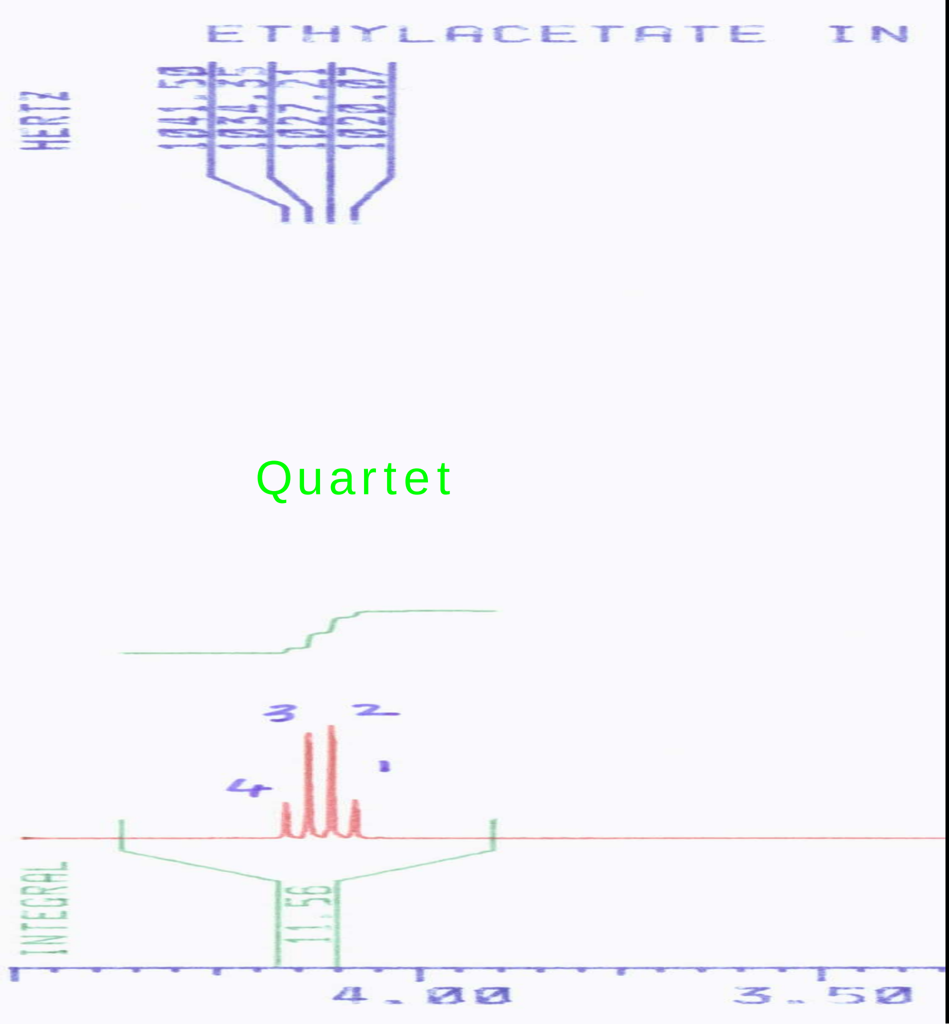
For Group 2 (CO) gives no peak as there is no ^1H present hence would not interact with neighbour. No signal at all.

For Group 3 (O) No signal at all. Same as above.

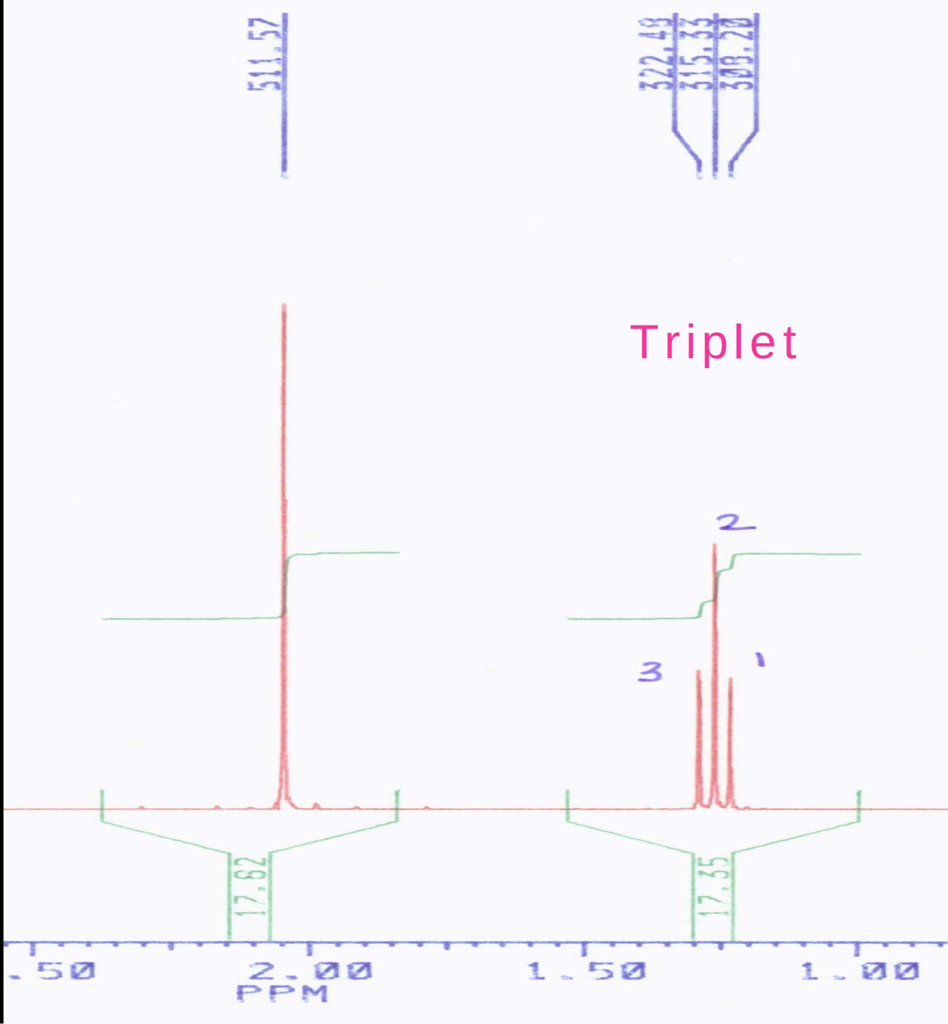
For Group 4 (CH2) No. Of peaks = 2 x 3 x ½ + 1 = 3 + 1 = 4 (Quartet)

For Group 5 (CH3) No. of peaks = 2 x 2 x ½ + 1 = 2 + 1 = 3 (Triplet)

Measurement of the Coupling Constants.
Let us analyse the Quartet and Triplet of Ethyl Acetate



Quartet



Triplet

Read The Position of each peak in Quartet and Triplet. Now calculate the difference between each peak.

Pattern	Position in Hz	Difference
Quartet peak 1	1020 . 07	
		7.14 Hz (P2 – P1)
,, peak 2	1027 . 21	
		7.14 Hz (P3 - P2)
,, peak 3	1034 . 35	
		7.15 Hz (P4 - P3)
,, peak 4	1041 . 50	
Triplet peak 1	308 . 20	
		7.13 Hz (P2 – P1)
,, peak 2	315 .33	
		7.15 Hz (P3 – P2)
,, peak 3	322 .48	

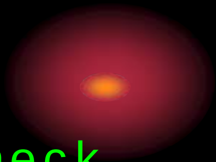
Coupling Constant

- What is the Coupling Constant ?
- The spacing between each adjacent peaks in Quartet and triplet are equal and constant
- (7 .14 Hz) This spacing is known as Coupling
- Constant which is denoted by J_{Hz} and it is independent of applied magnetic field H_0 or B_0
- J $CH_3 - CH_2$ = 7 .14 Hz (in Ethyl Acetate)

Note :- The intensity of Quartet and Triplet can be predicted using Pascal 's Triangle.

Quartet Intensity Ratio	1 : 3 : 3 : 1
Triplet Intensity Ratio	1 : 2 : 1

Theoretical Prediction of NMR Spectrum

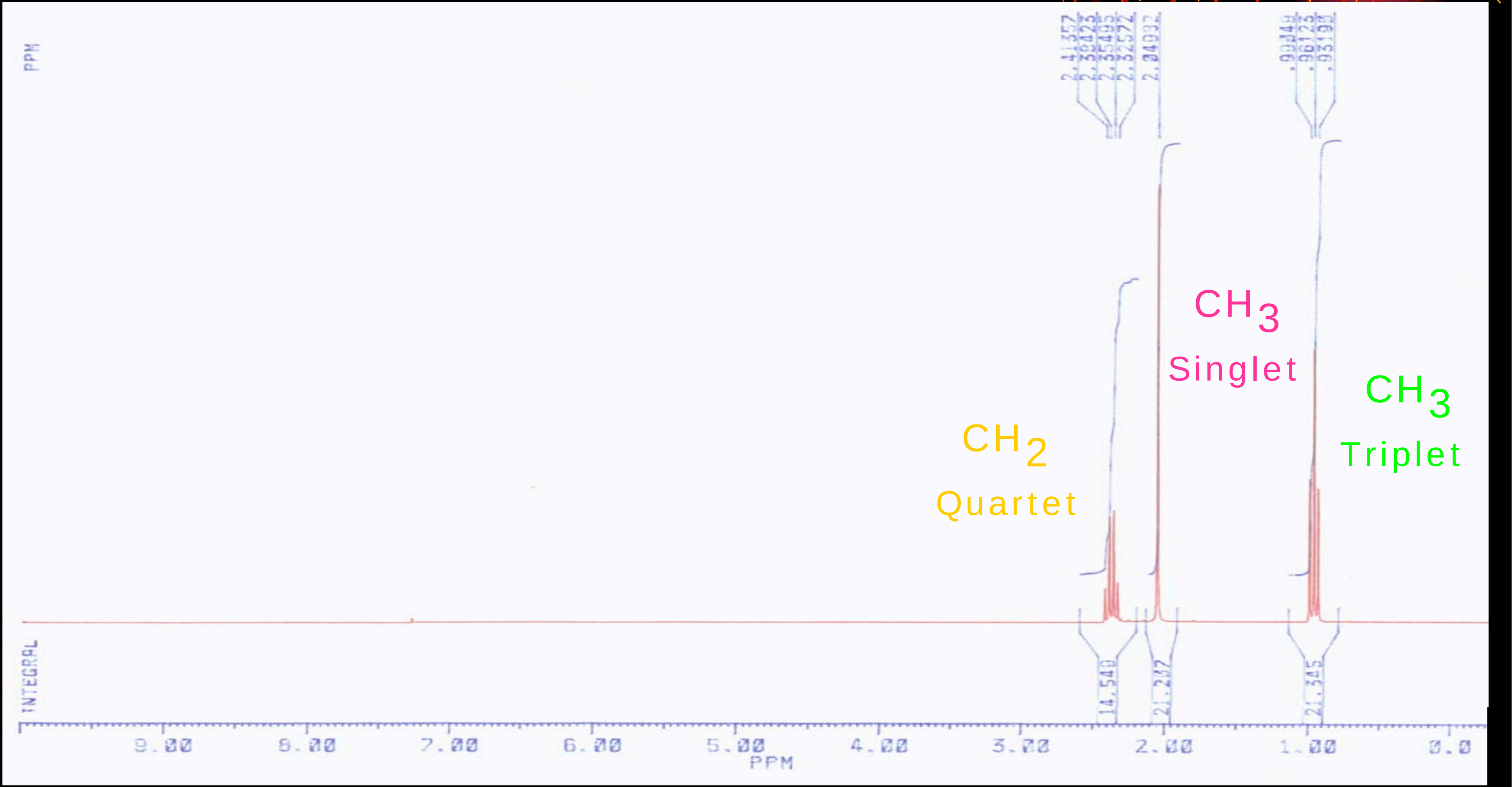


- Butan-2-one $\overset{1}{CH_3}\,\overset{2}{CO}\,\overset{3}{CH_2}\,\overset{4}{CH_3}$

Group No.	Structure of a group	Spin Active neighbouring nuclei n =	No. of Peaks = $2nI + 1$	Remarks
1	CH_3	0	1 (singlet)	Check Integration
2	CO	5	no signal	
3	CH_2	3	4 (quartet)	Check J =
4	CH_3	2	3 (Triplet)	J =

In $CDCl_3$ (0.0 to 10.00 PPM) 1 2 3 4

^1H NMR of Butan-2-one CH_3 CO CH_2 CH_3



CH_2
Quartet

CH_3
Singlet

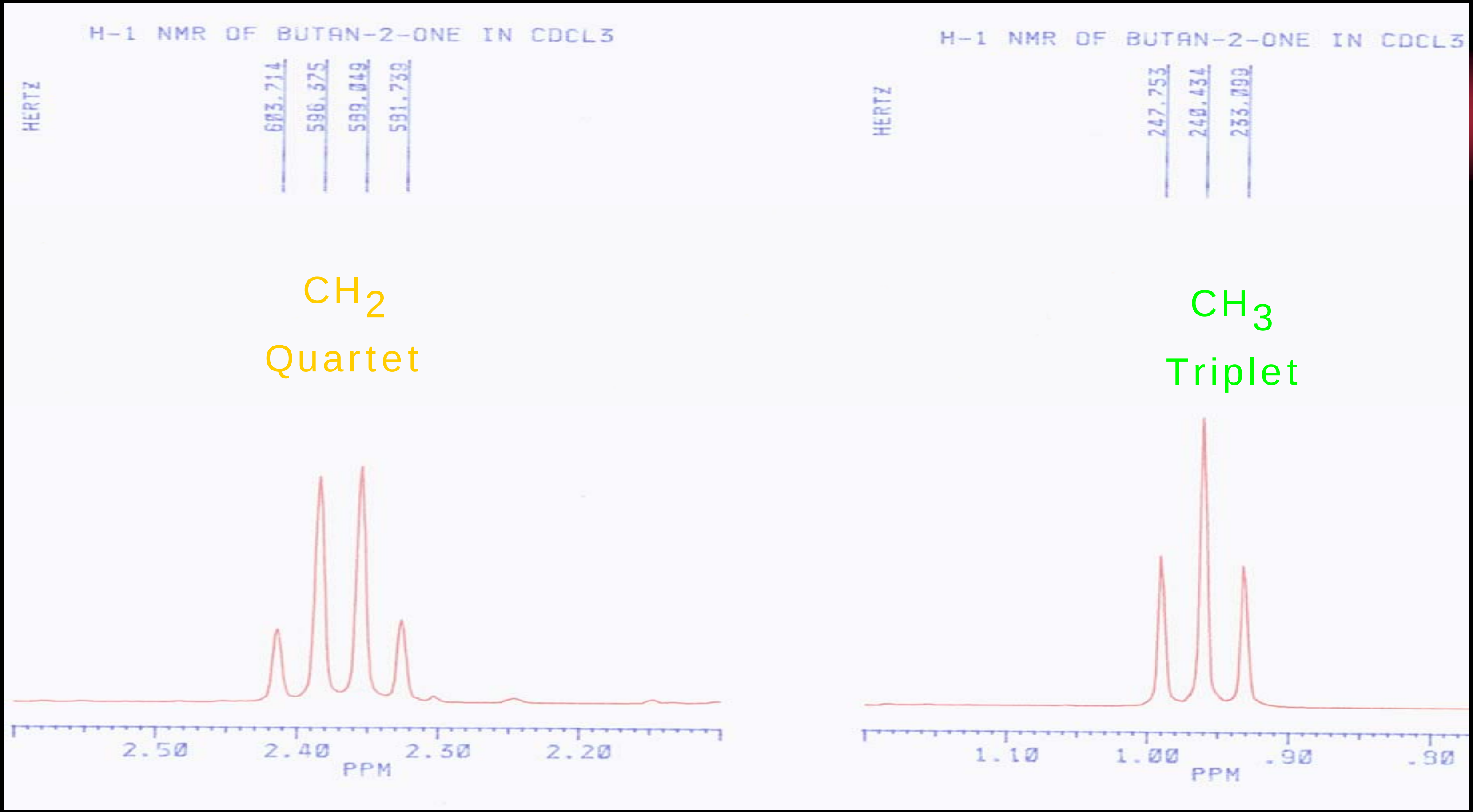
CH_3
Triplet

Expansion of Triplet and Quartet for calculating coupling constant.

J = 247.753 – 240.434 =7.319 Hz 240.434 – 233.099 =7.335 Hz (triplet)

J = 603.714 – 569.375 =7.339 Hz 596.375 – 589.049 =7.326 Hz (quartet)

J = 589.049 – 581.739 =7.310 Hz (quartet)



CH_2

Quartet

CH_3

Triplet

Analysis and Interpretation of ^{1}H NMR of Butan-2-one

1 2 3 4

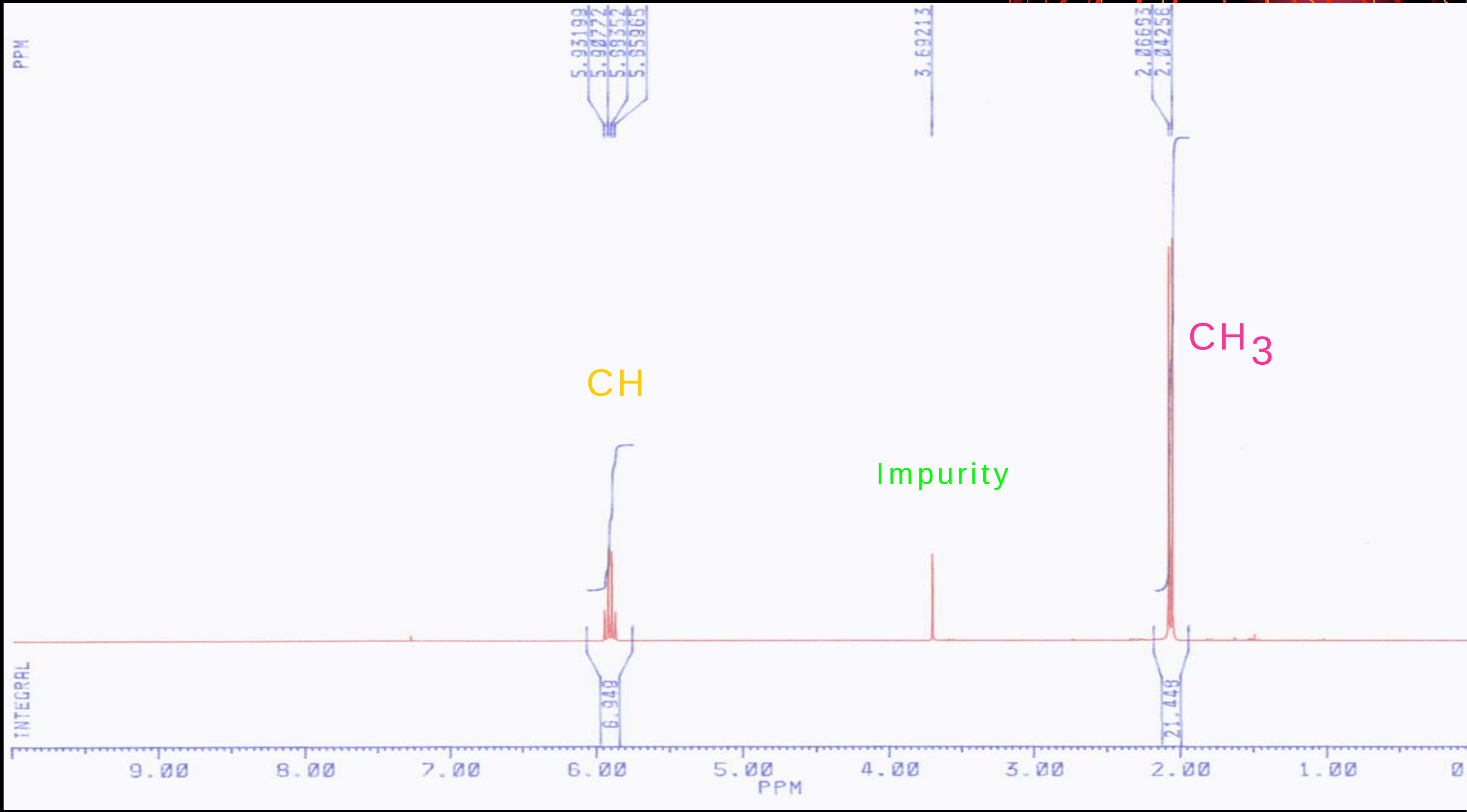
CH_3 CO CH_2 CH_3

Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J =	Neighbouring Groups
1	Singlet	2 . 05	21.28 3	CH_3	None	CO
2	No signal	N/A	N/A	CO	N/A	N/A
3	Quartet	2 . 37	14.54 2	CH_2	7.32 Hz	CH_3
4	Triplet	0 . 96	21.34 3	CH_3	7.32 Hz	CH_2
5			Divide by 7 7 = 1 H		As J=7.32 Hz for gr. 3 & 4 hence neighbours	

^{1}H NMR of 1,1 Dichloroethane in $CDCl_3$

1 2

CH_3 $CHCl_2$ 0.0 to 10.00 PPM Range

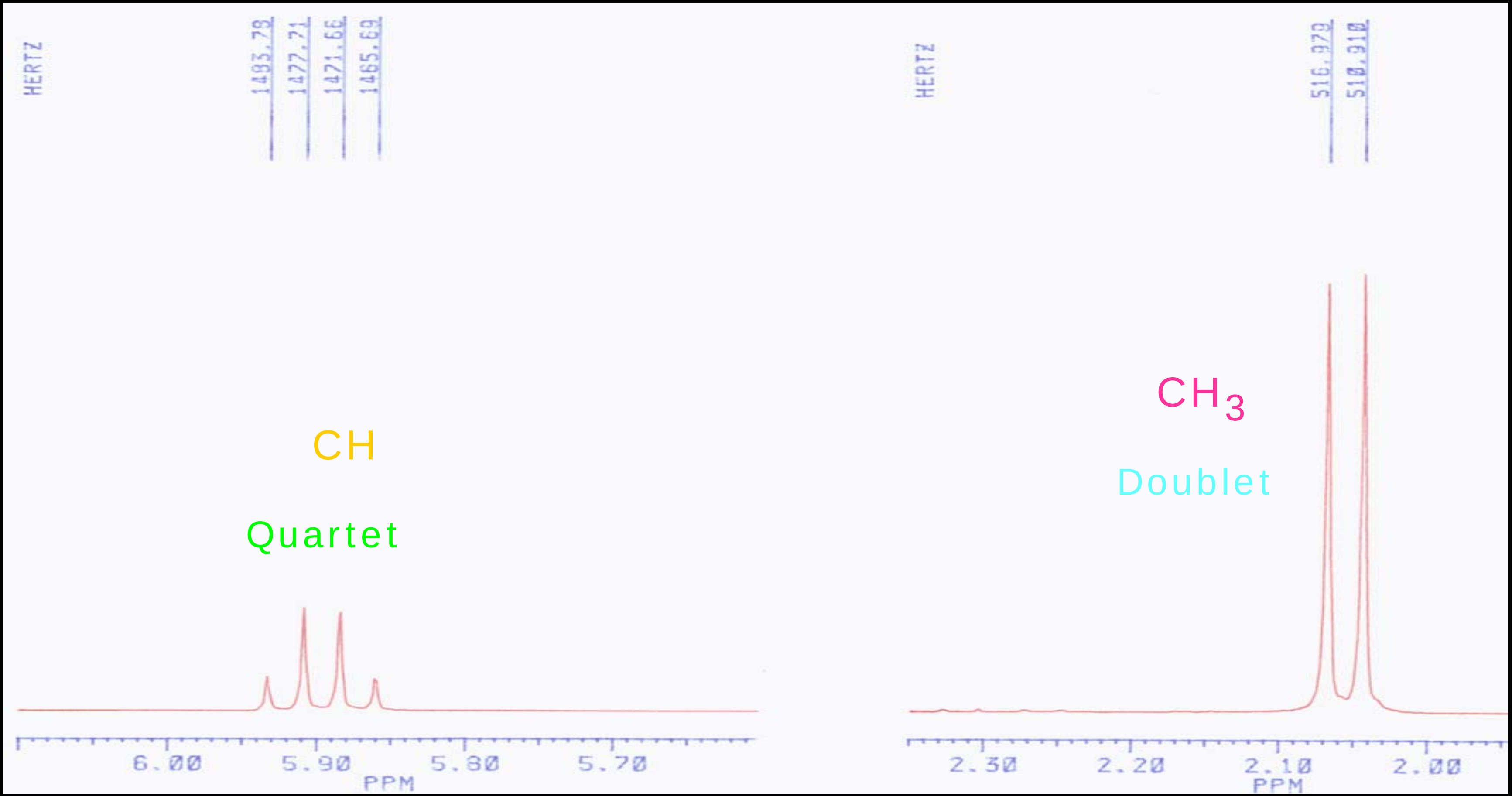


Expansion of Doublet and Quartet of 1,1-Dichloroethane

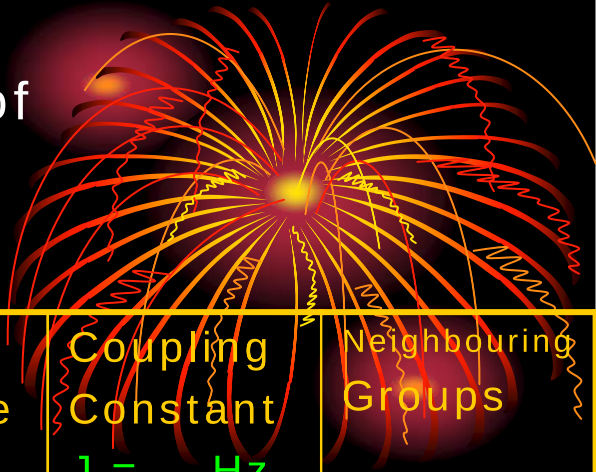
J = 516.979 – 510.910 =6.069 Hz = 6.07 Hz (Doublet)

J = 1483.78 – 1477.71 =6.07 Hz 1477.71 – 1471.66 =6.05 Hz

J = 1471.66 – 1465.69 =5.97 Hz (Quartet)

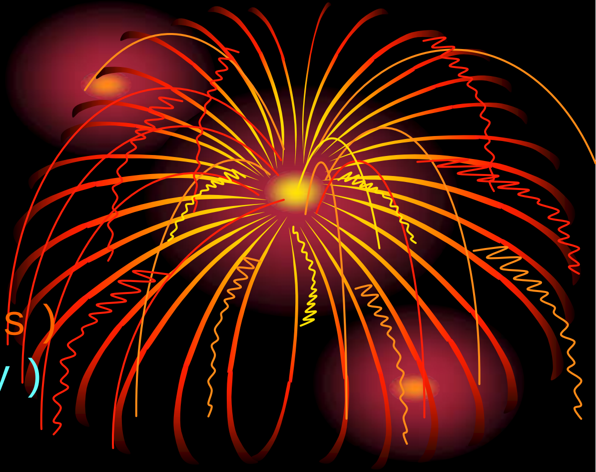


Analysis and Interpretation of ^{1}H NMR of 1,1-Dichloroethane

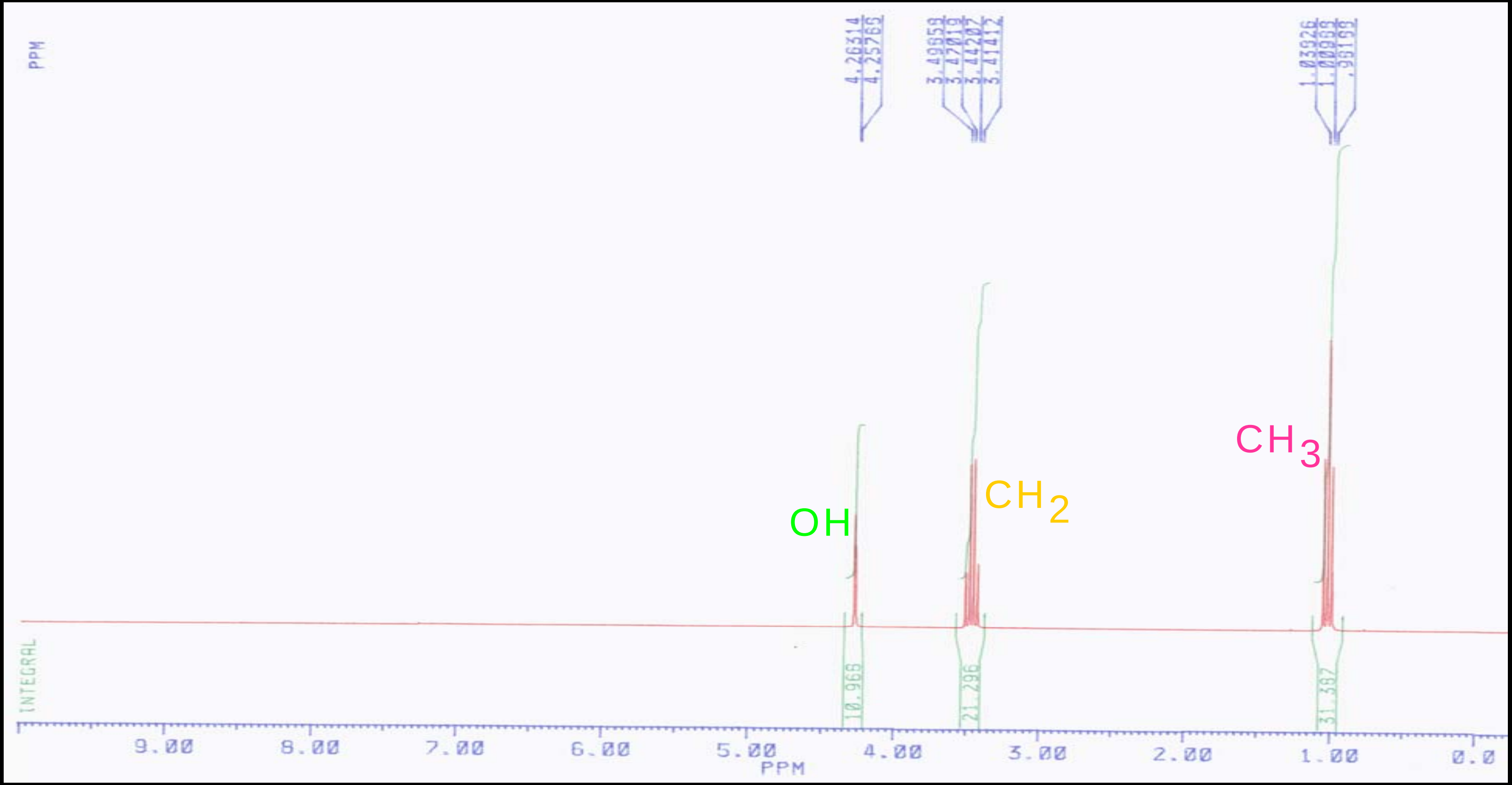


Group No.	NMR Signal	Chemical Shift in PPM	Integration	Related Structure	Coupling Constant J = Hz	Neighbouring Groups
1	Doublet	2 . 05	21.45 3	CH_3	6.07 Hz	CH
2	Quartet	5 . 89	6.95 1	CH	6.07 Hz	CH_3
	Intensity 1 : 1 Doublet 1 : 3 : 3 : 1 Quartet		6 .95 = 7 7 = 1 H		As the J Values are Equal hence neighbours	Cl_2 give No NMR Signal in ^{1}H NMR

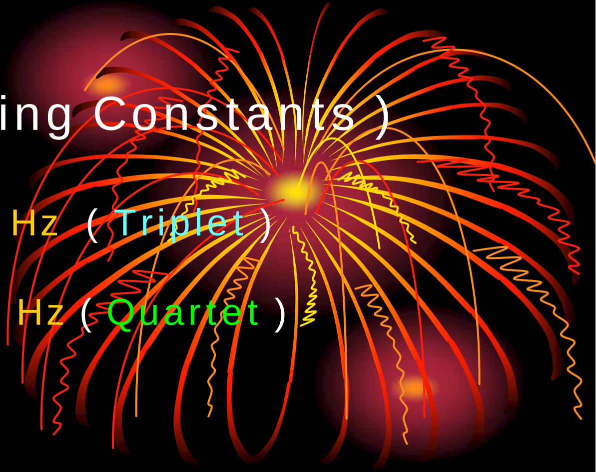
^1H NMR of Ethanol in $CDCl_3$



	1	2	3	
	CH_3	CH_2	OH	
PPM	1.01	3.46	4.26	(Chemical Shits)
Integration	30	20	10	(Approximately)
No. of H	3	2	1	

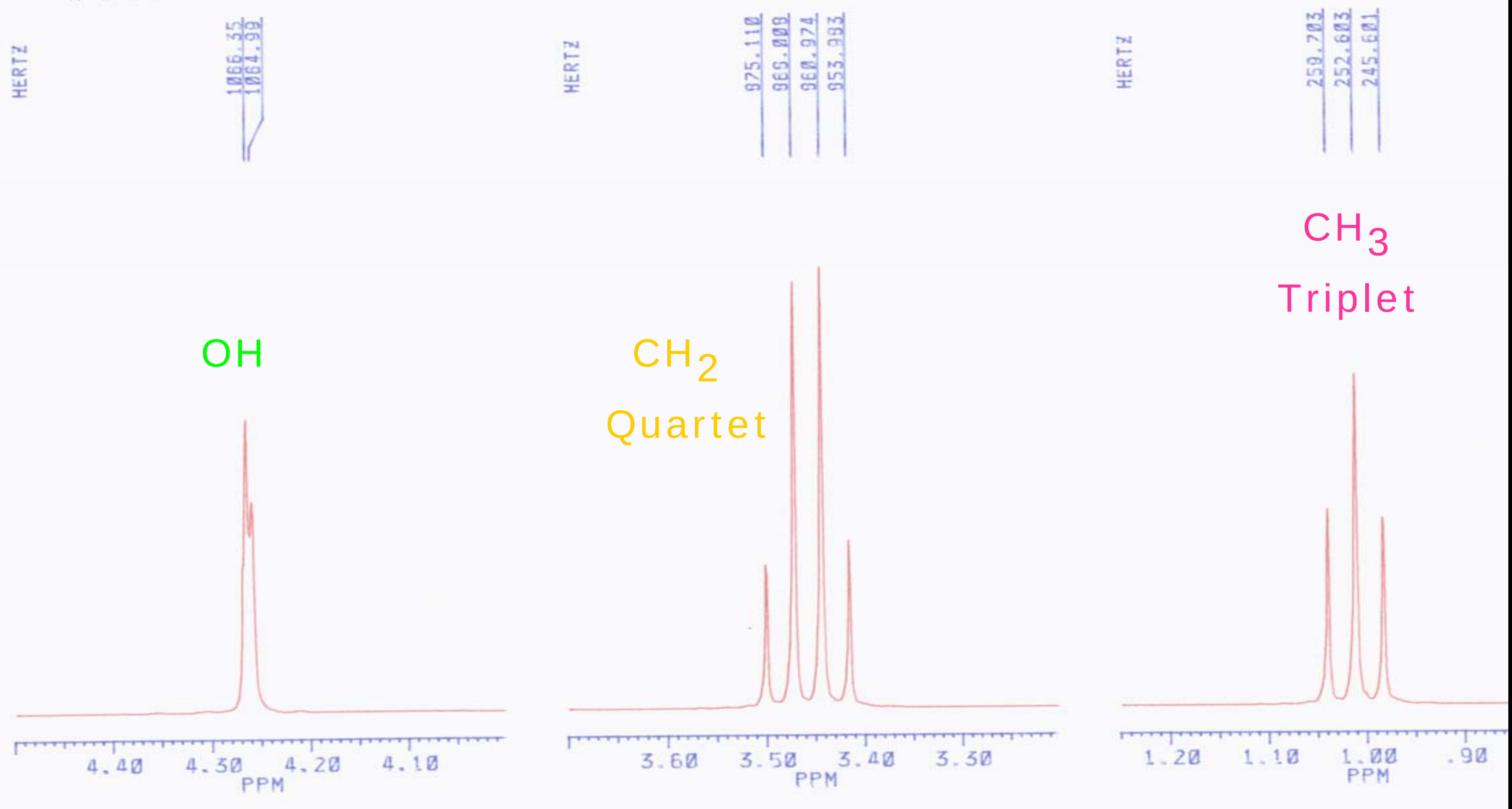


Expansion of ^{1}H NMR of Ethanol (Coupling Constants)



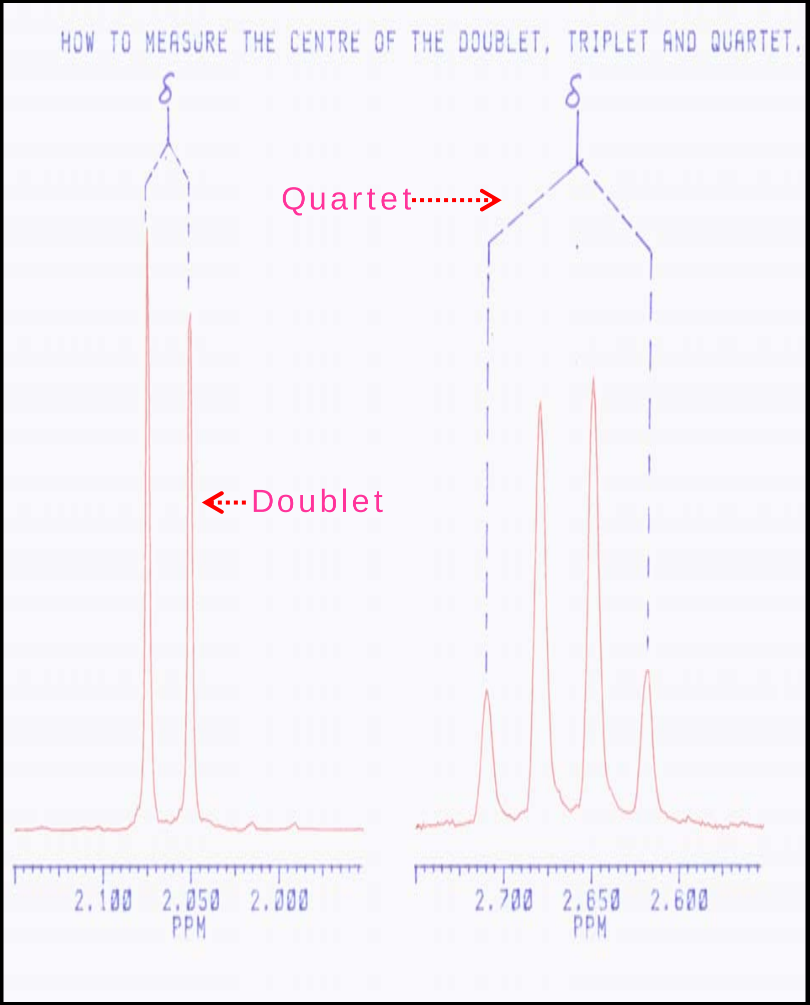
J = 259.70 – 252.60 = 7.10 HZ 252.60 – 245.60 = 7.00 Hz (Triplet)

J = 875.11 – 868.01 = 7.10 Hz 868.01 – 860.97 = 7.04 Hz (Quartet)



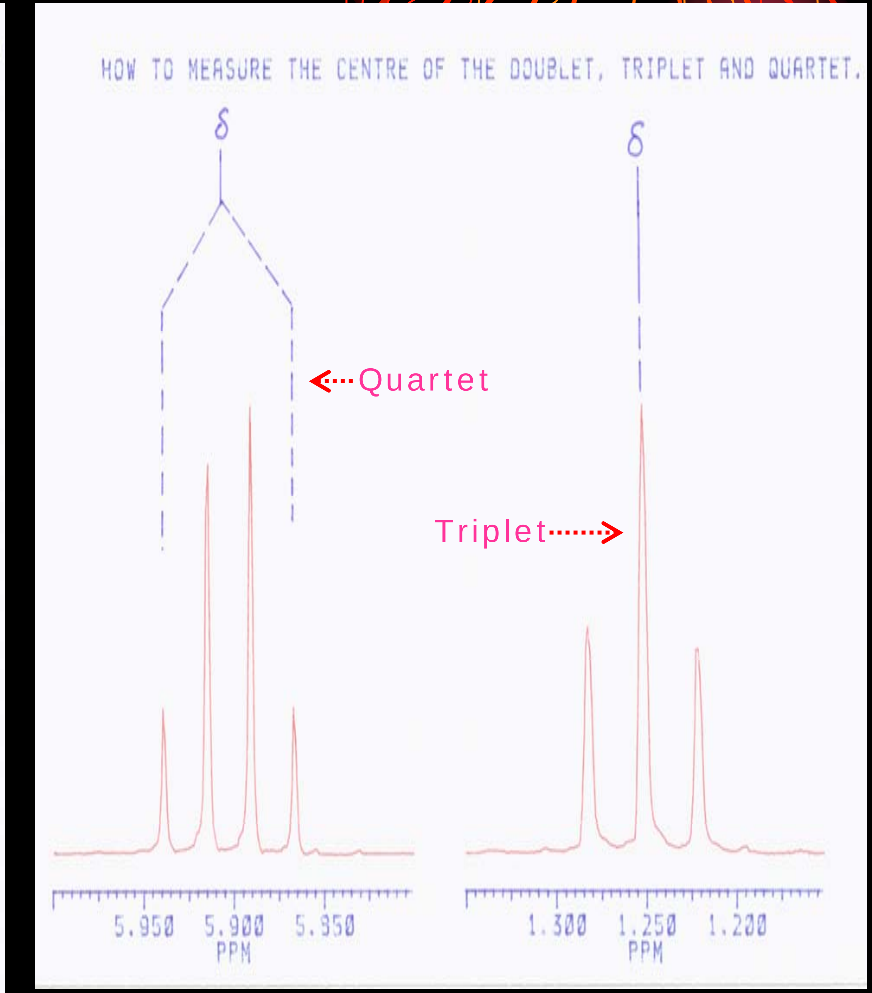
How to calculate the Chemical shifts of Doublet, Triplet and Quartet

Chemical shift = Centre of the multiplet (Doublet, Triplet , Quartet Etc.)



Quartet

Doublet

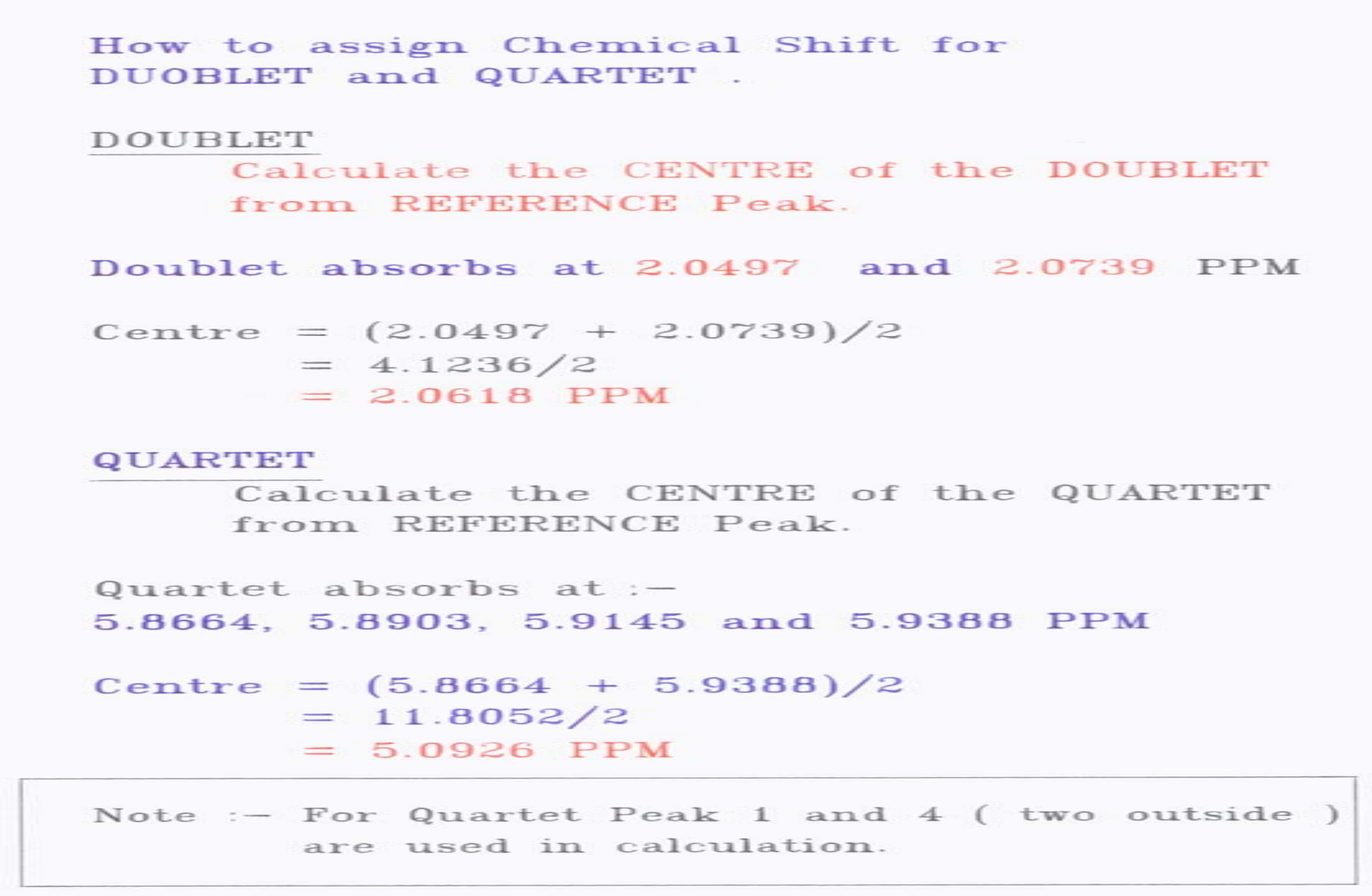


Quartet

Triplet

Chemical shifts Calculation.

For Triplet it is easy to assign the chemical shift. The position of the middle peak is the chemical shift for Triplet.



How to assign Chemical Shift for DUOBLET and QUARTET .

DOUBLET

Calculate the CENTRE of the DOUBLET from REFERENCE Peak.

Doublet absorbs at 2.0497 and 2.0739 PPM

Centre = (2.0497 + 2.0739)/2
= 4.1236/2
= 2.0618 PPM

QUARTET

Calculate the CENTRE of the QUARTET from REFERENCE Peak.

Quartet absorbs at :–
5.8664, 5.8903, 5.9145 and 5.9388 PPM

Centre = (5.8664 + 5.9388)/2
= 11.8052/2
= 5.0926 PPM

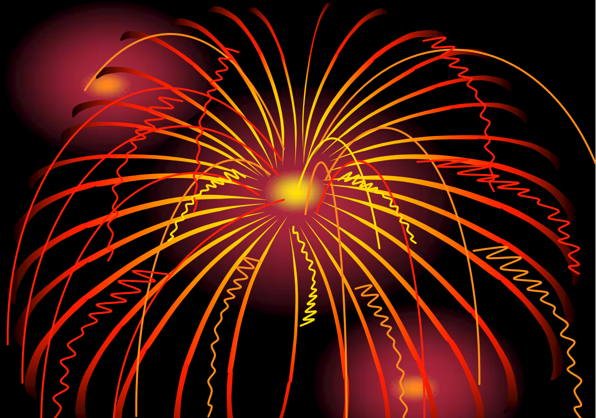
Note :– For Quartet Peak 1 and 4 (two outside) are used in calculation.

Analysis and Interpretation of ^{1}H NMR of Butan-2-one

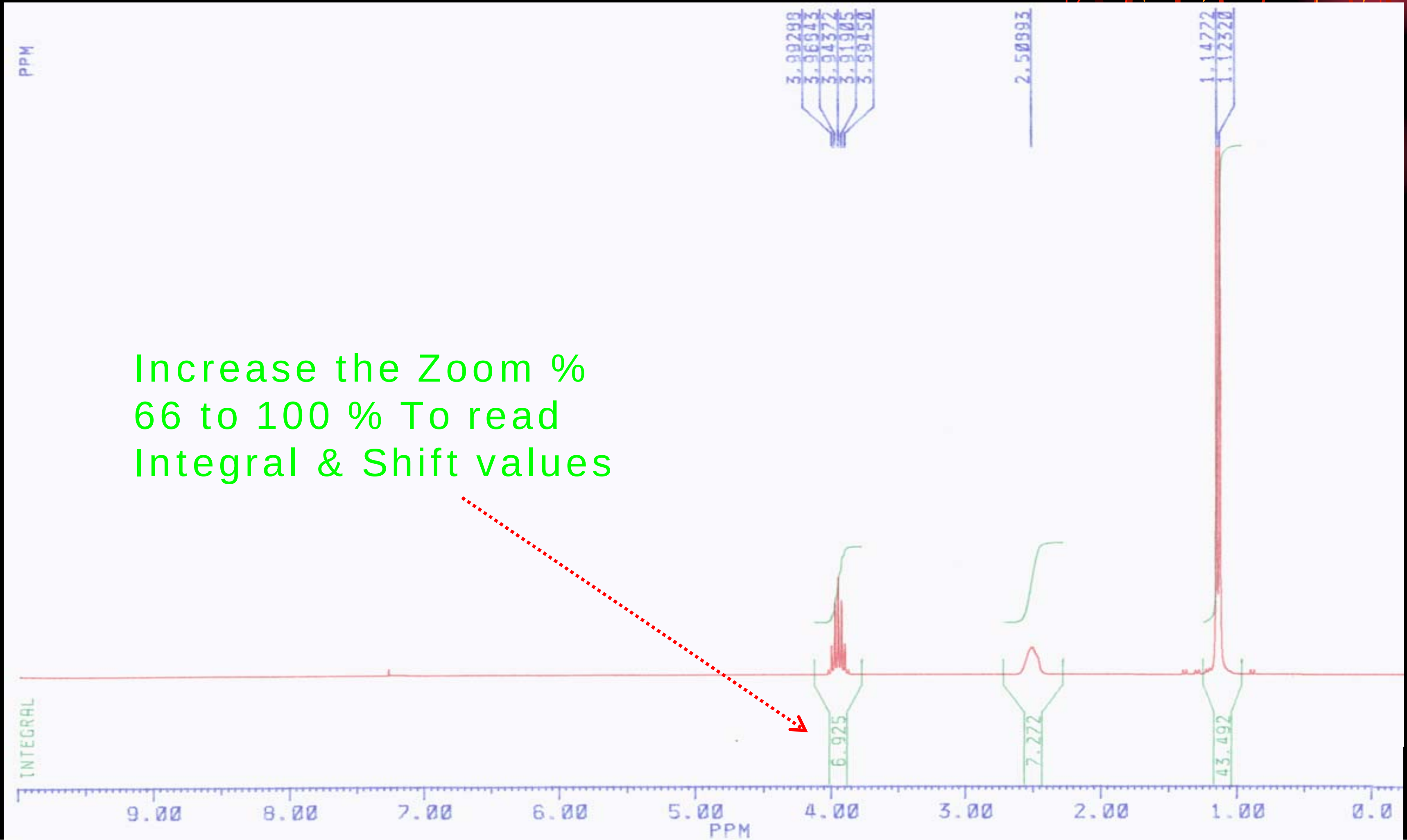
$\overset{1}{CH_3}\ \overset{2}{CO}\ \overset{3}{CH_2}\ \overset{4}{CH_3}$

Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J =	Neighbouring Groups
1	Singlet	2 . 05	21.28 3	CH_3	None	CO
2	No signal	N/A	N/A	CO	N/A	N/A
3	Quartet	2 . 37	14.54 2	CH_2	7.32 Hz	CH_3
4	Triplet	0 . 96	21.34 3	CH_3	7.32 Hz	CH_2
5			Divide by 7 7 = 1 H		As J=7.32 Hz for gr. 3 & 4 hence neighbours	

^1H NMR of Propan-2-ol in $CDCl_3$



	1	2	3	4
	CH_3—	CH	OH--	CH_3
PPM	1.13	3.94	2.51	1.13
Integration	21	7.0	7.0	21
No. of H	3	1	1	3



Increase the Zoom %
66 to 100 % To read
Integral & Shift values

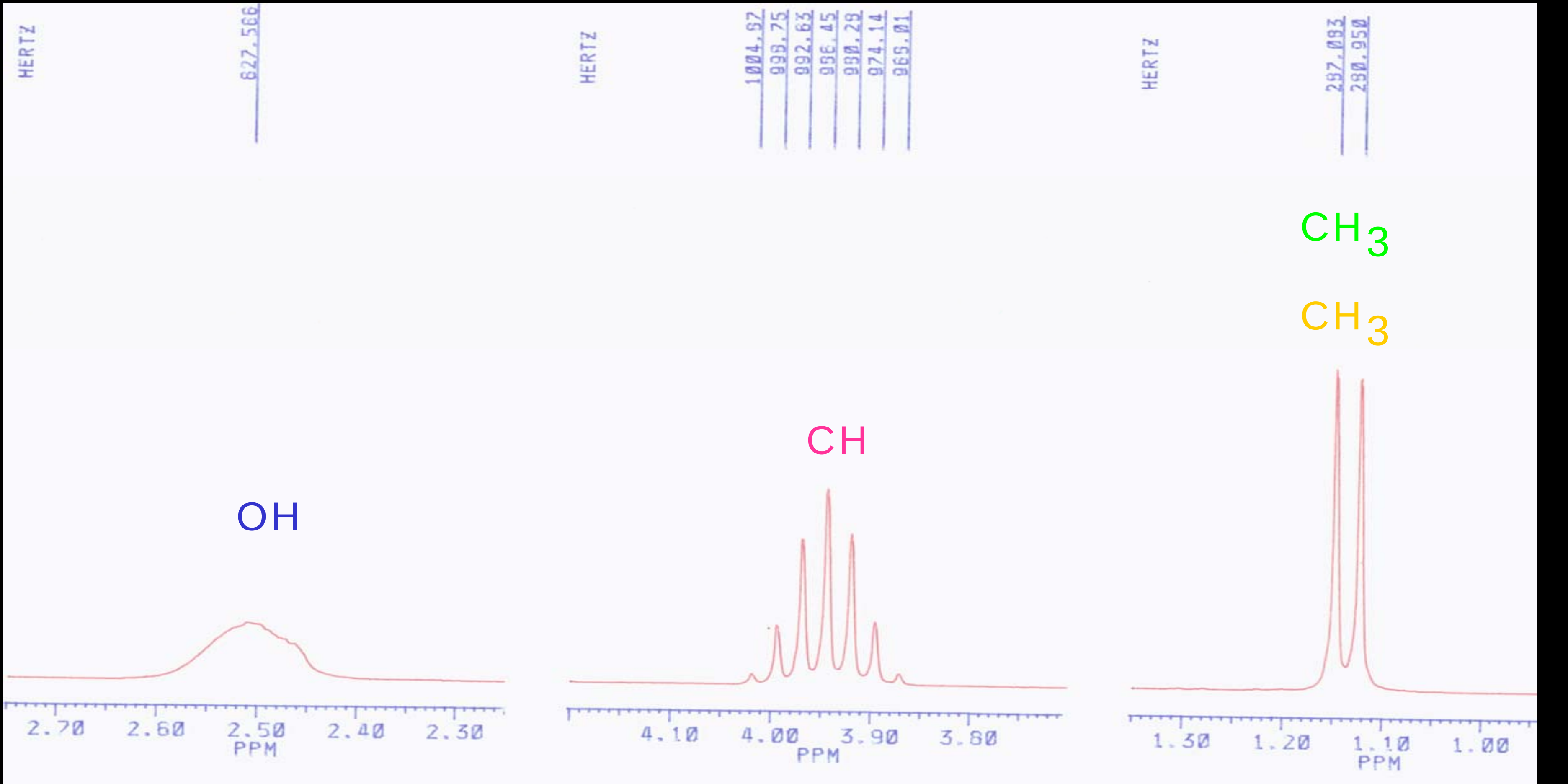
Expansion of ^{1}H NMR of Propan-2-ol CH_3-CHOH-CH_3

J = 287.083 – 280.950 = 6.133 Hz (Doublet)

J = 1004.87 – 998.75 = 6.12 Hz 992.63 – 986.45 = 6.18 Hz (Septet)

980.28 - 974.14 = 6.14 Hz 997.14 – 968.01 = 6.13 Hz (,,)

Both CH_3 & CH_3 are chemically and magnetically equivalents



Analysis and Interpretation of ^{1}H NMR of Propan-2-ol

1 2 3 4

CH_3-CHOH-CH_3

Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J =	Neighbouring Groups
1	Doublet	1.13	43.49 6	CH_3 & CH_3	6.13 Hz	CH
2	Septet	3.94	6.93 1	CH	6.13Hz	CH_3 & CH_3
3	Broad Singlet	2.51	7.22 1	OH	N/A	CH
4						
5			Divide by 7 7 = 1 H	Both CH3 groups are identical	As J=6.13 Hz for gr. 1 & 2 2 & 4 hence neighbours	

^{1}H NMR of Methyl Benzene (Toluene) In $CDCl_3$

1 2

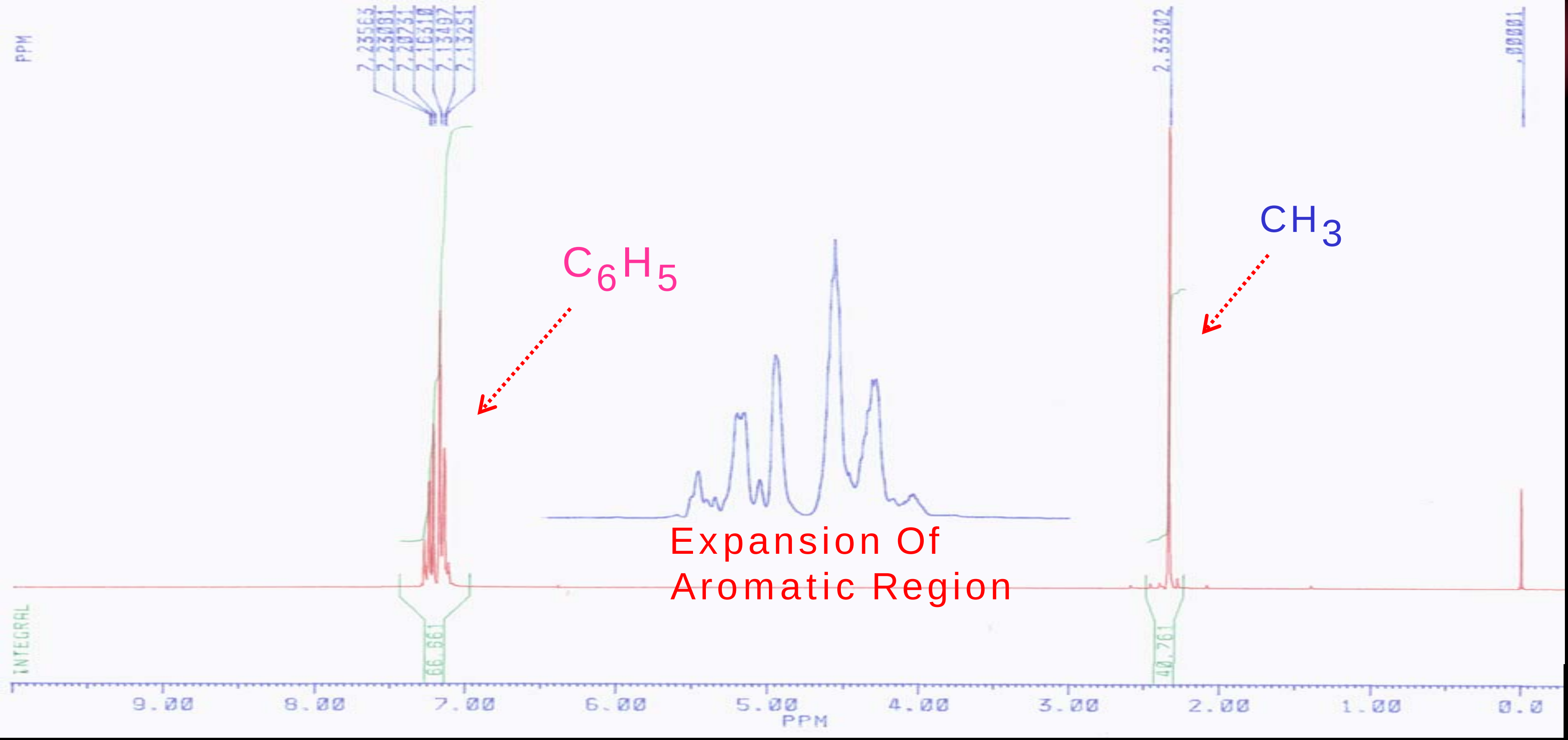
C_6H_5--CH_3

Aromatic NMR signal is complex at this stage treat as a one signal

PPM 7.16 2.33

Integration 66.66 : 40.76 = 1.63 :1.00 = 3 x (1.63 : 1.00) = 5 : 3

No. of H 5 3



C_6H_5

CH_3

Expansion Of Aromatic Region

^{1}H NMR of Ethyl Benzene in $CDCl_3$

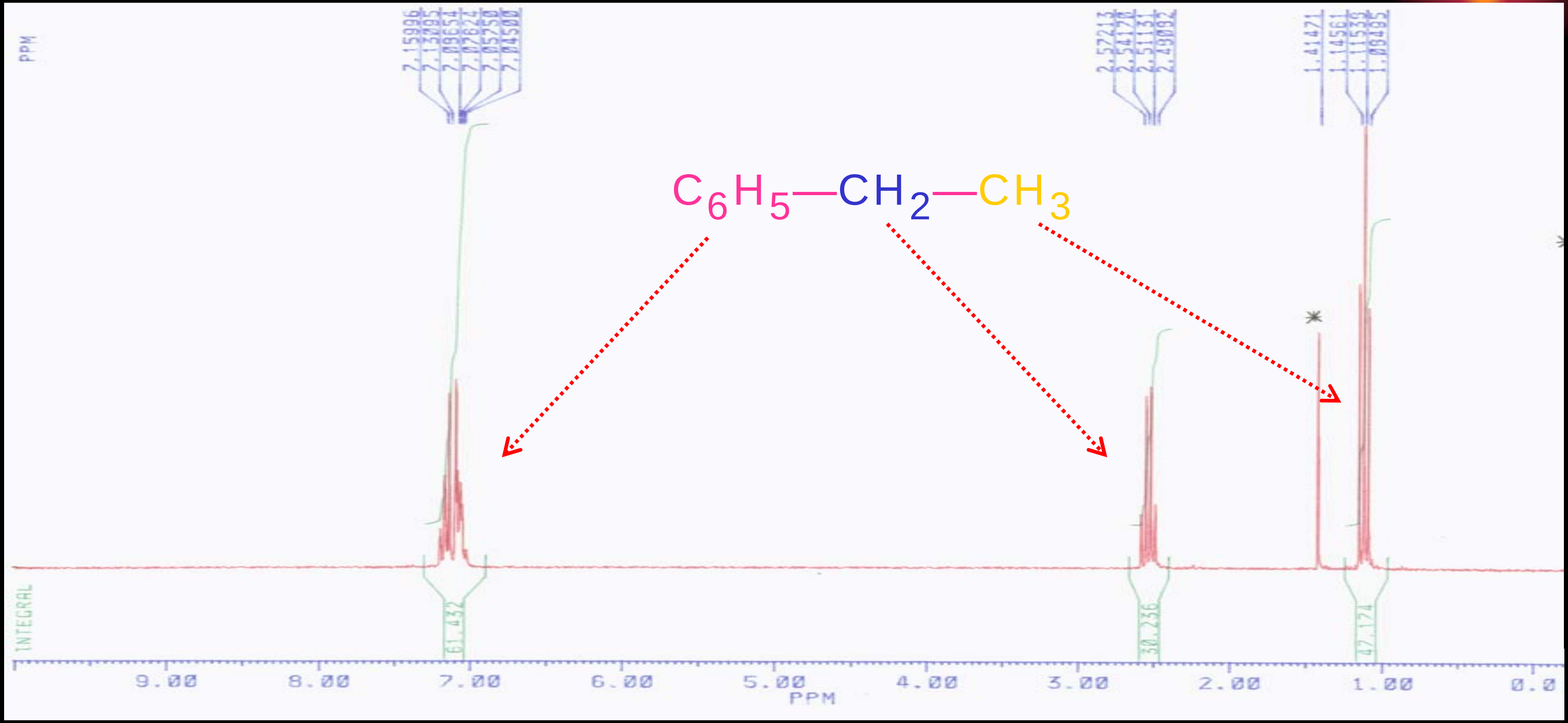
$$\overset{1}{C_6H_5}—\overset{2}{CH_2}—\overset{3}{CH_3}$$

PPM 7.08 2.53 1.12

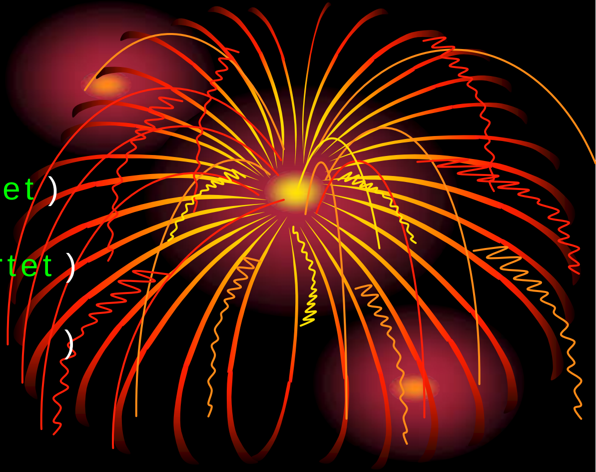
Integration 2.03 : 1.00 : 1.56 = 4.06 : 2.00 : 3.12 = 4 : 2 : 3 **

No. of H 5 2 3

** Integration for aromatic is slightly out due relaxation process. Before the next acquisition, the delay should be enough to allow the molecule to return to ground state otherwise Integration will be incorrect.



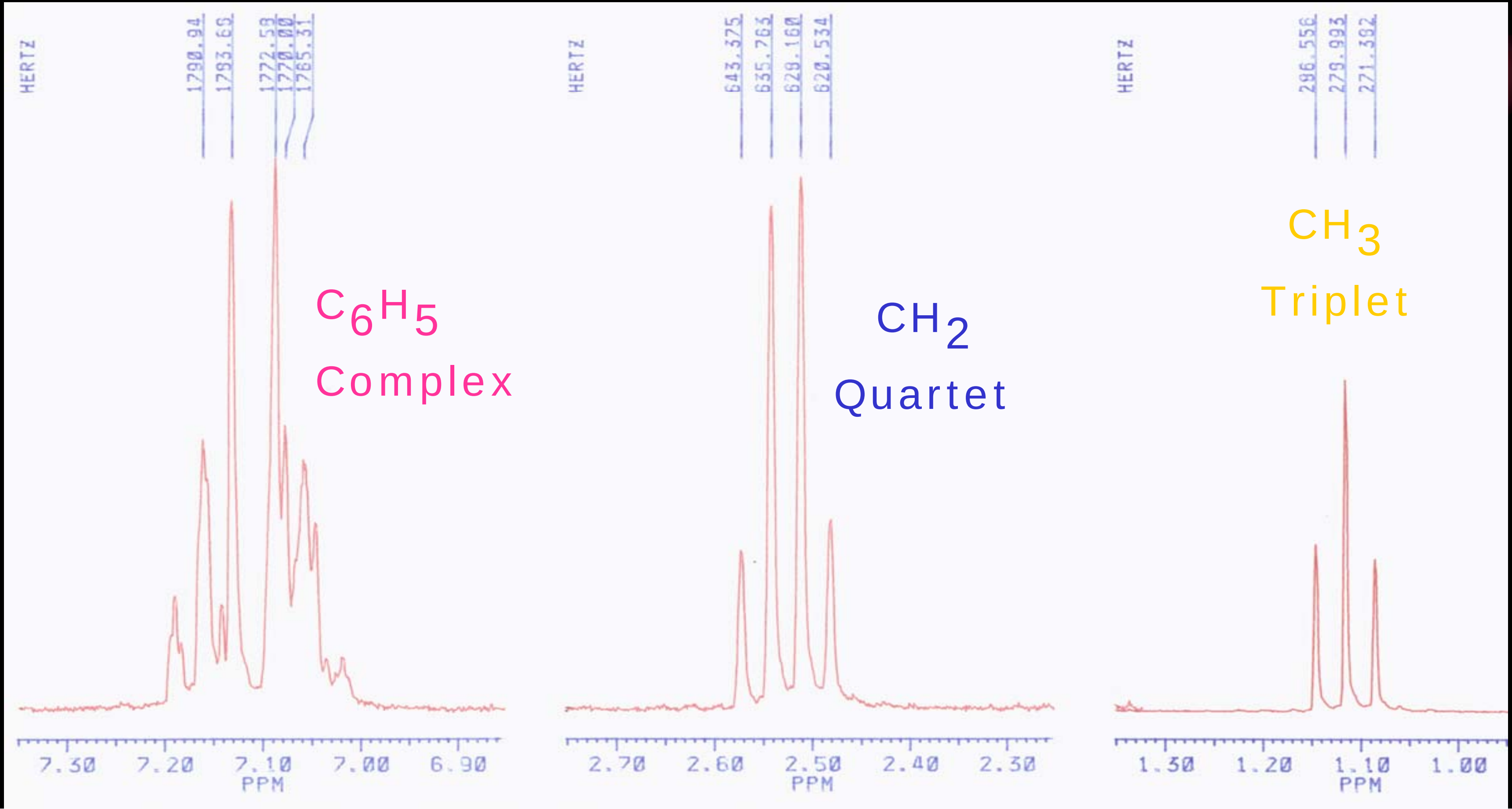
Expansion of ^{1}H NMR of Ethyl Benzene



J = 286.556 – 278.993 =7.56 Hz 278.993 – 271.382 =7.61 Hz (Triplet)

J = 643.375 – 635.763 = 7.59 Hz 635.763 – 628.160 = 7.60 Hz (Quartet)

J = 628.160 – 620.534 = 7.63 Hz (,,)



Analysis and Interpretation of ^{1}H NMR of Ethyl Benzene

1 2 3

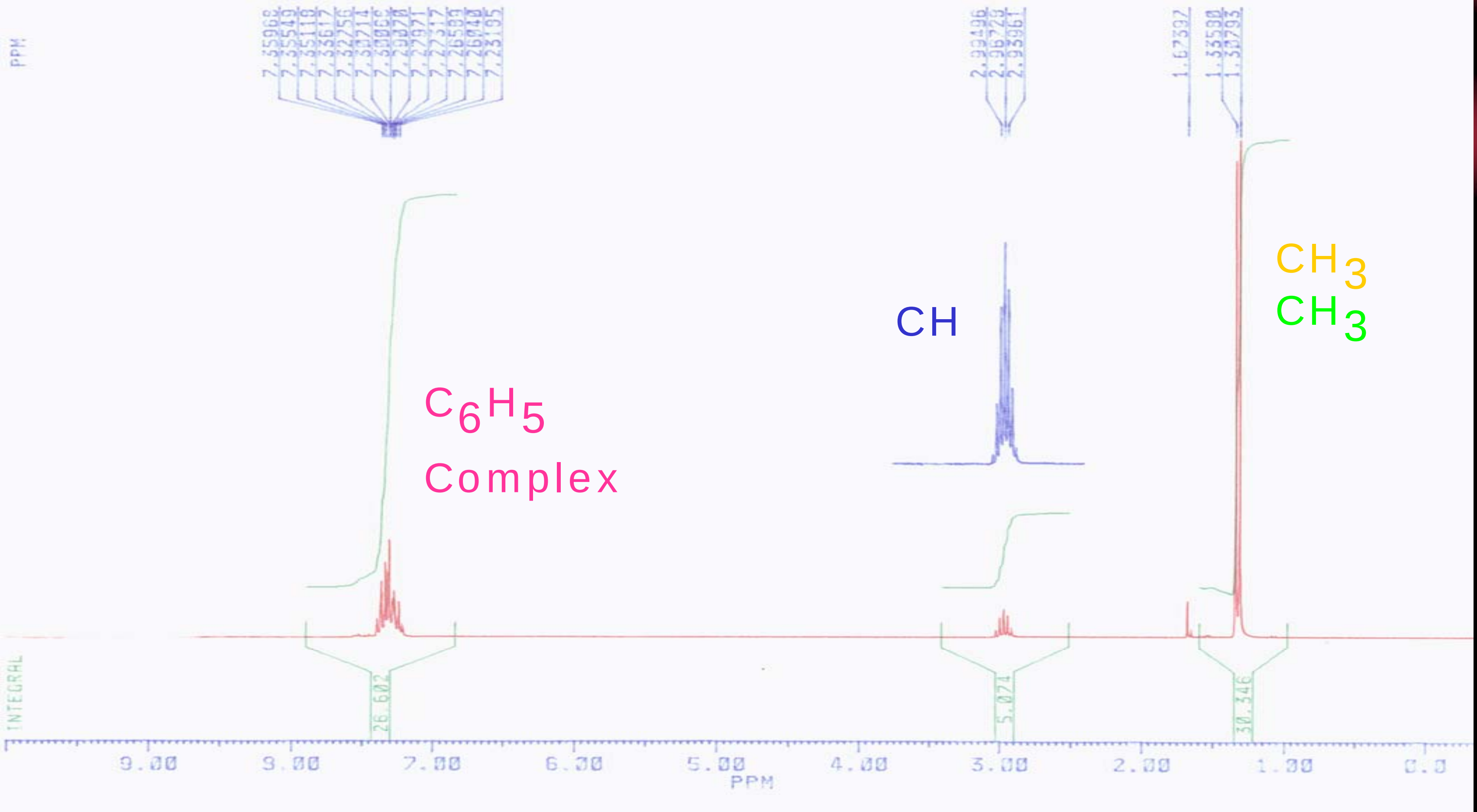
$C_6H_5—CH_2—CH_3$

Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J = Hz	Neighbouring Groups
1	Complex	7.08	5 **(4.06)	C_6H_5	N/A	CH_2
2	QUARTET	2.53	2	CH_2	7.61 Hz	*C_6H_5 & CH_3
3	Triplet	1.12	3	CH_3	7.61 Hz	CH_2
4						
5			Divide by 15 15 = 1 H **Slightly out		As J=7.61 Hz for gr. 2 & 3 hence neighbours	* No Aromatic • Interactions • (Coupling)

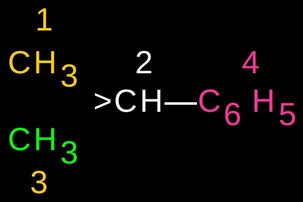
^{1}H NMR of Isopropyl Benzene in $CDCl_3$

1
CH_3 2 4
>CH—C_6 H_5
CH_3
3

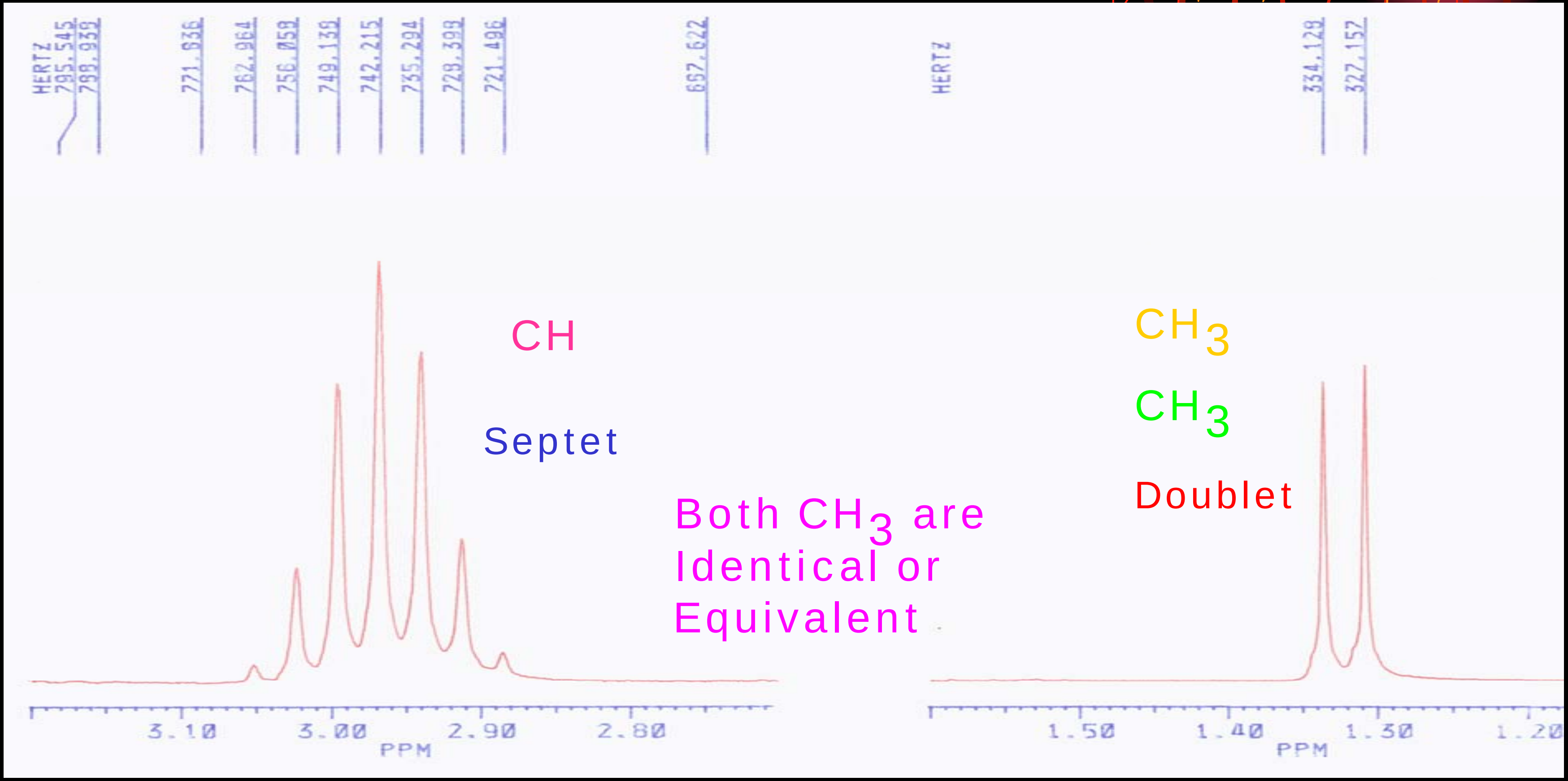
Group	PPM	Integral	J = Hz
CH3 & CH3	1.32	6	= 6.97
CH	2.97	1	= 6.97
C6 H5	7.29	5	= N/A



Expansion of ^{1}H NMR of Isopropyl Benzene



$$\begin{matrix} \overset{1}{CH_3} \\ \underset{3}{CH_3} \end{matrix} \!\! > \overset{2}{CH} - \overset{4}{C_6H_5}$$



CH

Septet

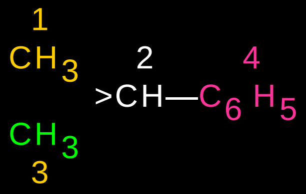
Both CH_3 are Identical or Equivalent

CH_3

CH_3

Doublet

^1H NMR of Isopropyl Benzene in $CDCl_3$



$$\begin{matrix}\overset{1}{CH_3} \\ \underset{3}{CH_3}\end{matrix} > \overset{2}{CH}-\overset{4}{C_6H_5}$$

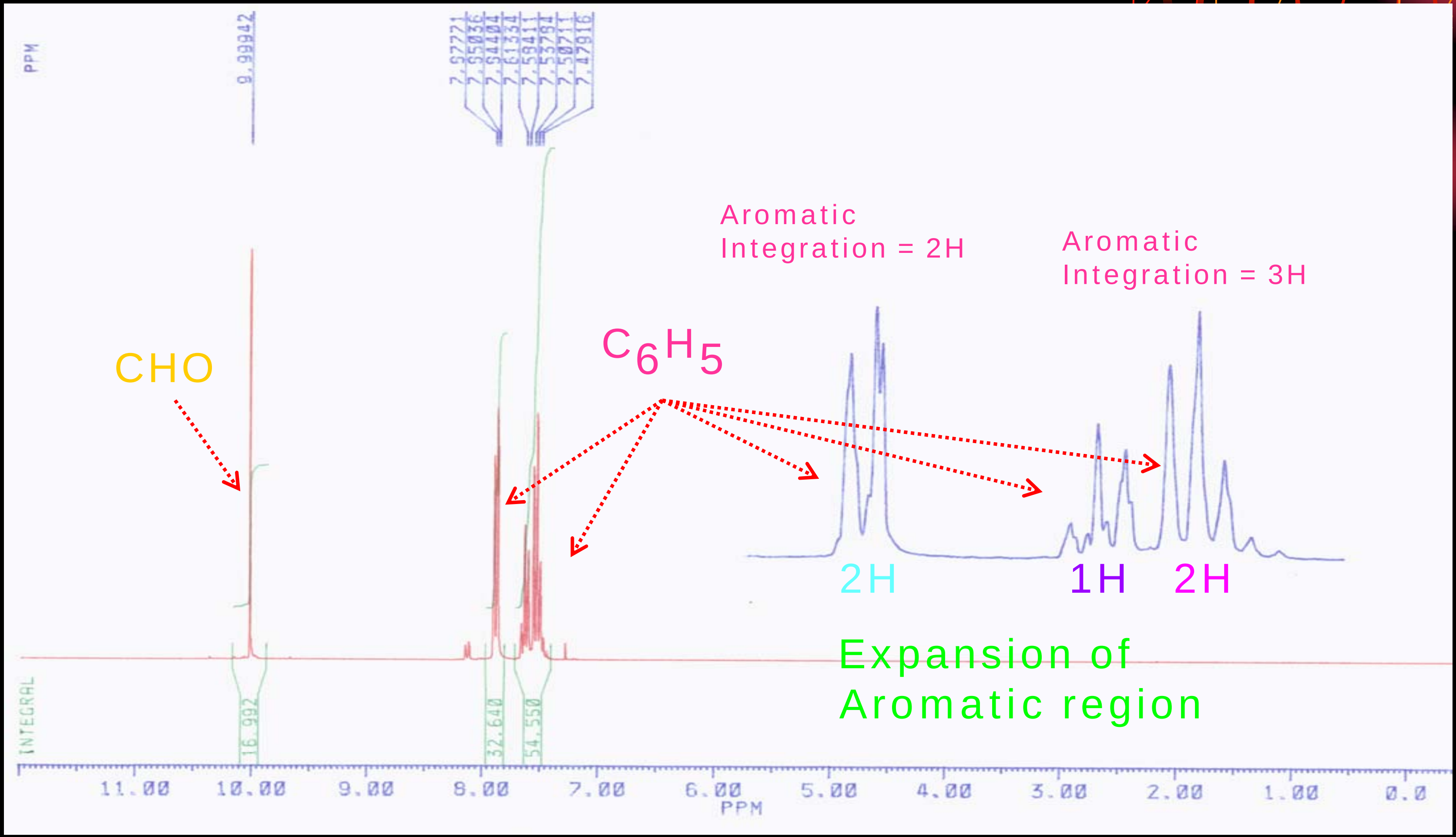
Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J = Hz	Neighbouring Groups
1	Doublet	1.32	6	CH_3 & CH_3	6.97 Hz	CH
2	Septet	2.97	1	CH	6.97 Hz	CH_3 & CH_3 * C_6H_5
3						
4	Complex	7.29	5	C_6H_5	N/A	CH
5			Divide by 5 5 = 1 H		As J=6.97 Hz for gr. 1 & 2 hence neighbours	* C_6H_5 No Coupling

^{1}H NMR of Benzaldehyde In $CDCl_3$

1 2

$C_6 H_5$—CHO

Group	PPM	Integral	J = Hz
C6 H5	7.60	5	N/A
CHO	10.00	1	N/A



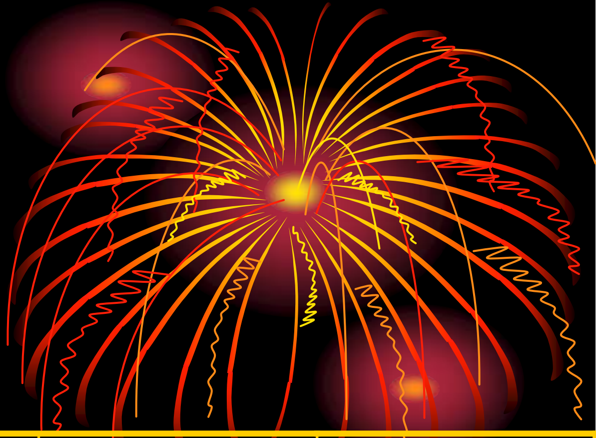
Aromatic Integration = 2H

Aromatic Integration = 3H

Expansion of Aromatic region

^{1}H NMR of Benzaldehyde In $CDCl_3$

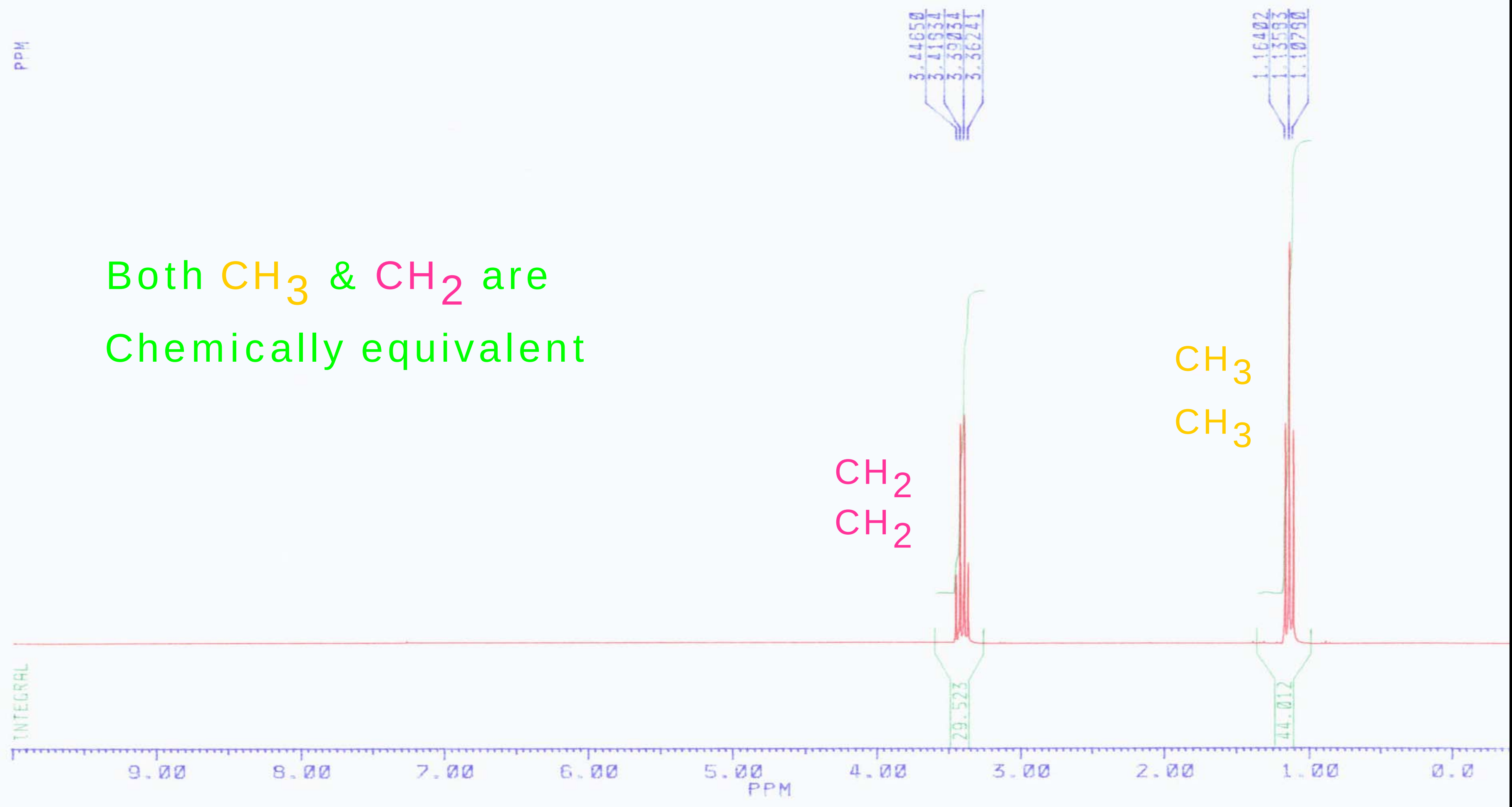
$\overset{1}{C_6H_5}\text{—}\overset{2}{CHO}$



Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J = Hz	Neighbouring Groups
1	Complex **	7.60	5	C_6H_5	N/A	CHO
2	Singlet	10.00	1	CH	N/A	N/A
3						
4						
5	**Resolve Into Aromatic 2H,1H & 2H due to CHO Group	Singlet at 10.00 PPM due deshielding Effect on H	Divide by 16 16 = 1 H			

^{1}H NMR of Diethyl Ether in CDCl3

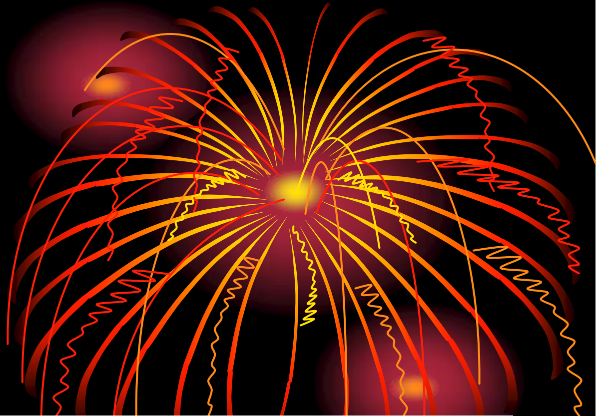
$CH_3—CH_2—O—CH_2—CH_3$



Both CH_3 & CH_2 are Chemically equivalent

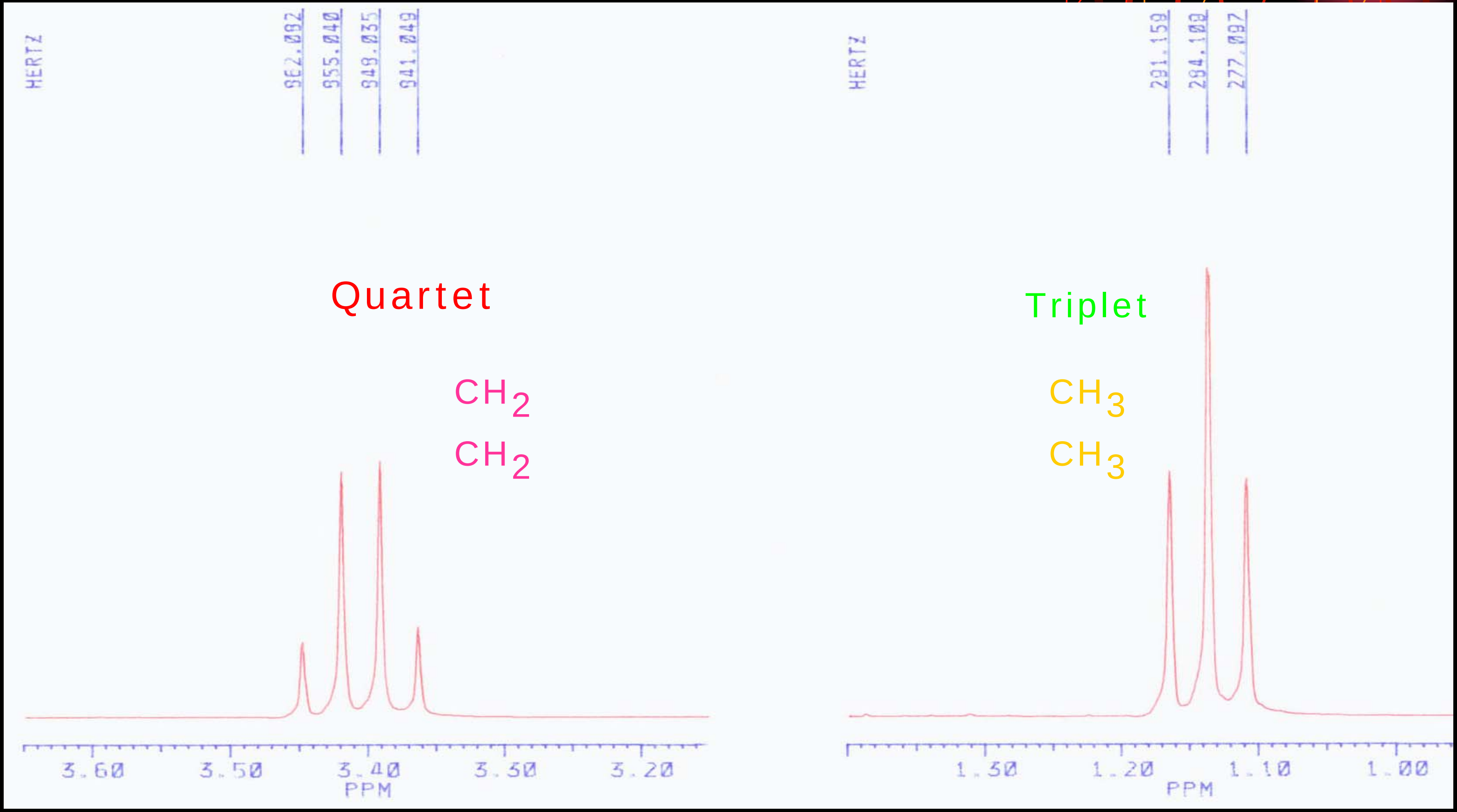
CH_2
CH_2

CH_3
CH_3



Expansion of ^{1}H NMR of Diethyl Ether

$CH_3—CH_2—O—CH_2—CH_3$



Quartet

CH_2

CH_2

Triplet

CH_3

CH_3

Analysis and Interpretation of ^{1}H NMR of Diethyl Ether

$CH_3—CH_2—O—CH_2—CH_3$

Both CH_3 and CH_2 groups are identical hence only one set of signals are observed.

Group No	Signal Structure	Chemical Shift PPM	Relative Area Integration	Possible Group Structure	Coupling Constant J = Hz	Neighbouring Groups
1	Triplet	1.14	1.50 x 4 = 6.00	CH_3	7.01 Hz	CH_2
2	Quartet	3.40	1.00 x 4 = 4.00	CH_2	7.01 Hz	CH_3
3						
4						
5			Divide by 30 30 = 4 H		As J=7.01 Hz for gr. 1 & 2 hence neighbours	