Citrus College

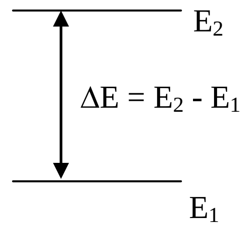
<u>**Spectroscopy**</u> ***Prof. Badieh Farahani***

Absorption of energy by a molecule & the subsequent response.

<u>**IR:**</u> Two different vibrational state.

<u>**NMR:**</u> Two different spin state of atomic nucleus.

<u>**UV – Visible:**</u> Two different electronic energy state.



<u>**IR:**</u> Functional Group.

<u>**NMR:**</u> Molecular Structure; C-H Map.

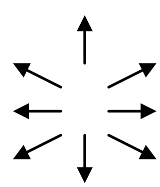
<u>**UV – Visible:**</u> Π System.

<u>**Nuclear Magnetic Resonance:**</u> ^{1}H – NMR (Proton NMR), ^{13}C – NMR (C – NMR)

^{1}H – NMR: Transition between nuclear spin states.

Proton (spinning positive charge) ⟶ spin (2 spin states) ↗ - 1/2 ; ↘ + 1/2] same Energy (E)

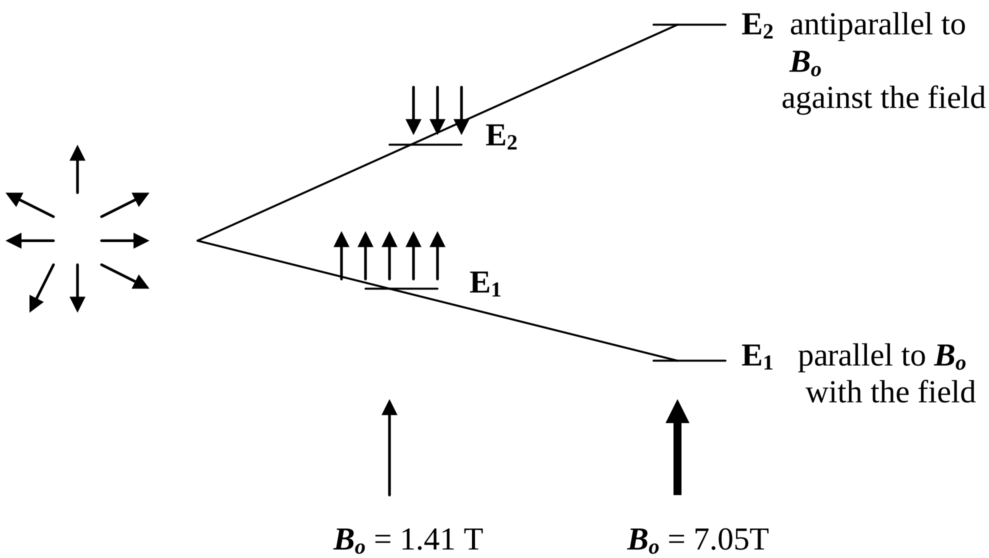
Proton ⟶ produce magnetic moment; ***I***



randomly distributed

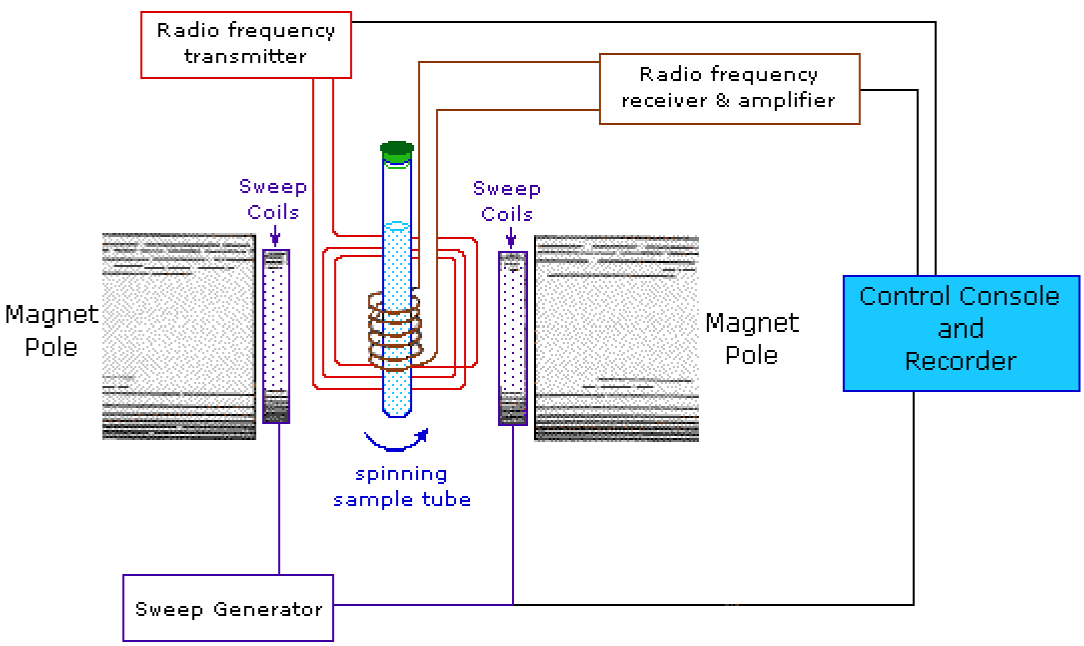
In the presence of a strong external magnetic field (***B_o***), some nuclei align themselves:

With the field – parallel (lower E)   against the field – antiparallel (higher E)

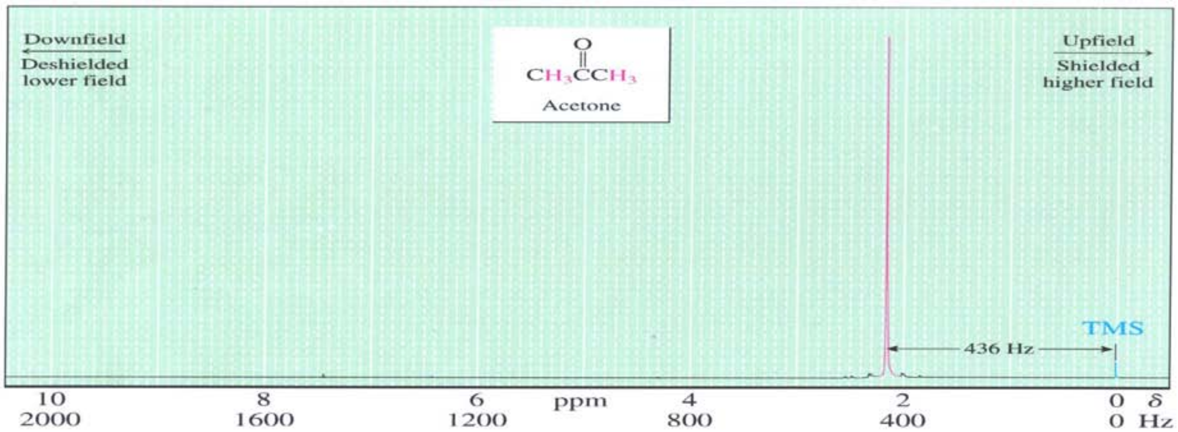


@ $\boldsymbol{B_o}$ = 1.41T → $\Delta E = 5.72 \times 10^{-6}$ kcal/mol = $h\nu$ → ν = 60 MHz (radio frequency)

This ΔE is absorbed & nuclei undergo spin flip from $\mathbf{E_1}$ to $\mathbf{E_2}$ (resonance)



FT - NMR



The 1H-NMR spectrum of acetone @ 200 MHz

Nuclear Shielding:

Bare proton (deshielded) → ν = 60 MHz → resonance @ 1.41T

e^-s of the bond shield the nucleus → proton (shielded) → resonance at > 1.41T

Chemical Shift (δ): A change in resonance position of a nucleus which is the result of its molecular environment.

How is chemical shift (δ) measured? Pick a standard → $(CH_3)_3Si$ – **TMS** (protons are most shielded**). TMS** is assigned δ = 0 & peaks position are measured in Hz downfield from **TMS**.

$$\delta = \frac{436}{200 \times 10^6 Hz} \times 10^6 = 2.18 \text{ (ppm)} \quad \text{for acetone}$$

This peak occurs @ 2.18 δ on any other instrument regardless of operating frequency.

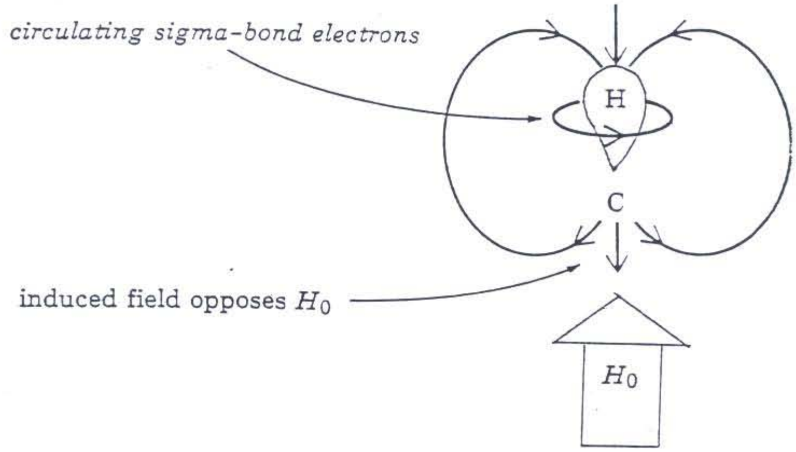
Inductive Effect: Electronegativity

	CH_3**F**	CH_3Cl	CH_3**Br**	CH_3**I**
δ	4.3	3.1	2.7	2.2

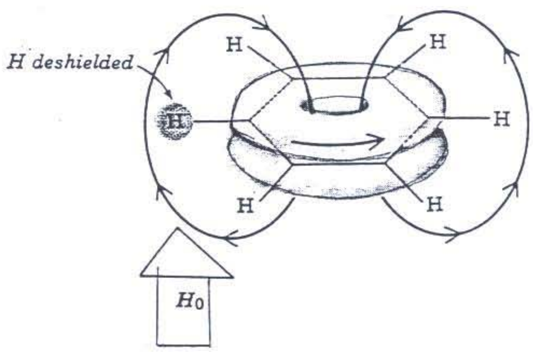
	CH_3F	CH_3**O**CH_3	$(CH_3)_3$**N**	CH_3CH_3
δ	4.3	3.2	2.2	0.9

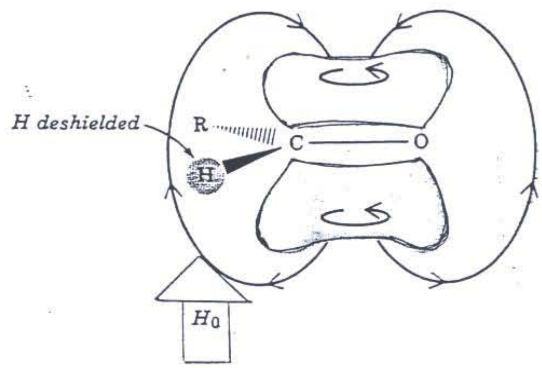
<u>Pi Electron Effect:</u>

Induced field of circulating σ bond electrons opposes H_o

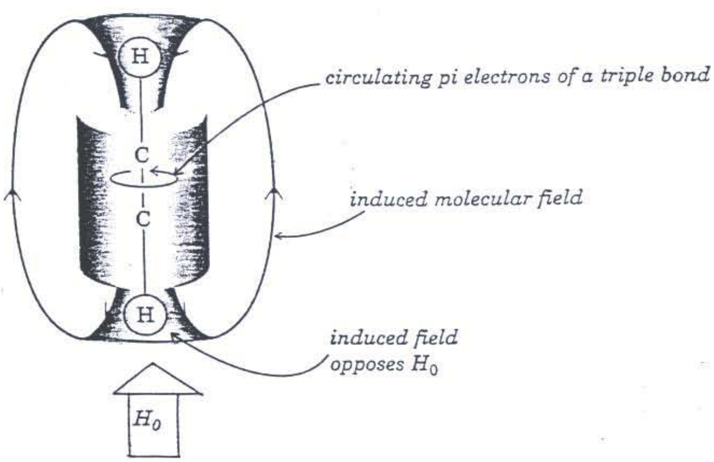


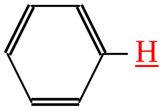
Circulating Π electrons in benzene & aldehydes

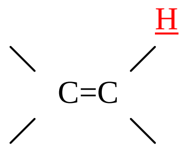




Shielded alkyne proton

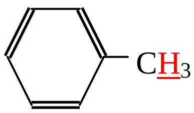


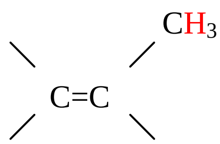




CH_3CH_3

7.3 δ 5.3 δ 0.9 δ





CH_3CH_3

2.2 δ 1.7 δ 0.9 δ

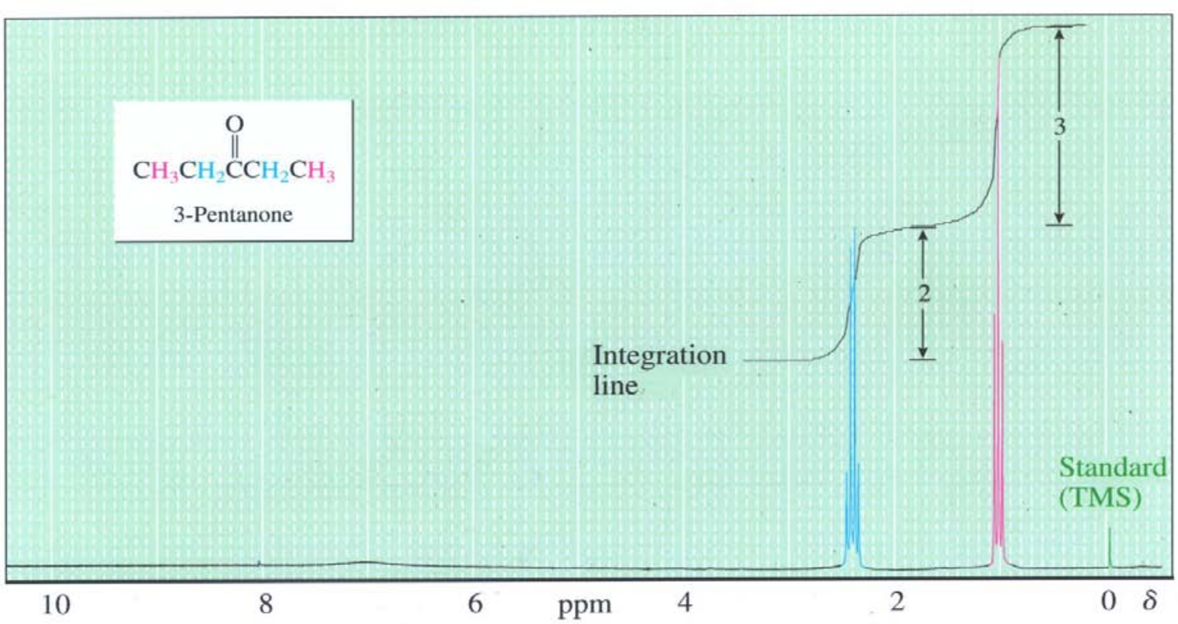
Interpreting Proton NMR Spectrum

* Location of signals

* Number of signals

* Intensity of signals as measured by the area under each peak

* Multiplicity (splitting of each signal)



<u>Multiplicity, Spin-Spin Splitting in NMR:</u> The number of peaks into which the signal a particular proton is split (due to the presence of neighboring protons) is called ***Multiplicity***.

Multiplicity of a signal = n+1 n = # of neighboring protons

H_a
|
-C-C-
|
H_b

H_b ↑ helps $\boldsymbol{H_o}$ → resonance @ lower $\boldsymbol{H_o}$

↓ against $\boldsymbol{H_o}$ → resonance @ higher $\boldsymbol{H_o}$

→ **Doublet**
Intensities 1:1

| ← the signal for $\mathbf{H_a}$ will break into

| | ← 2 signals

↑ H_o

H_a
|
H_b-C-C-
|
H_b

H_b

↑↓

↑↑ ↓↑ ↓↓

→ **Triplet**

Intensities 1:2:1

↑ H_o

H_b

↑↑↓ ↓↓↑

↑↓↑ ↓↑↓

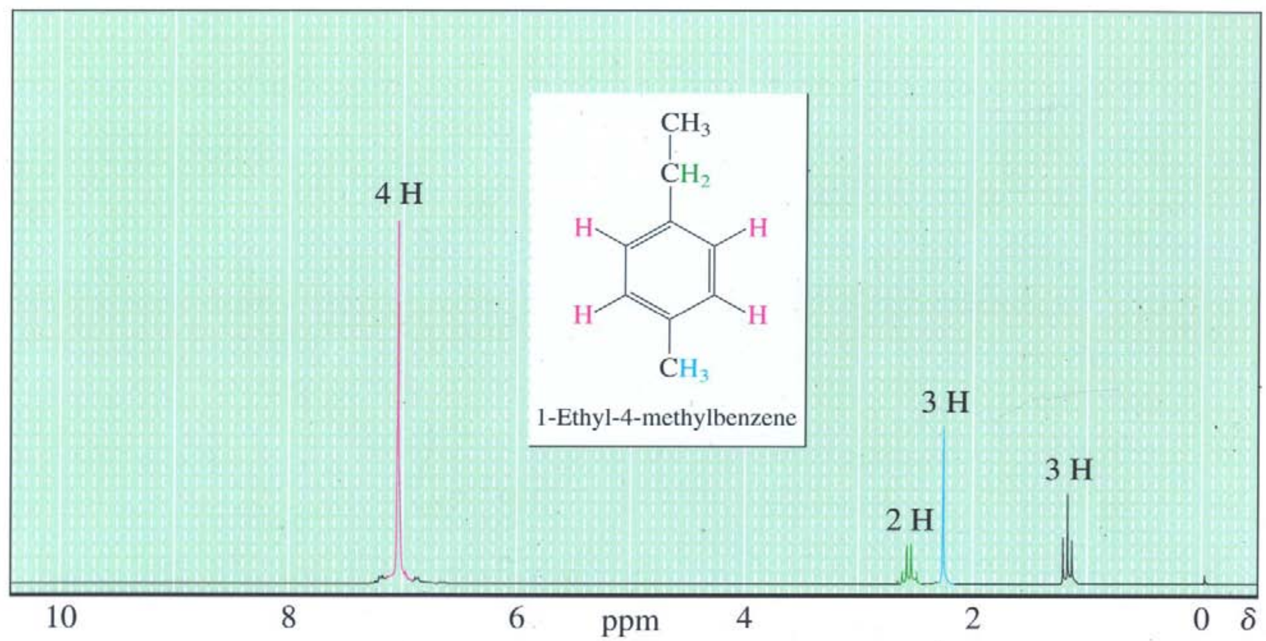
↑↑↑ ↓↑↑ ↑↓↓ ↓↓↓

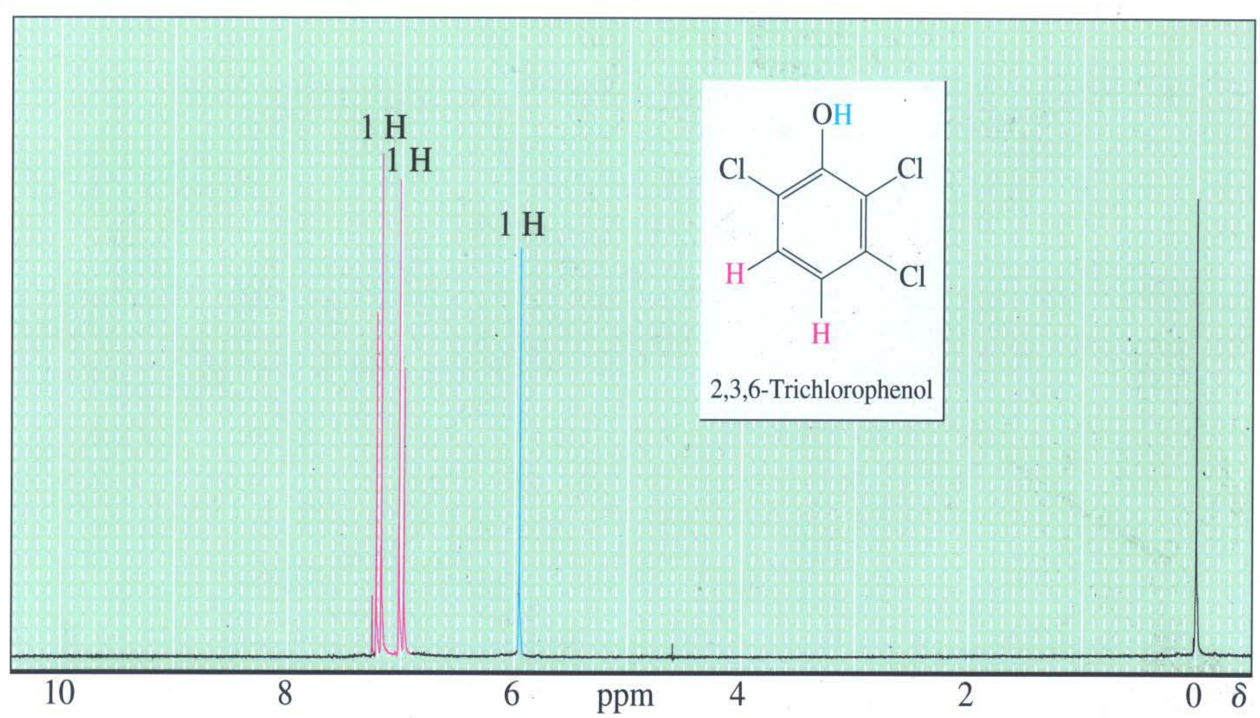
H_b
|
H_b-C-C-**H_a**
|
H_b

↑ H_o

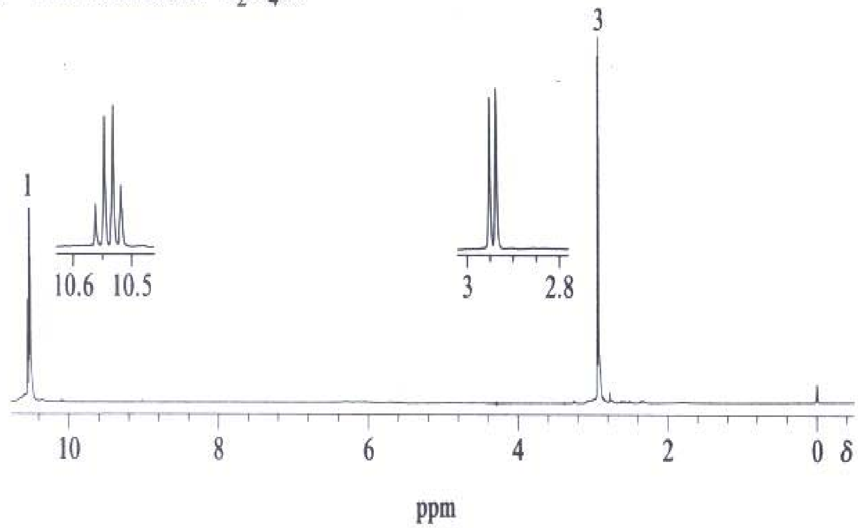
→ **Quartet**

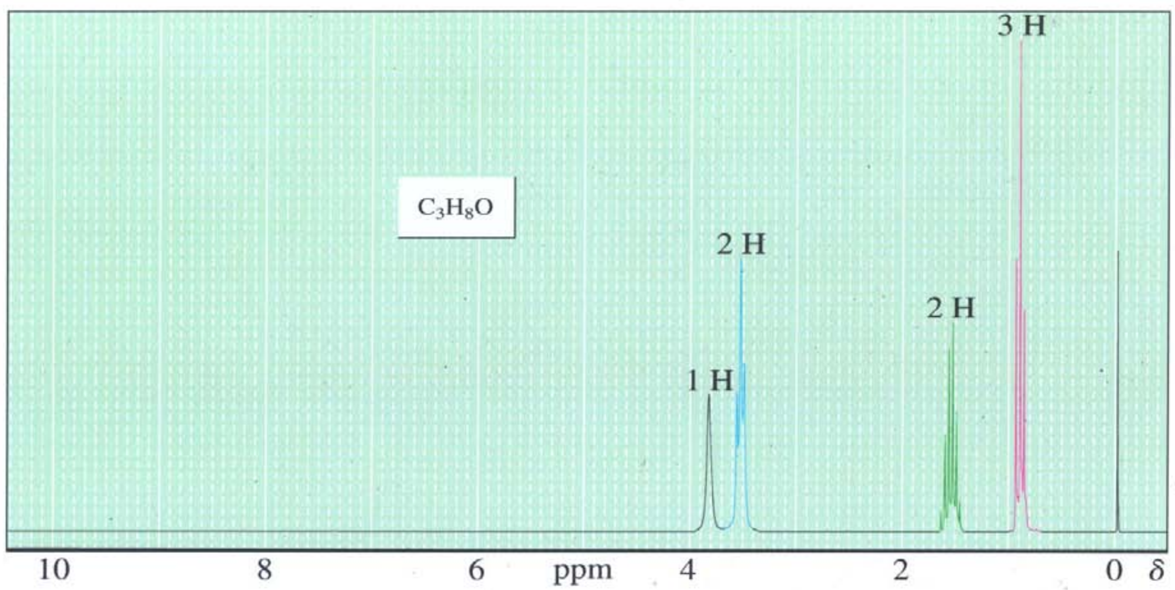
Intensities 1:3:3:1


CH3
CH2
H
H
H
H
CH3
1-Ethyl-4-methylbenzene
4 H
3 H
3 H
2 H
10
8
6
ppm
4
2
0
δ

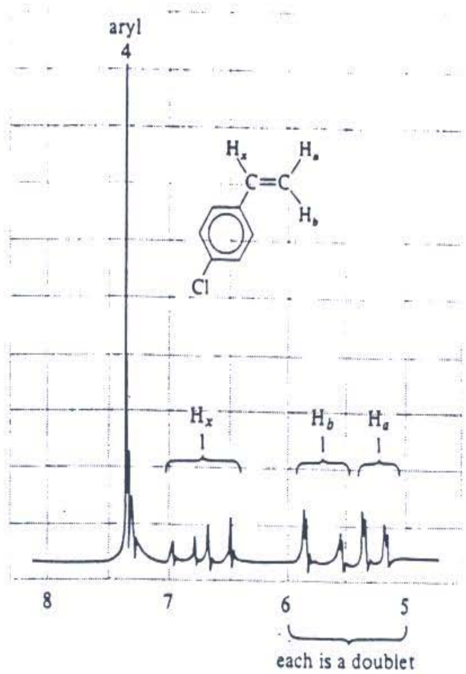

OH
Cl
Cl
H
Cl
H
2,3,6-Trichlorophenol
1 H
1 H
1 H
10
8
6
ppm
4
2
0
δ

c) The formula is C_2H_4O.

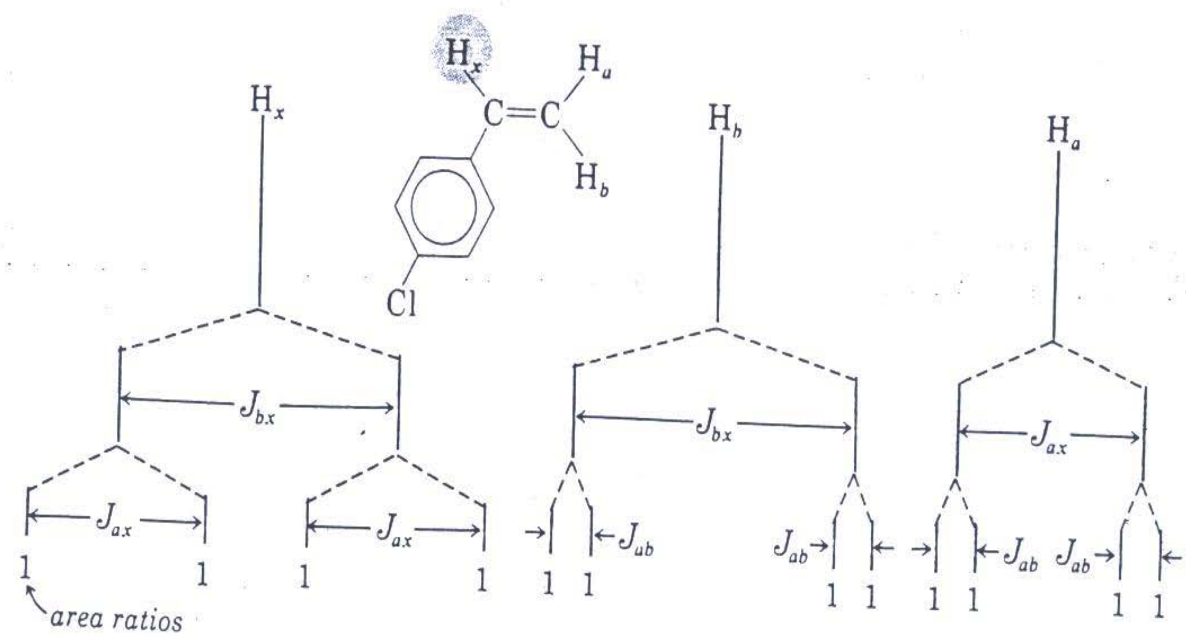




Partial ^{1}H NMR spectrum of *p*-chlorostyrene

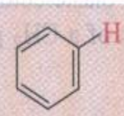


Splitting patterns of three alkenyl protons



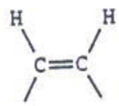
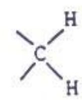
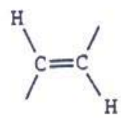
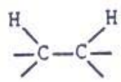
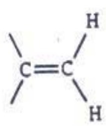
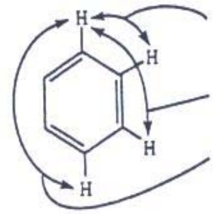
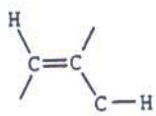
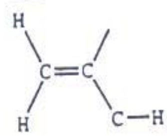
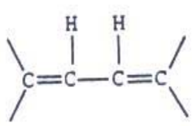
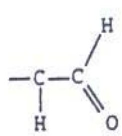
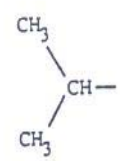
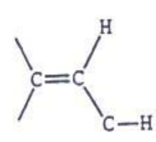
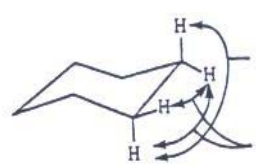
J_{ax} = 11 Hz, J_{ab} = 2 Hz, J_{bx} = 18 Hz

Typical Chemical Shift in NMR Spectra

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$-C-CH_3$	0.9	$Br-CH_3$	2.7
$C{=}C-CH_3$	1.6	$Cl-CH_3$	3.0
$C{\equiv}C-H$	1.8	$O-CH_3$	3.3
$N-H$	1–3	$C(=O)-O-CH_3$	3.7
$O-H$	2–5	O_2N-CH_3	4.1
$C-O-C(=O)-CH_3$	2.0	$F-CH_3$	4.2
$C(=O)-CH_3$	2.2	$C{=}C-H$	5.5–6.5
$N-CH_3$	2.2		7–8
$I-CH_3$	2.2	$C(=O)-H$	10
$N{\equiv}C-CH_3$	2.2	$C(=O)-O-H$	12
$Ph-CH_3$	2.3		

Note that these positions are only approximate. Furthermore, most of these positions are given for CH_3 groups. CH_2 groups appear farther downfield by about 0.3 ppm and CH groups by about 0.7 ppm.

Spin – Spin Coupling Constants for Various Geometries

Fragment	*J* (Hz)	Fragment	*J* (Hz)
	7–12		12–15
	13–18		0–10
	0.5–3		6–9 1–3 0–1
	0.5–2.5		0
	9–13	CH_3-CH_2-	6.5–7.5
	1–3		5.5–7
	4–10		5–9 2–4