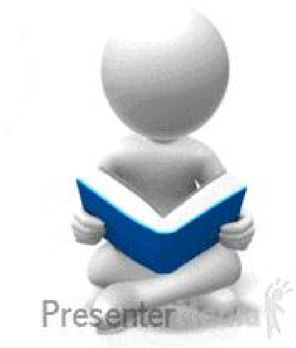
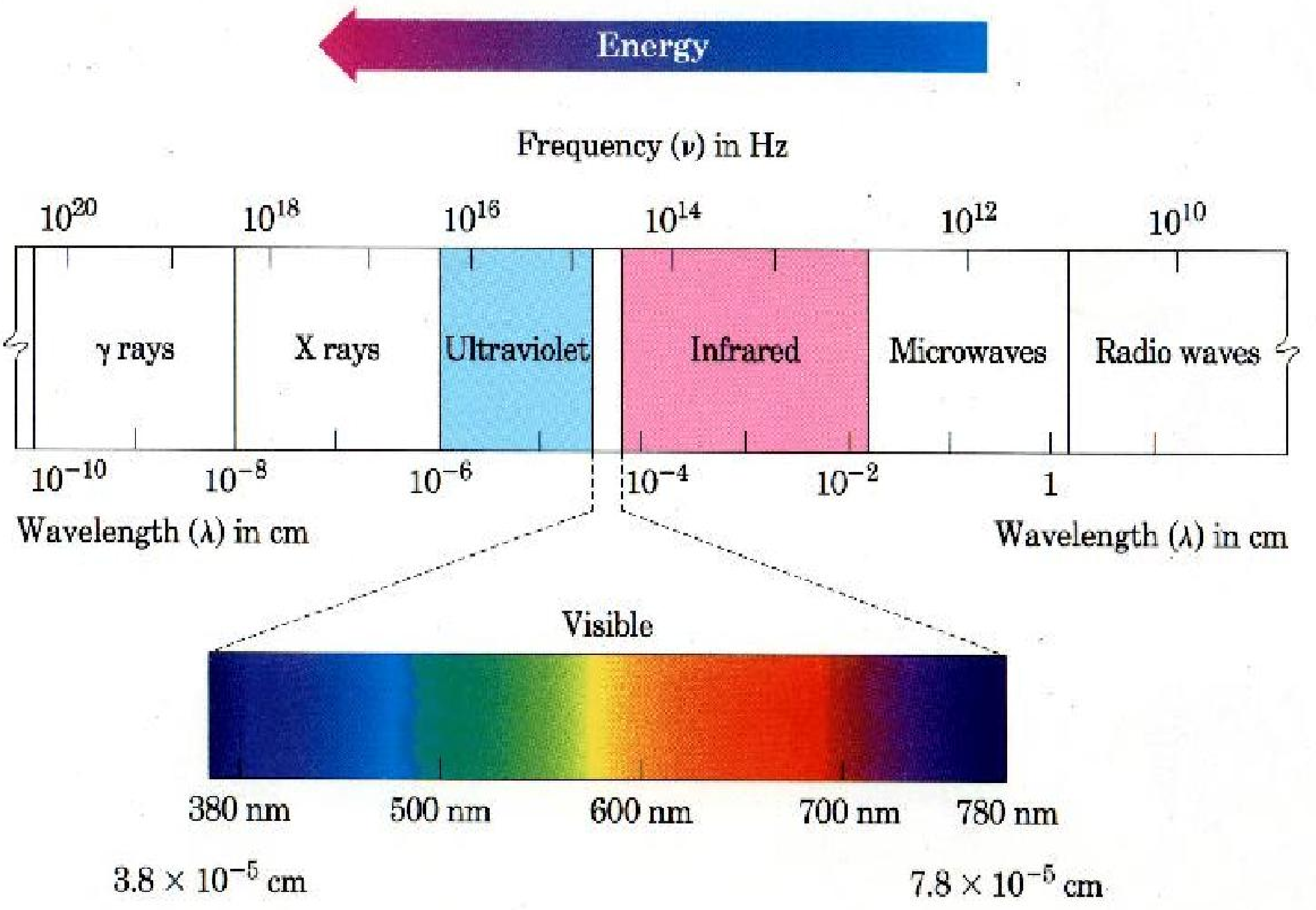


Spectroscopic Technique

Mr. Swapnilkumar Subhashrao Kale
Assistant Professor
Department of Chemistry
Shri Shivaji Science and Arts College, Chikhli
Dist.-Buldana
E-mail: kaleswapnilkumar02@gmail.com

The electromagnetic spectrum



NMR
What is it Good for?

Natural Product Chemistry

Environmental Chemistry

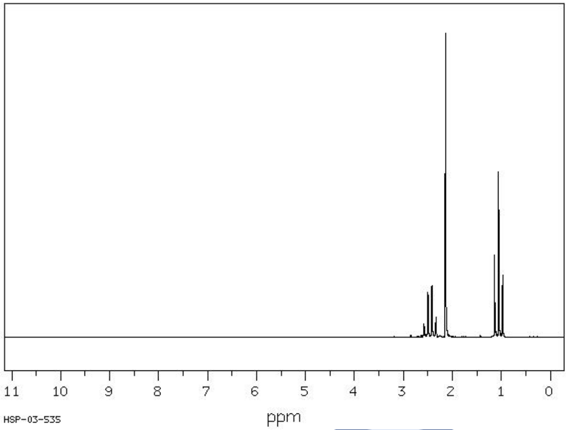
Determine Solution Structure of Small Molecules

Polymer Chemistry

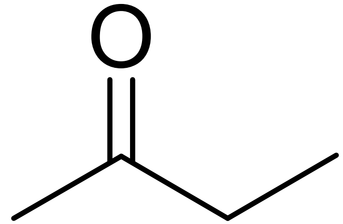
Molecular Dynamics – Quantifying Motional Properties – Exchange Rate/Activation Energy/ΔH/ ΔS

DNA and Protein Structure Determination

From Here……..



To here!



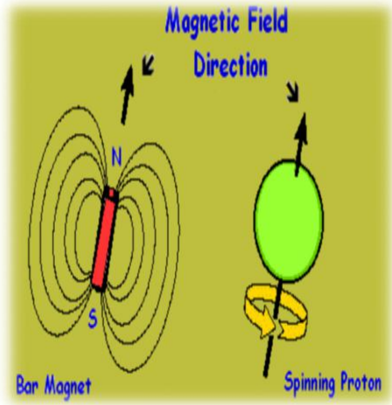
Lets start the study of NMR spectroscopy…….

The Nuclear Magnetic Moment

- Nuclear spin quantum number, I.

'I' can be ≥ 0 and any multiple of ½.

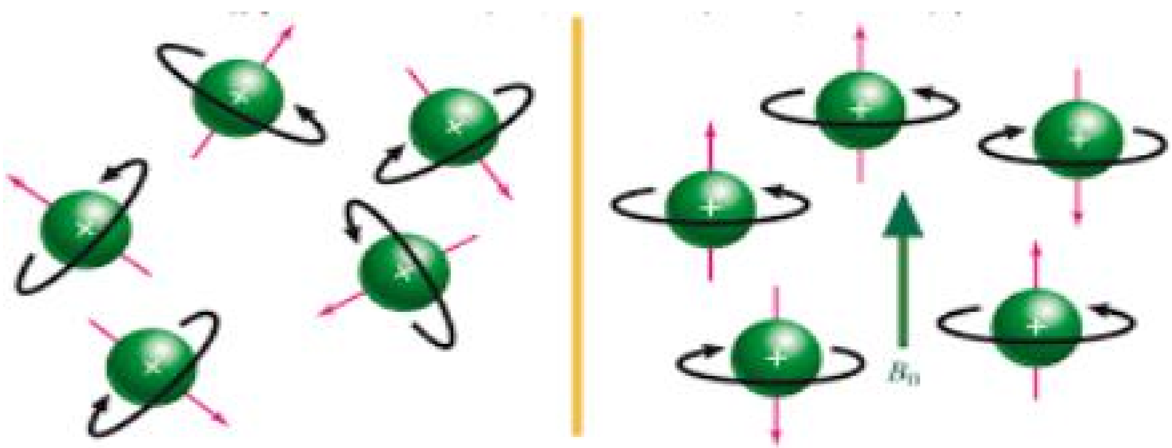
- NMR silent or NMR inactive nuclei
- NMR active Nuclei:



Element	$^{1}H_{1}$	$^{2}H_{1}$	$^{12}C_{6}$	$^{13}C_{6}$	$^{14}N_{7}$	$^{16}O_{8}$	$^{17}O_{8}$	$^{19}F_{9}$	$^{31}P_{15}$
Nucleur spin quantum number	1/2	1	0	½	1	0	5/2	1/2	1/2
No of spin states	2	3	0	2	3	0	6	2	2

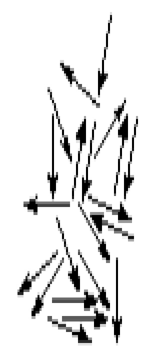
NMR Concepts – Spin States

- Nucleus produces magnetic field.
- NMR active nuclei as tiny bar magnet
- Random orientation and spin aligned or spin opposed.
- lower energy spin state: spin aligned situation: highly populated one.
- Higher spin energy state: spin opposed situation: less populated one.

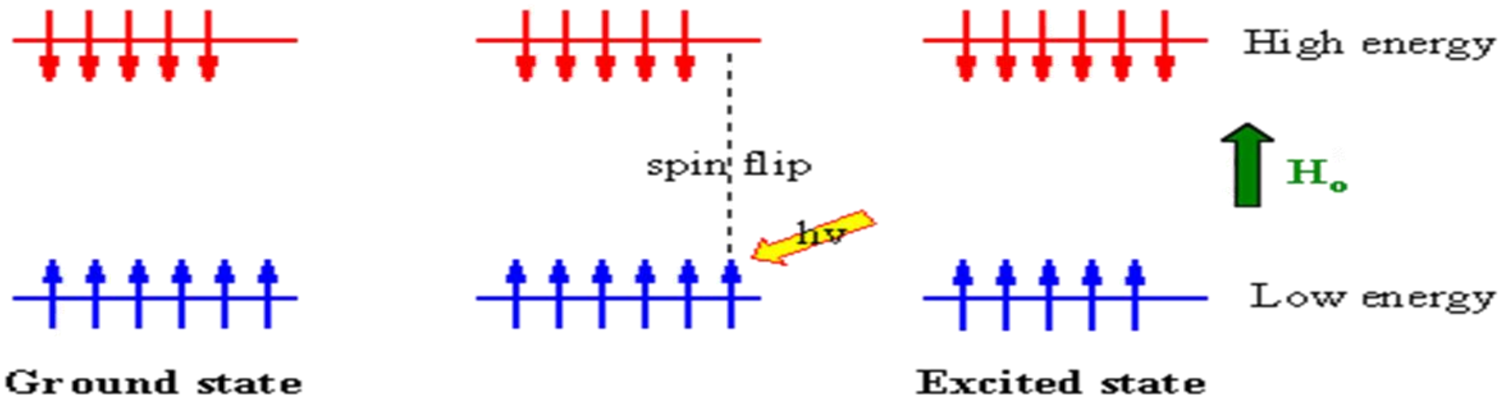


Without external magnetic field

With external magnetic field



Nuclear Transition

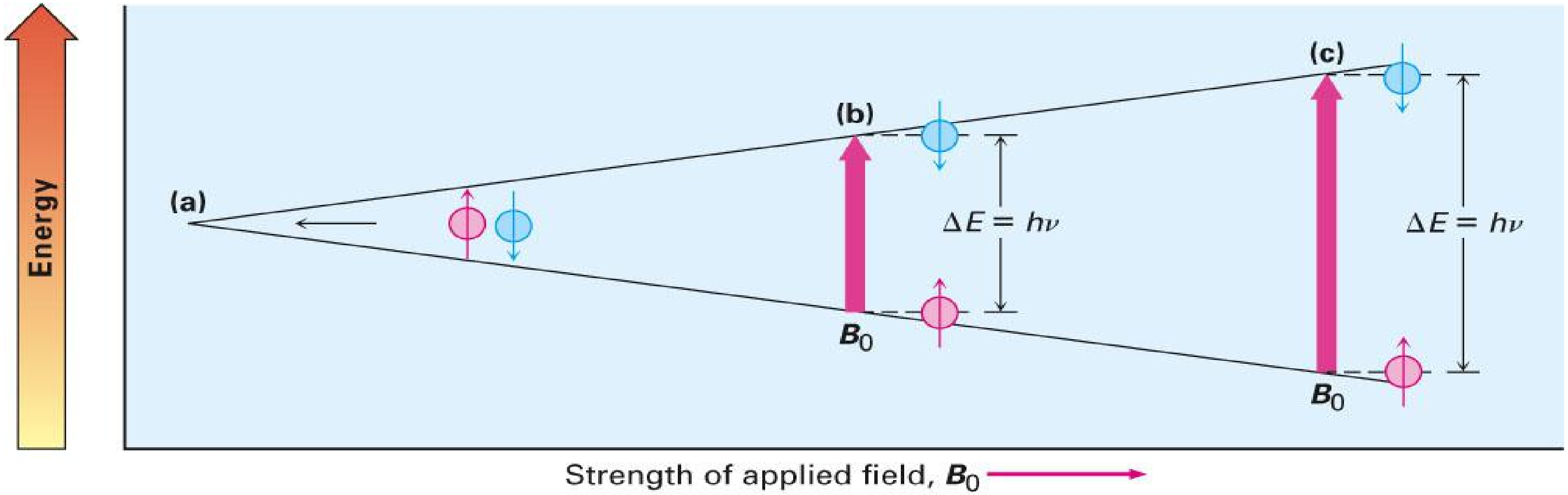


Strength of External magnetic field:
Energy required for nuclear transition ∝ strength of external applied magnetic field

Nature of the nucleus:
Frequency required to nuclear transition ∝ magnetogyric ratio of the nucleus

$$\vartheta = \frac{\gamma H_0}{2\pi}$$

Dependence of the difference in energy between lower and higher nuclear spin levels of the hydrogen atom.

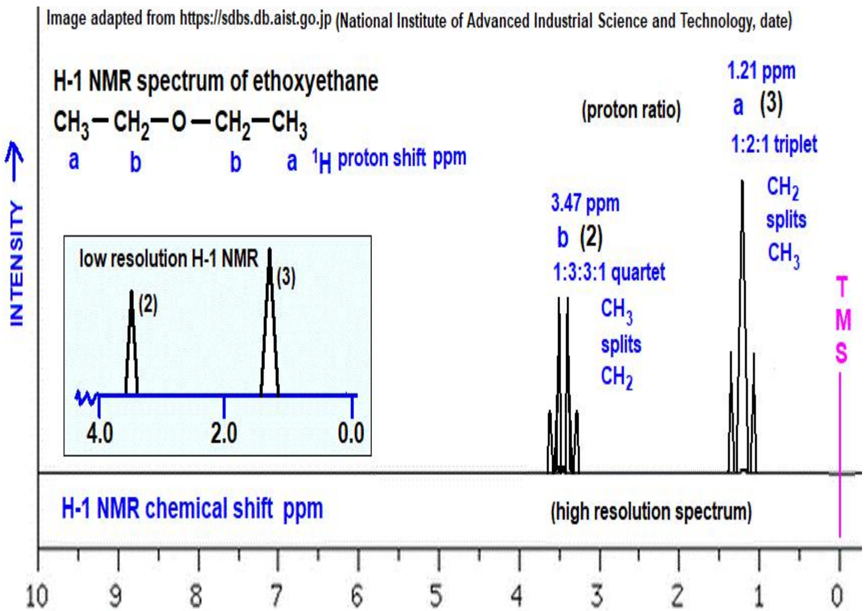


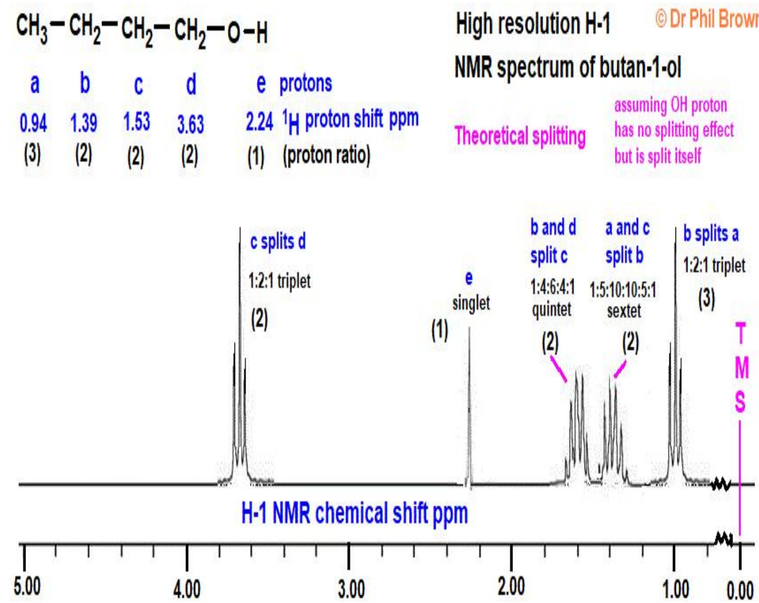
- Nuclear Magnetic resonance: At some values of magnetic field strength, the energy required to excite a proton matches the energy of incident radiation is called resonance, an absorption of energy occurs and a NMR spectrum is obtained.
- Effective field strength

Information from proton-NMR Spectrum

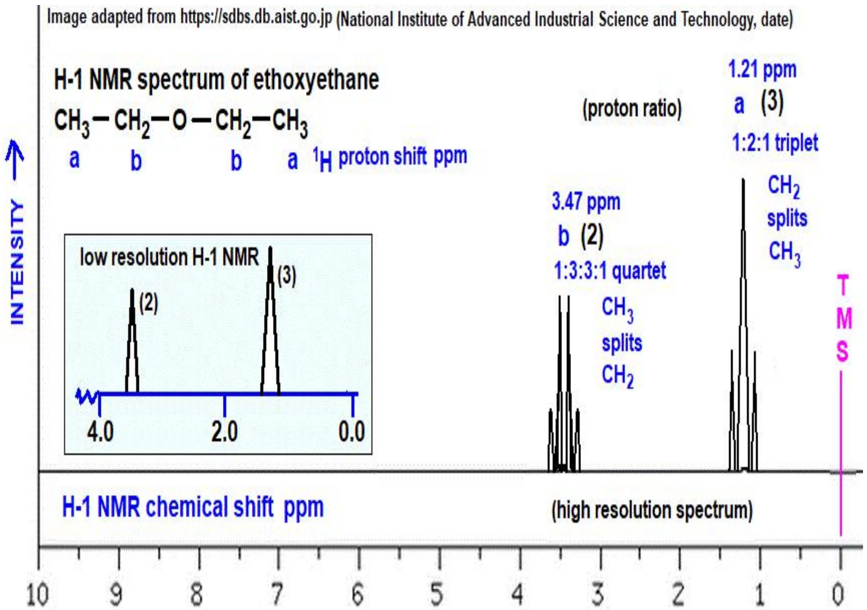
1. **The number of signals:** how many different types of proton present in given organic molecules

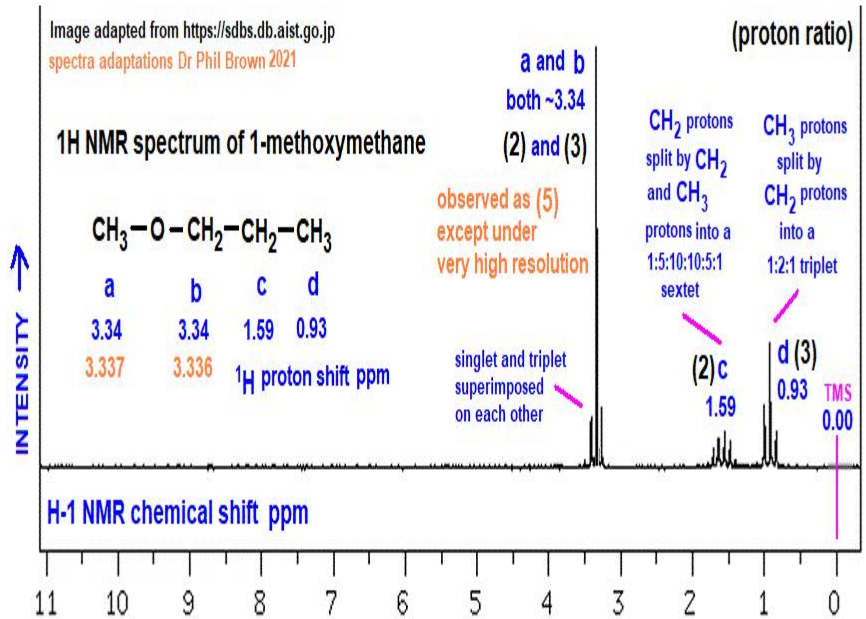
   No. of signal in the spectrum = the number of kinds of proton





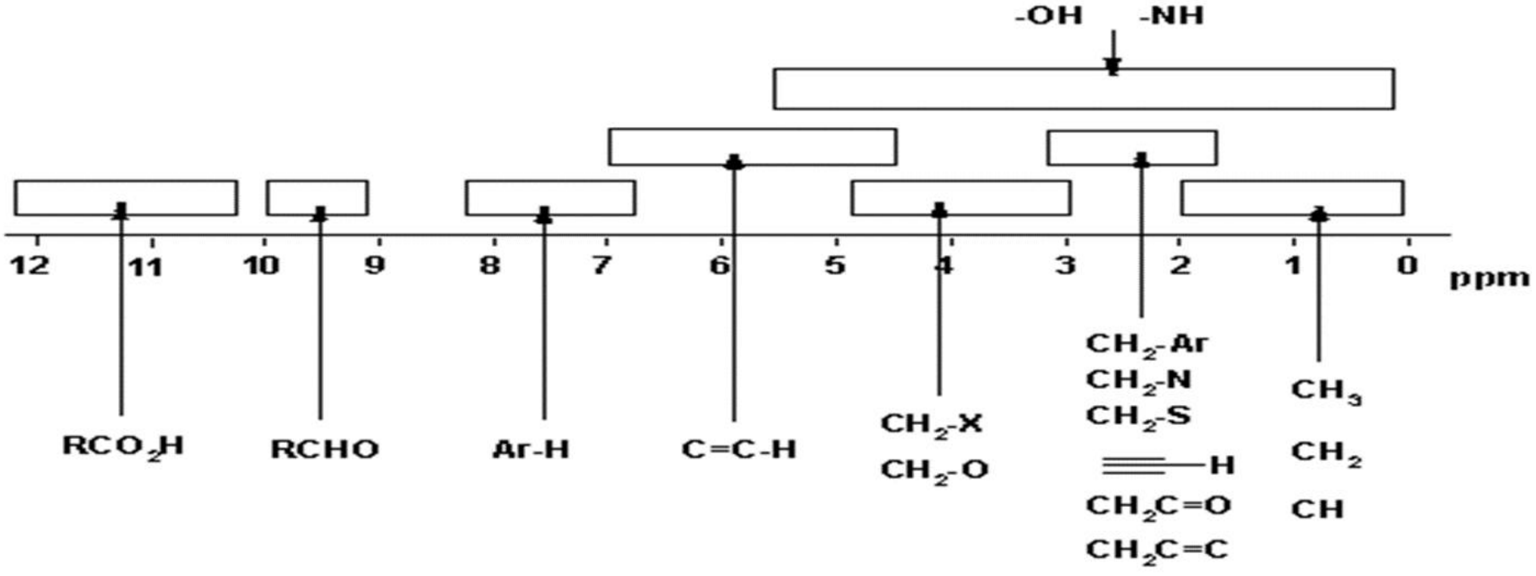
2. Position of Signals: tells us about the electronic environment of each type of proton





Chemical Shift

- Tells us about the kinds of protons
- Tells about the electronic environment which determine spectrum where a proton absorbs.
- Unit: ppm
- Shielded and deshielded proton
- Chemical Shift
- TMS: standard for NMR spectrum



Electronegativity Effects

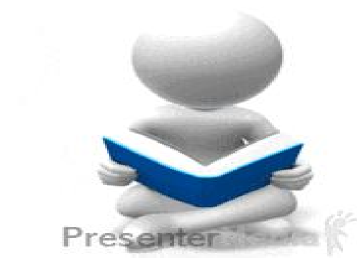
The chemical shift simply increases as the electronegativity of attached element on the carbon to which protons of interest are present given in Table A

Multiple substituents have a stronger effect that a single substituents given in Table B

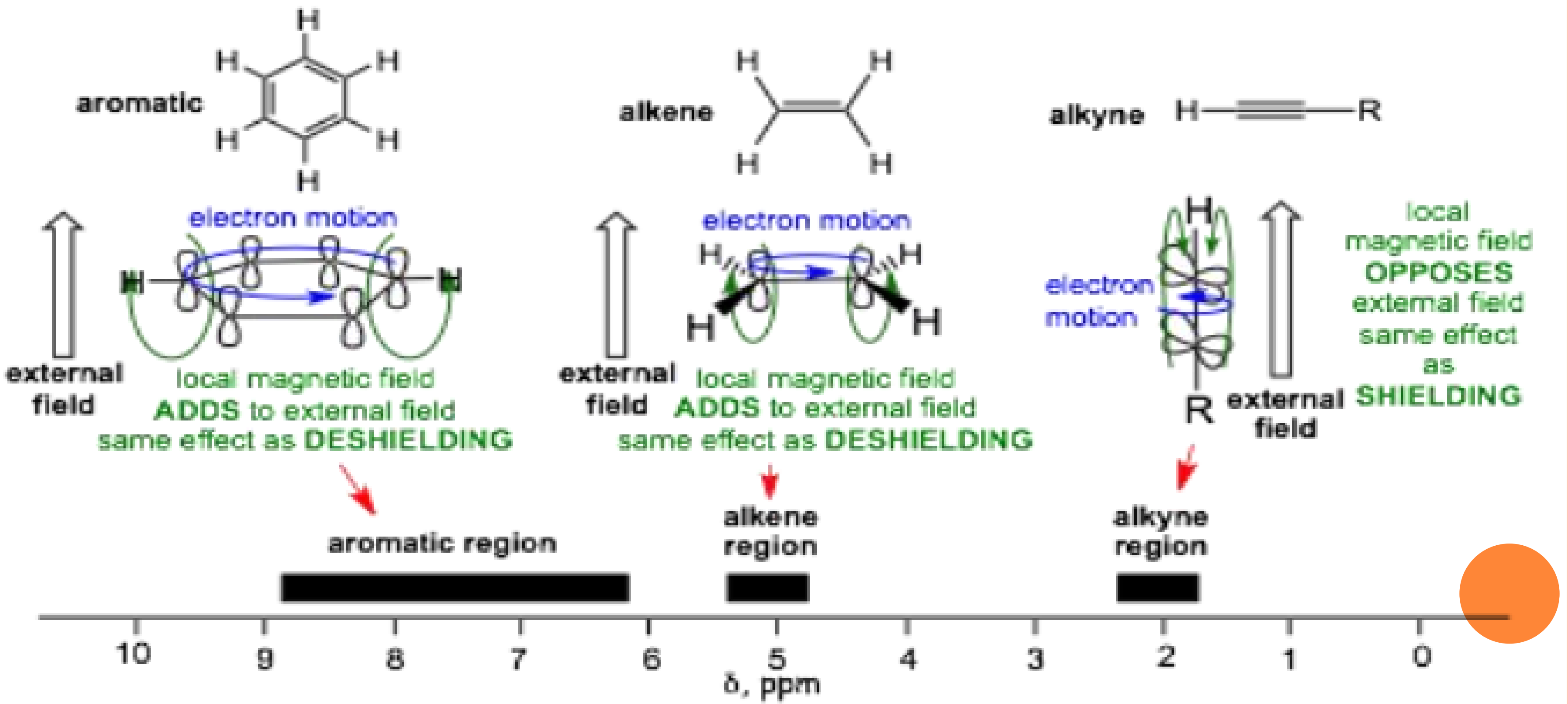
Dependence of the chemical shift of alkyl halide (Table A)

Compound CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4$ Si
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

Other Factors that affects Chemical Shift

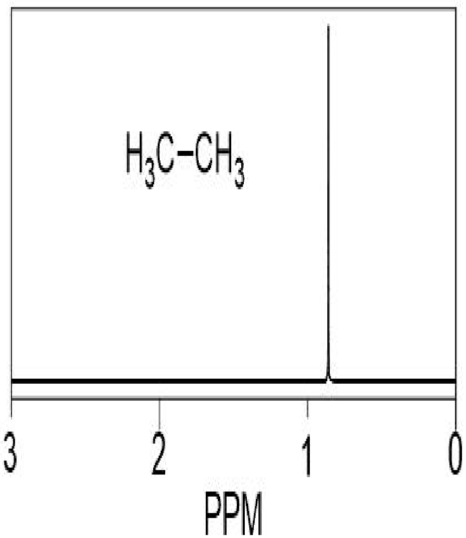


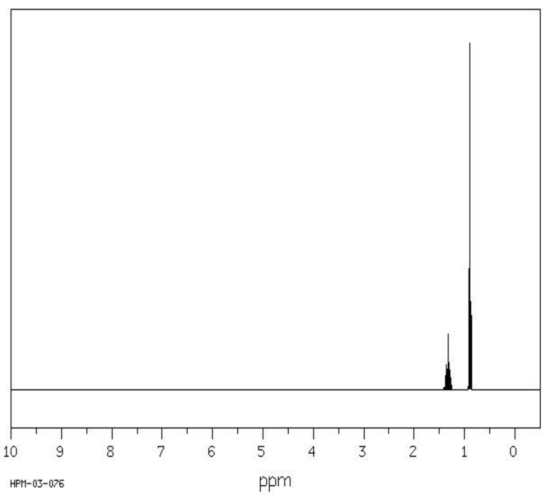
– **Magnetic anisotropy** of neighboring bonds and ring currents – π electrons of triple bonds and aromatic rings are forced to rotate about the bond axis creating a magnetic field which counteracts the static field.

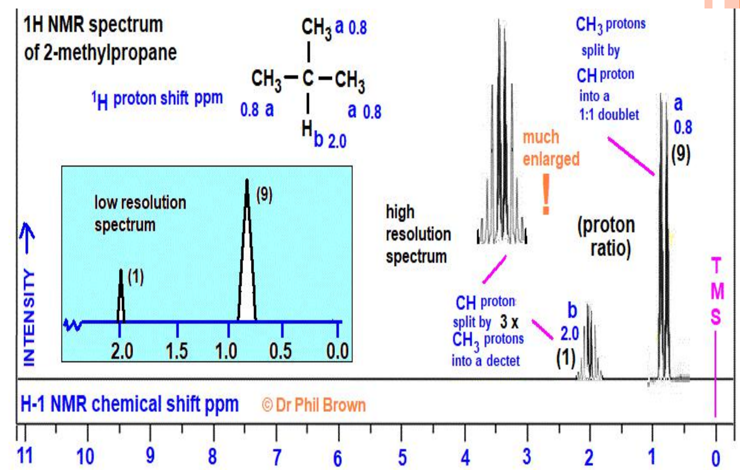


Substitution Effect

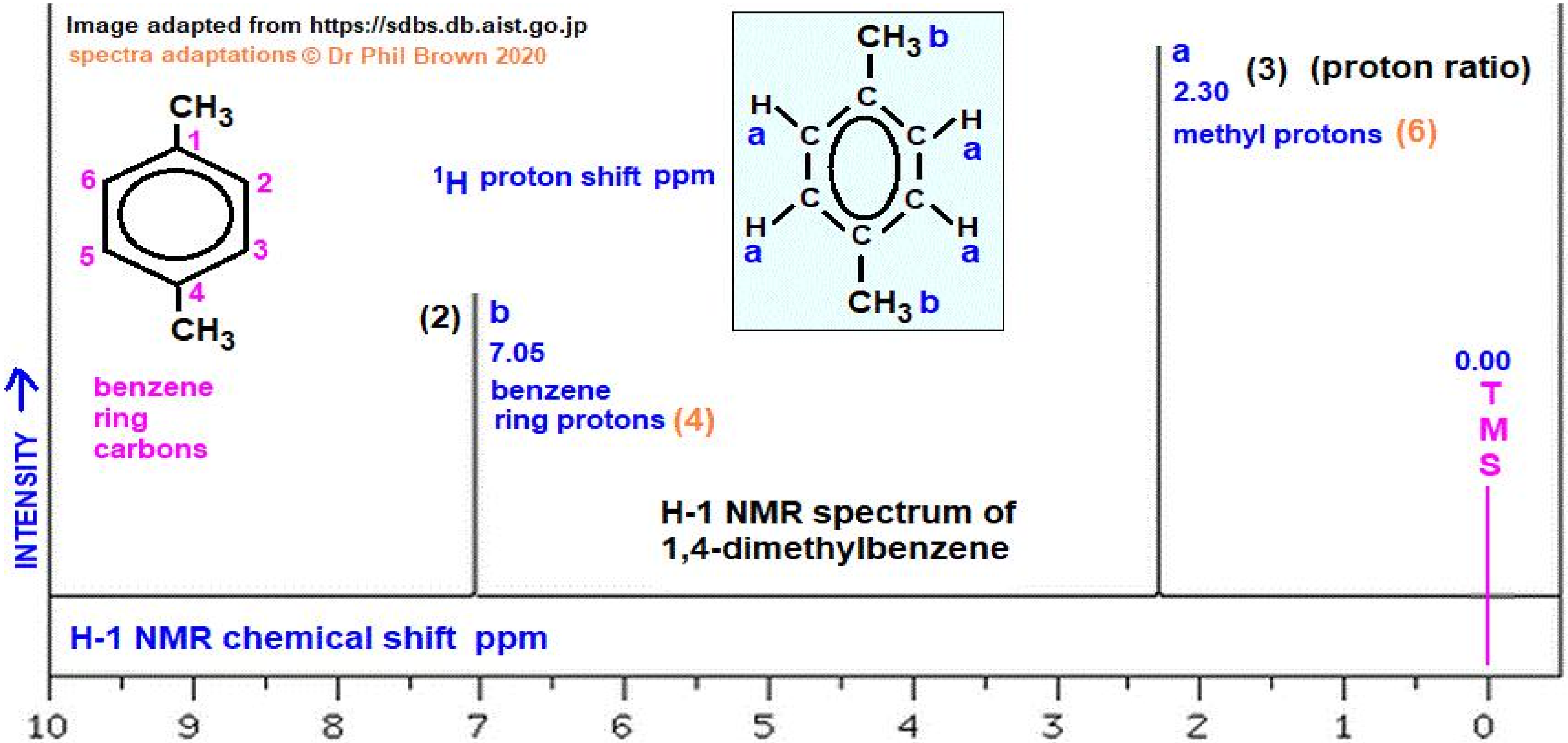
R-C<u>H</u>$_3$	<u>R$_2$</u>CH$_2$	<u>R$_3$</u>CH
0.7-1.1 ppm	1.2-1.4 ppm	1.4-1.7 ppm







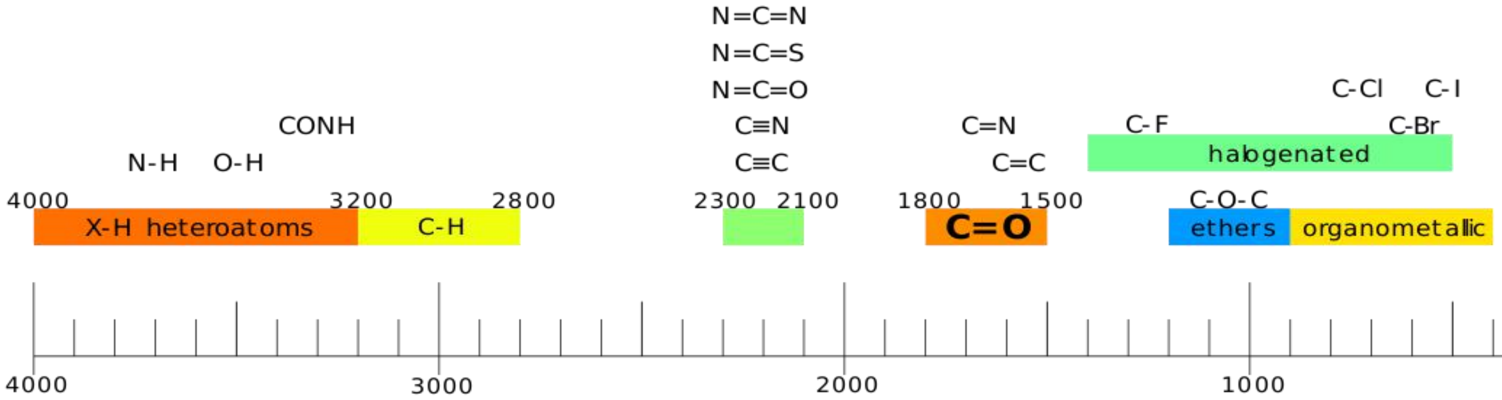
3. The intensities of signals ∝ total number of protons giving rise to the signal.

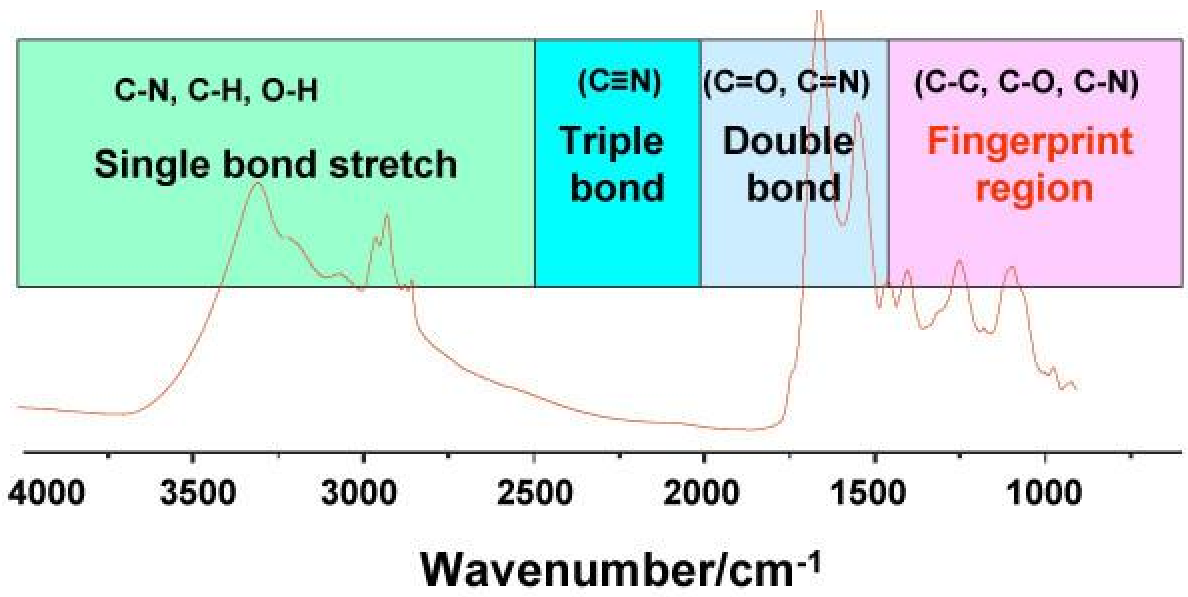


Splitting of Signals: Spin-Spin Coupling

- Multiplicity and spin-spin coupling
- Gives an idea about adjacent environment of proton
- Spin-spin coupling for one adjacent non-equivalent proton
- Spin-spin coupling for two adjacent non-equivalent proton
- Spin-spin coupling for three adjacent non-equivalent proton
- Multiplets
- n+1 rule
- $(n_a + 1)(n_c + 1)$ rule

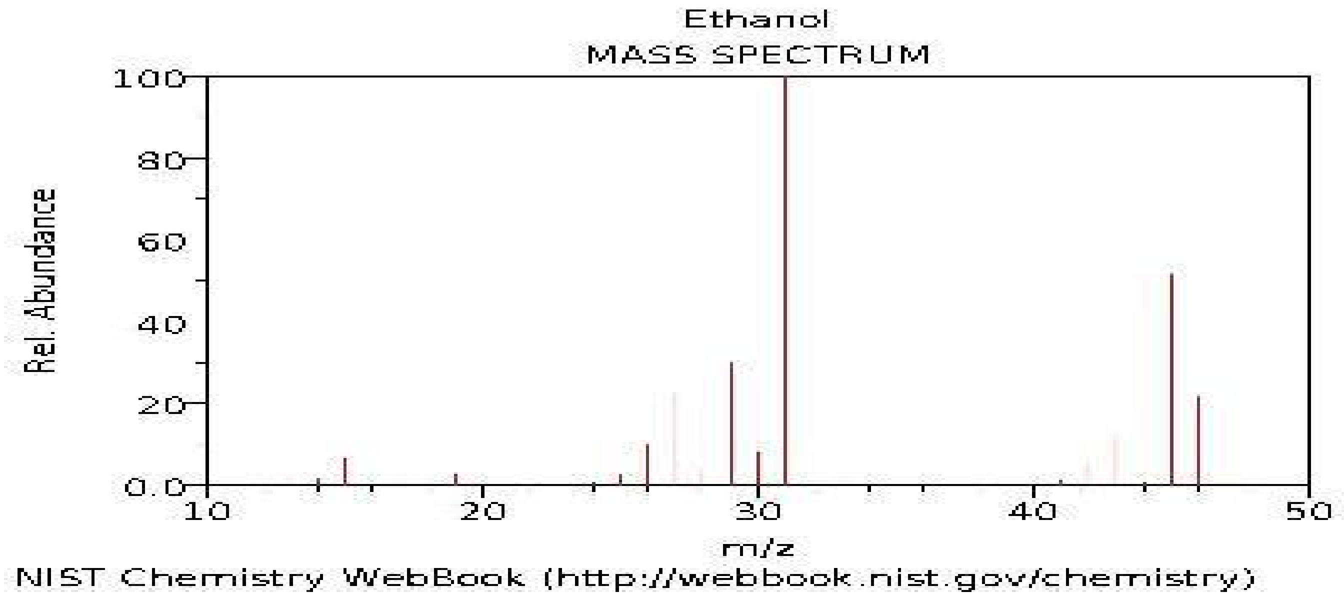
IR Spectroscopy





Mass Spectroscopy

- Principle: Bombardment of sample with electron and detection of molecular fragment
- Provide information about molecular mass and atom connectivity



UV Spectroscopy

- Principle: Promotion of electron to higher energy level through irradiation of matter with UV light
- Provides information of about the presence of conjugated system and the presence of double and triple bond

X-ray Spectroscopy

- Principle: Bombardment of sample with X-ray radiation
- Provide information about bond angles and bond length

Thank

You