



**BITS Pilani**  
Pilani Campus

# **CHEM F111 : General Chemistry**

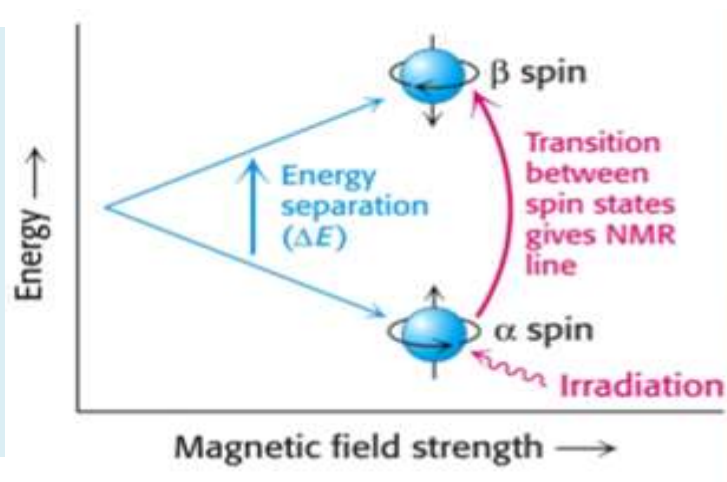
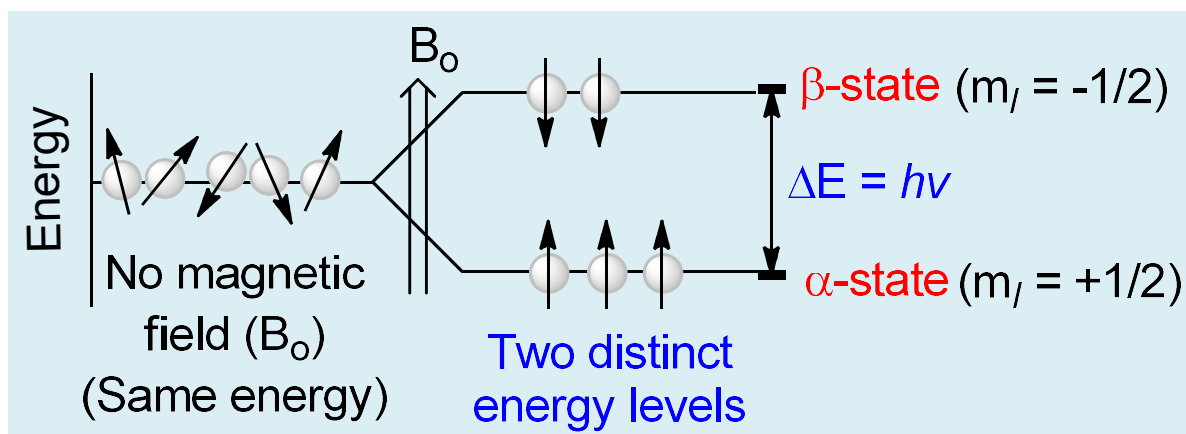
## **Semester II: AY 2017-18**

### **Lecture 18 (21-02-2018)**

# Summary of Lecture 17



- Not all nucleus are NMR active.
- $I = \frac{1}{2}$  are the most suitable nucleus for NMR.
- When placed in a magnetic field ( $B_0$ ) nuclei that possess **spin** align themselves according to their energy states (***Zeeman Effect***).



- Nuclei transit from  $\alpha$ -state to  $\beta$ -state by absorbing energy corresponding to the radio frequency region of EMR. **This phenomenon is called Resonance. (Resonance: A general phenomenon for energy pumping)**

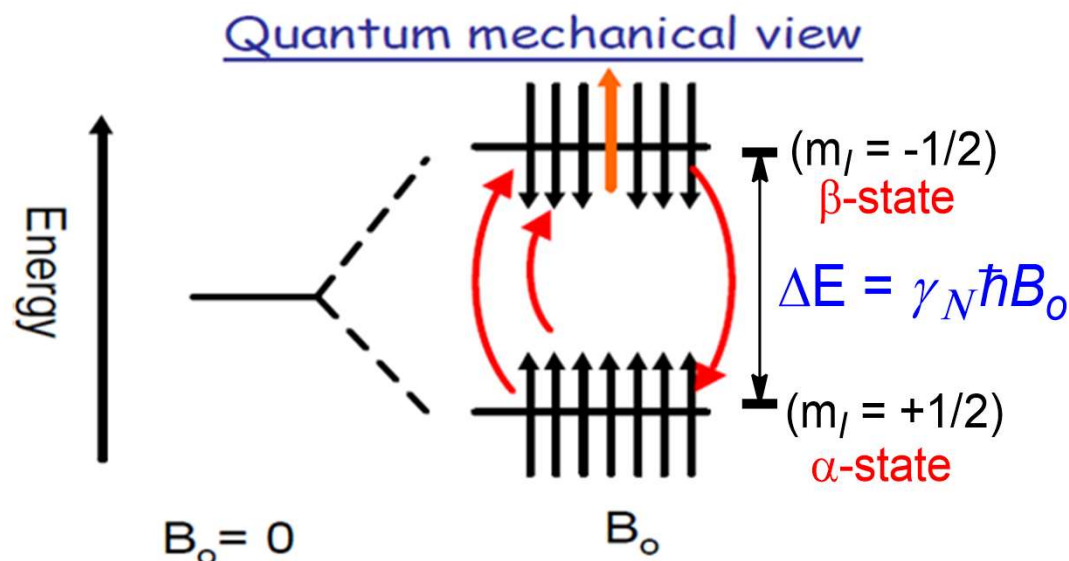
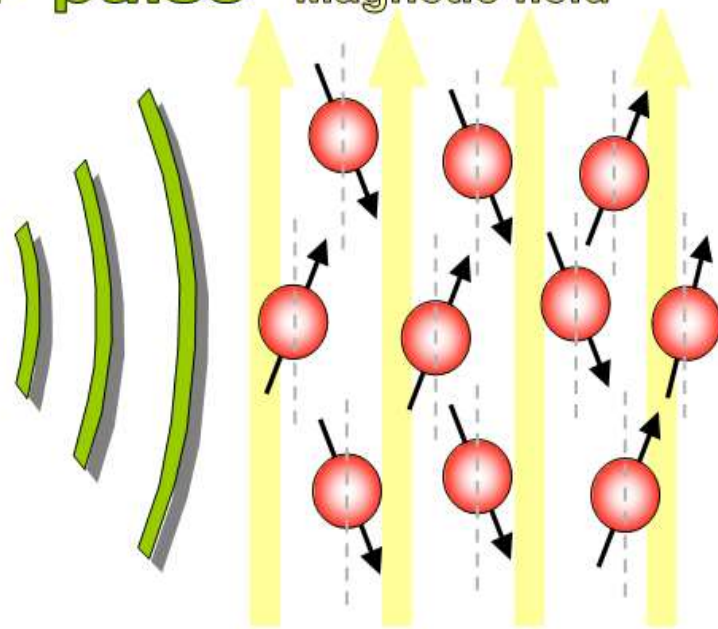
## Summary of Lecture 17



$$E_{m_I} = -\gamma_N \hbar B_o m_I; \Delta E = E_{\beta} - E_{\alpha} = \gamma_N \hbar B_o$$

$h\nu = \gamma_N \hbar B_o$  Thus,  $\nu = \gamma_N B_o / 2\pi$  (selection rule:  $\Delta m_I = 1$ )

RF pulse      Magnetic field



• Nuclei transit from  $\alpha$ -state to  $\beta$ -state by absorbing energy corresponding to the radio frequency region of EMR. [Resonance]

Do all the nuclei with  $I = 1/2$  resonate at same radio frequency ( $\nu$ )?

## Sensitivity: Gyromagnetic Ratio ( $\gamma$ )



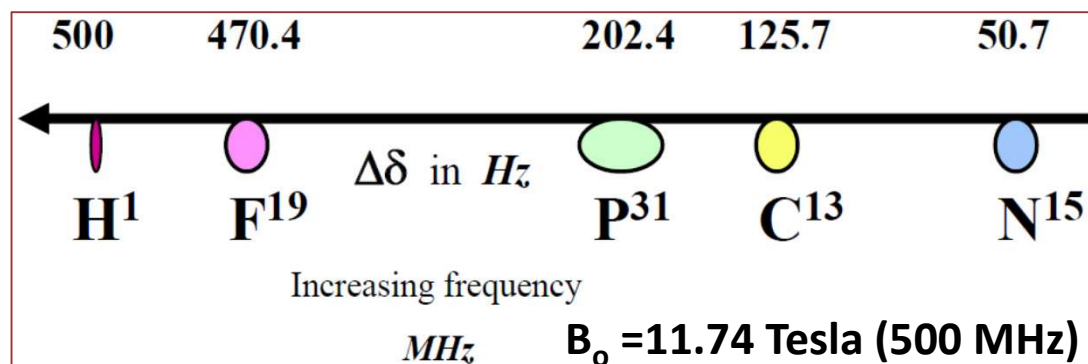
Not all the nucleus with  $I = 1/2$  resonate at same radio frequency region.

Nucleus	$I_N$	$\gamma [10^8 \text{ T}^{-1}\text{s}^{-1}]$	Nat. Abd. [%]
$^1\text{H}$	$1/2$	2.675	99.98
$^{13}\text{C}$	$1/2$	0.673	1.11
$^{15}\text{N}$	$1/2$	-0.2712	0.37

$^1\text{H}$  is 5672 times more sensitive than  $^{13}\text{C}$ . That's why you need many more  $^{13}\text{C}$  scans to get a decent spectrum.\*\*

$$h\nu = \gamma_N \hbar B_0 \text{ OR } \nu = \gamma_N B_0 / 2\pi$$

The frequency of absorbed electromagnetic radiation is different for different elements.

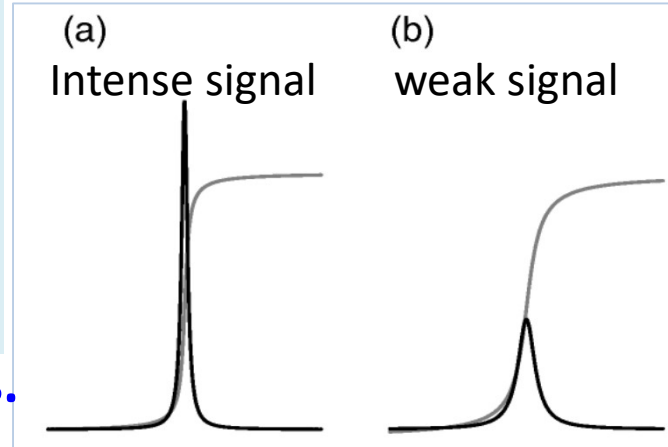
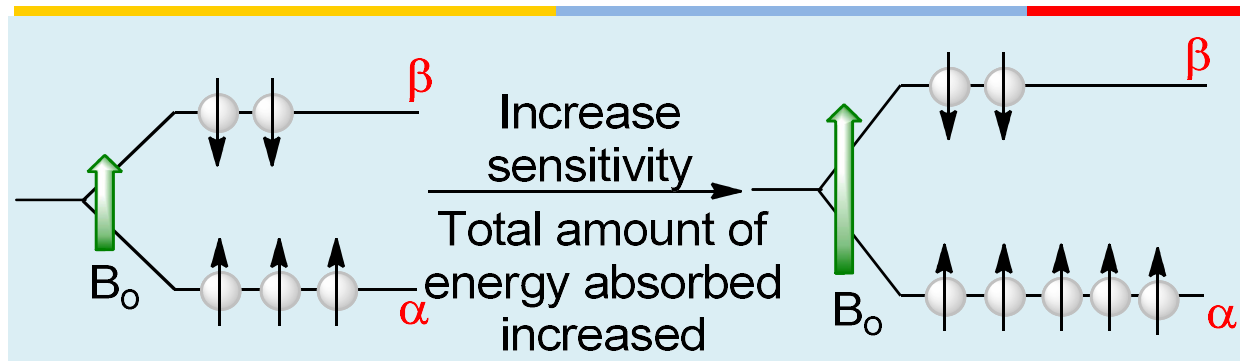


Different nuclei resonate at different frequencies in MHz.

–When talking about 500 MHz NMR, we are referring to the resonance frequency of proton in that particular strength magnetic field.

**\*\*You can see why  $^1\text{H}$  (proton) easy to “see” in NMR –high abundance, and large  $\gamma$ \*\***

# Sensitivity: Nuclei Population(s) difference in two states

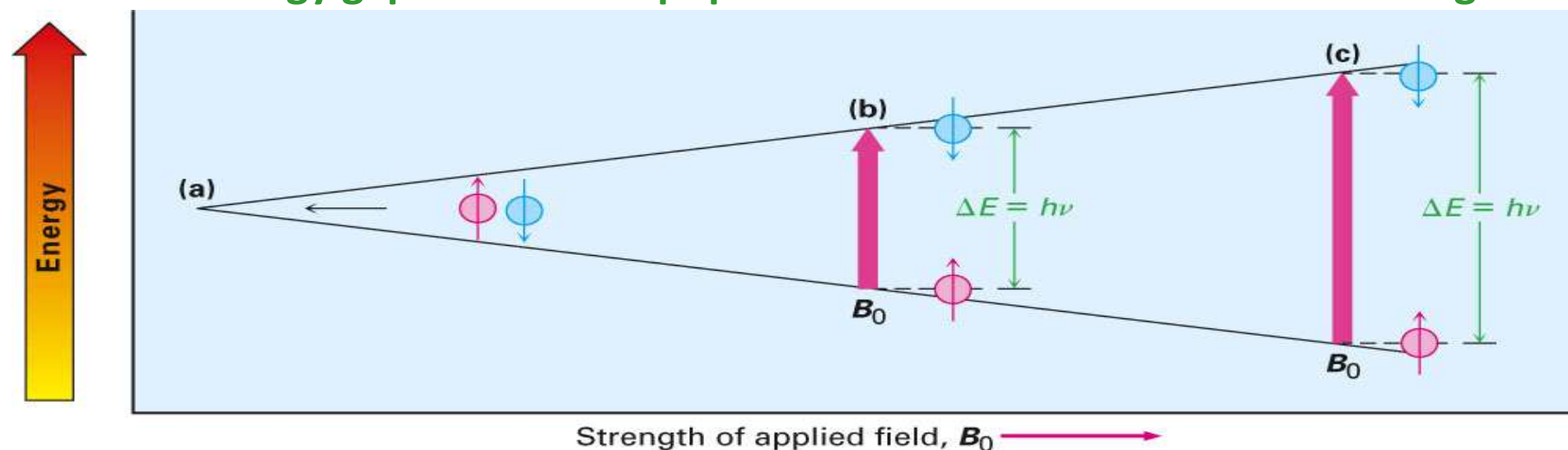


- Small population difference: weak NMR signals.

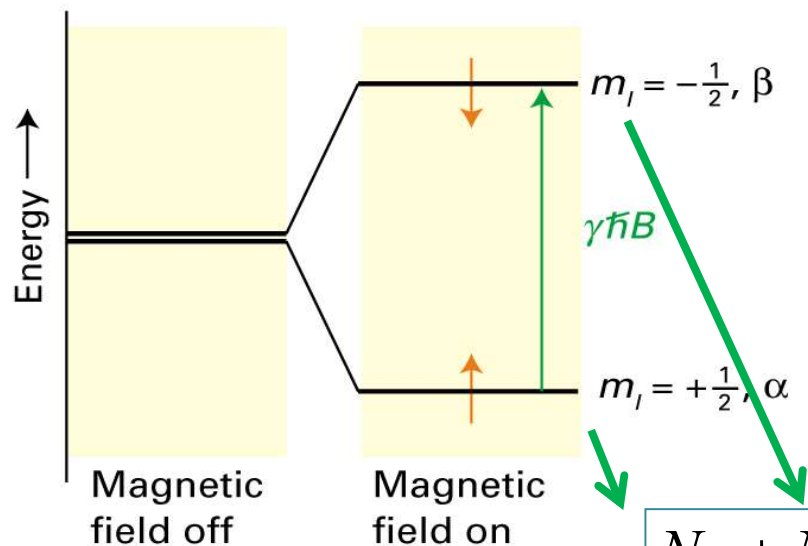
$$\uparrow \Delta E \equiv \uparrow B_0 \equiv \uparrow \gamma$$

- Increase population difference: more sensitivity, strong NMR signals

Increase energy gap -> Increase population difference -> Increase NMR signal



## Sensitivity: Nuclei population(s) difference in two states



- The population difference between two energy states ( $\alpha$  and  $\beta$ ), on applying an external magnetic field could be estimated using a very famous law termed as **Boltzmann distribution Law**, as universal law obeyed in nature.

$$N_{\alpha} + N_{\beta} = N$$

$$\frac{N_{\beta}}{N_{\alpha}} = e^{\frac{-\Delta E}{kT}} = e^{\frac{-h\nu}{kT}} = e^{\frac{-\gamma_N \hbar B_0}{kT}}$$

$$\frac{N_{\alpha} - N_{\beta}}{N_{\alpha} + N_{\beta}} = \frac{N_{\alpha} \left[ 1 - \frac{N_{\beta}}{N_{\alpha}} \right]}{N_{\alpha} \left[ 1 + \frac{N_{\beta}}{N_{\alpha}} \right]} \rightarrow N_{\alpha} - N_{\beta} \approx \frac{N \gamma_N \hbar B_0}{2kT} = \frac{N \mu_N g_N B_0}{2kT}$$

$B_0 = 1.41 \text{ T}$  ( $\nu_0 = 60 \text{ MHz}$ ),  $T = 298 \text{ K}$ ;  $\gamma_N$  (Hydrogen nuclei)  $= 2.67 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$ ;  $N_{\alpha} - N_{\beta} = 9$  (excess of just 9 nuclei in lower (favored) spin state, in approximately 2 million nuclei).

$$\frac{N_{\beta}}{N_{\alpha}} = 0.999991 = \frac{1000000}{1000009}$$



## Sensitivity: Intensity of signals

Intensity of Absorption,  $I \propto (N_\alpha - N_\beta) B_0$

$$(N_\alpha - N_\beta) \propto B_0/T$$

→ Intensity of Absorption,  $I \propto B_0^2/T$

Frequency (MHz)	Excess Nuclei (per 2 million nuclei)
60	9
80	12
100	16
200	32
300	48
600	96

- Number of nuclei in the ground state is more than the excited state at equilibrium. Hence, there is a net absorption. The strength of the signal is proportional to the net difference in population between two states.
- Decreasing T or Increasing  $B_0$ , → Population increases in  $\alpha$ -state.
- Increase the population difference → increase sensitivity.

Intensity  $\propto$  relative abundances of nucleus

Isotopic abundance  $^1\text{H}$  is also very high (99.98 %). Strong signal ( $^1\text{H}$ ) Recorded in lesser time.

Isotopic abundance  $^{13}\text{C}$  is less (1.10 %) rest is  $^{12}\text{C}$  (NMR inactive;  $I = 0$ ); weak signal ( $^{13}\text{C}$ ) Recorded in more time.

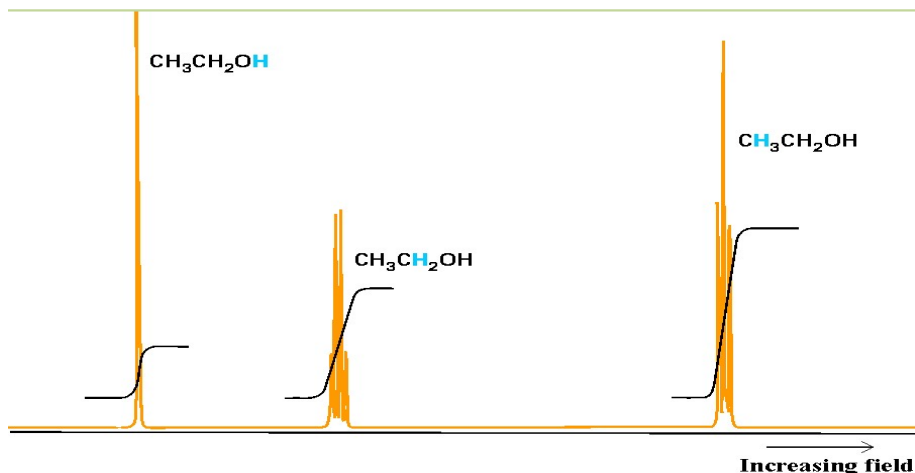


# Nuclear Resonance: Chemical shift



- $^1\text{H}$  nuclei resonate at a characteristic frequency dependent on the magnetic field strength  $B_o$ .
- You would think that all  $^1\text{H}$  absorb at same frequency.
- In practice, chemically different nuclei absorb at different frequencies.

$$\nu = \gamma_N B_o / 2\pi$$



- Why do we get different peaks for hydrogen nuclei in the NMR spectrum of a compound?
- Why should the hydrogen nuclei in different compounds behave differently in the NMR experiment?

- Chemically different hydrogens in an organic molecule do not experience the same magnetic field.
- The chemical shifts of different  $^1\text{H}$ -nuclei in a molecule arise due to differences in the local magnetic field or *shielding* ( $\sigma$ ) felt by the nuclei in different spots of the molecule.



# Typical $^1\text{H}$ and $^{13}\text{C}$ -NMR Spectrum



Recording  $^{13}\text{C}$  NMR

$B = 9\text{ T}$

$\nu \sim 100\text{ MHz } (^{13}\text{C})$

RF source required  
 $\nu \sim \text{approx. } 100\text{ MHz}$

Ethanol;  $\text{CH}_3\text{-CH}_2\text{-OH}$

Precessional freq.

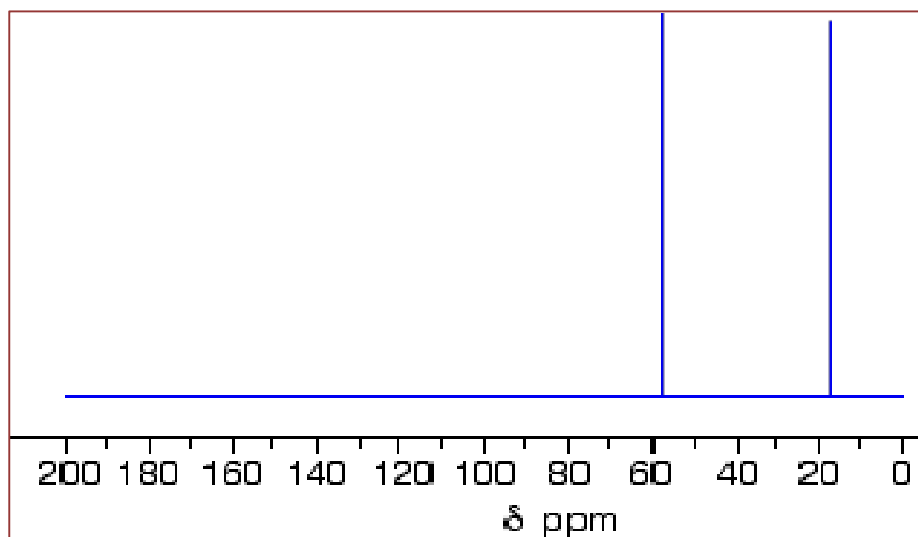
$$\nu = \gamma_N B_o / 2\pi$$

Recording  $^1\text{H}$  NMR

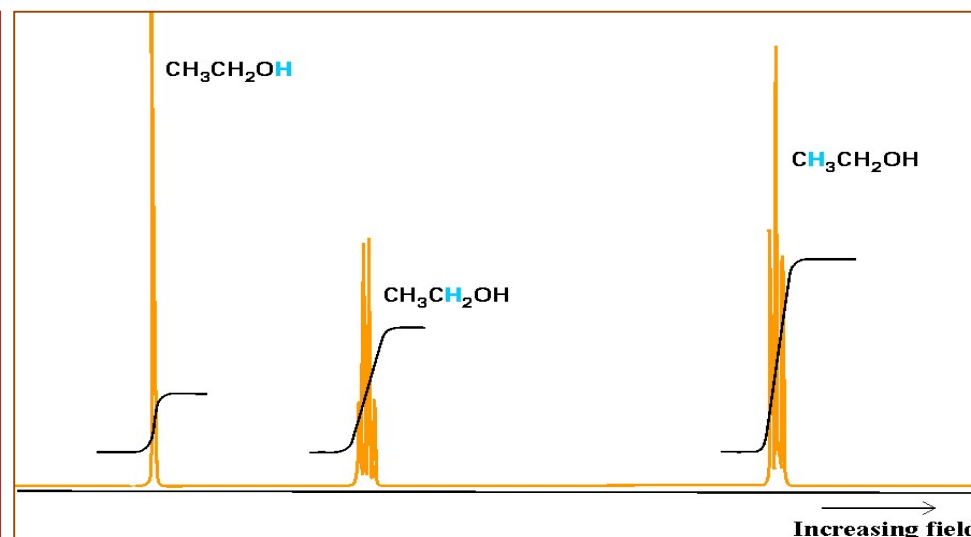
$B = 9\text{ T}$

$\nu \sim 400\text{ MHz } (^1\text{H})$

RF source required  
 $\nu \sim \text{approx. } 400\text{ MHz}$



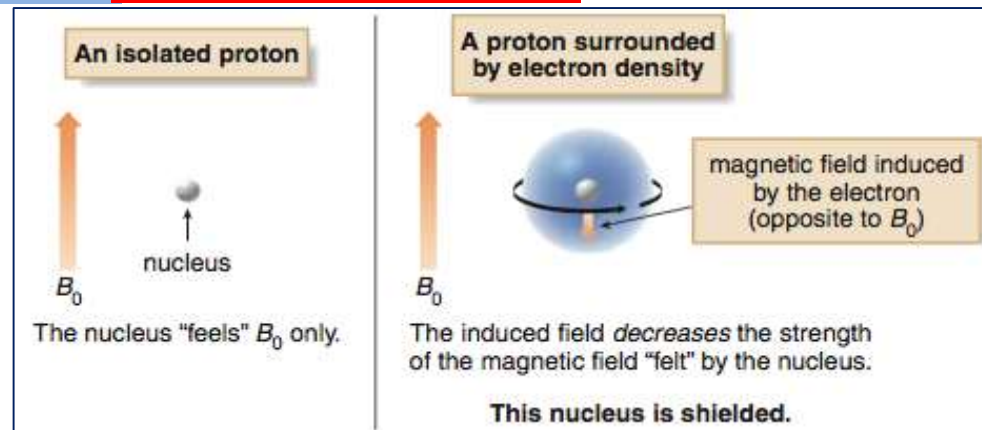
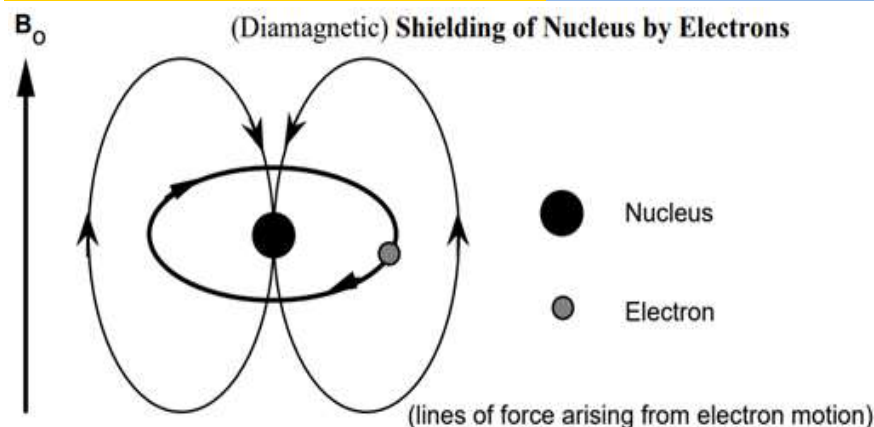
$^{13}\text{C}$  NMR of Ethanol



$^1\text{H}$  NMR of Ethanol

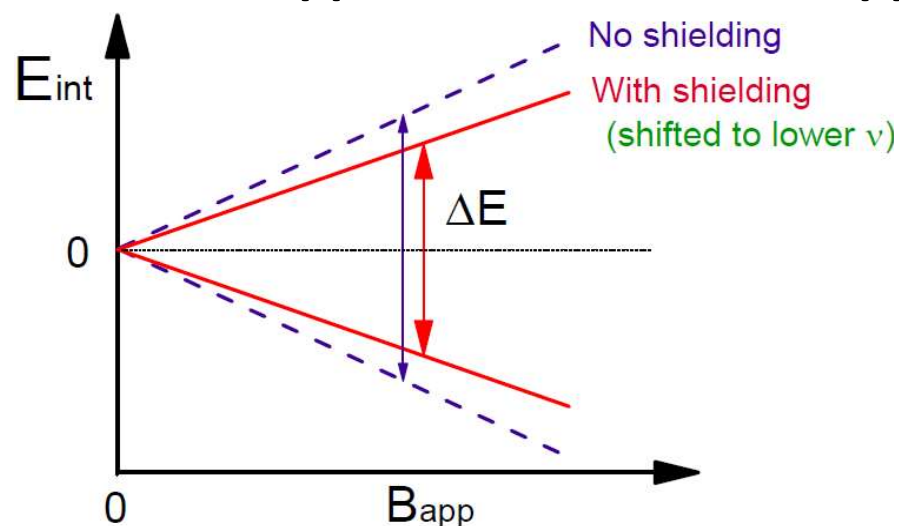
**WHY DIFFERENT PEAKS FOR DIFFERENT HYDROGENS (OR CARBONS) ?**

# Nuclear Resonance: What do we mean by "shielding"?



- An external magnetic field affects the motion of the electrons (spinning charged particles) and induced an additional magnetic field ( $B_{\text{add}}$ ) around the nucleus within the molecule. The direction of the induced magnetic field is opposite to that of the applied magnetic field.

$$B_{\text{add}} = -\sigma B_0$$



(Shielding factor  $\sigma$ ); It can be  $-ve$  or  $+ve$  depending upon whether the induced field adds to  $B_0$  or subtracts from the  $B_0$ . Thus, effective (net or local) magnetic field experienced by each nuclei is  $B_{\text{eff}}$  (not  $B_0$ )

## Nuclear Resonance: Reason for multiple peaks for proton



- Within a given external applied field  $B_o$ ,  $^1\text{H}$  nuclei in different chemical environments experience a slightly different effective (local or net) magnetic field due to chemical shielding from surrounding electrons and thus nucleus resonate at different frequency.
- Here, the shielding effect can be taken into account by expression:

$$B_{\text{eff}} = B_o + B_{\text{add}} = B_o - \sigma B_o \Rightarrow B_{\text{eff}} = B_o(1-\sigma)$$

$$\Delta E = \gamma_N \hbar B_{\text{eff}} \Rightarrow \nu = \gamma_N B_{\text{eff}} / 2\pi = \gamma_N B_o(1-\sigma)/2\pi$$

- The electron density around the  $^1\text{H}$ -nucleus have direct influence on the local magnetic field or *shielding factor* ( $\sigma$ ) exerted by the nucleus in a magnetic field, thus more electron density around nucleus means more diamagnetic shielding.
- Each chemically different  $^1\text{H}$  nuclei experience a slightly different effective field and thus, resonate at different frequency.

## Nuclear Resonance: "chemical shift"



- Resonant frequencies being dependent on strength of external magnetic field, are difficult to remember and vary with the field strength.

$$\nu = \gamma_N B_o / 2\pi$$

- It is inconvenient to refer to proton frequency as 300,000,900 Hz or 600,001,800 Hz and it will vary with the strength of the magnetic field.

### How to get rid of field-dependence?

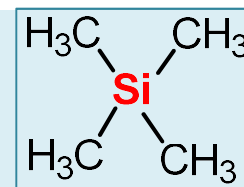
- Plot of spectrum could be in terms of a number that could be remembered easily rather than the exact value of resonant frequencies for nuclei on different environment.

## Nuclear Shielding and chemical Shifts



- Instead of actual frequencies of resonance, a reference is taken and the frequency are calibrated with respect to the reference and normalized with respect to the spectrometer frequency.

- **Tetramethyl silane ( $\text{Si}(\text{CH}_3)_4$ ) is used as reference in NMR spectra.**



- ✓ Hydrogen Nuclei are highly shielded. The chemical shift of TMS is lower than most of the protons in the organic compounds, so taken as zero.
- ✓ All the protons in TMS (no. 12) are equivalent (same chemical environment) and will resonate at same larmor frequency ( $\nu_0$ ) (i.e. one high signal intensity signal will be obtained) and we can set that ( $\nu_0 = 0$ ) as zero (while plotting).
- ✓ TMS is an inert, volatile liquid and miscible with most solvents. Thus, removed easily without any reaction with the sample.

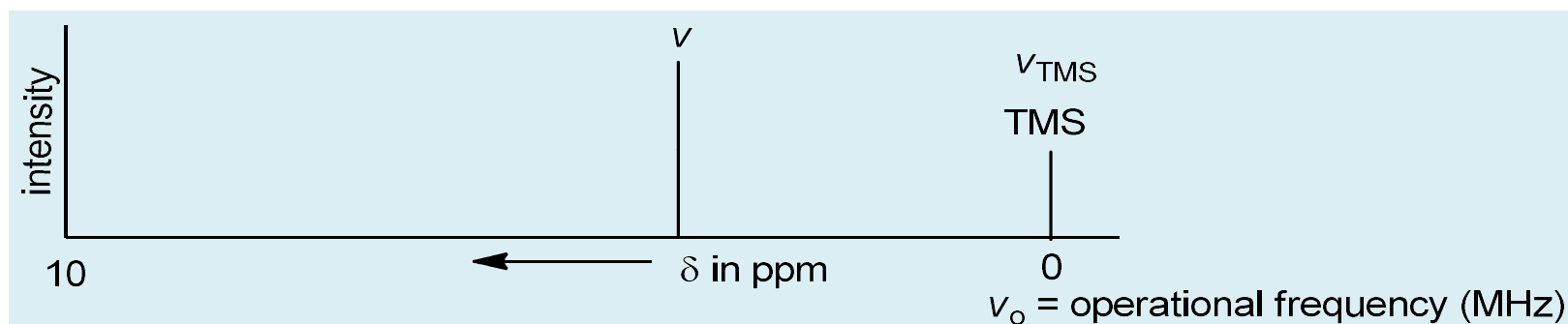
# Nuclear Shielding and chemical Shifts



- Measure the difference in the Resonant freq. of a nuclei ( $\nu$ ) with reference to the resonant frequency ( $\nu_0$ ) of the same nuclei of a reference compound and normalized to the spectrometer frequency.
- For example:  $B_0 = 9.3$  T, TMS protons resonate exactly equal to 400 MHz. Thus we can take this as a reference and determine the resonant frequencies of different  $^1\text{H}$  nuclei in a compound.

$$\text{Chemical shift: } \delta = \{(\nu - \nu_{\text{TMS}}) / \nu_0\} \times 10^6$$
$$= \{\text{chemical shift in Hz/operating frequency in MHz}\} \times 10^6$$

- Vertical scale = Intensity of the signal
- Horizontal scale = chemical shift ( $\delta$ ), independent upon the field strength of the external magnetic field. For  $^1\text{H}$  ( $\delta$ ) is usually from 1-10 ppm (parts per million).





# Nuclear Shielding and chemical Shifts



$$\text{Chemical shift: } \delta = \{(\nu - \nu_0) / \nu_0\} \times 10^6$$

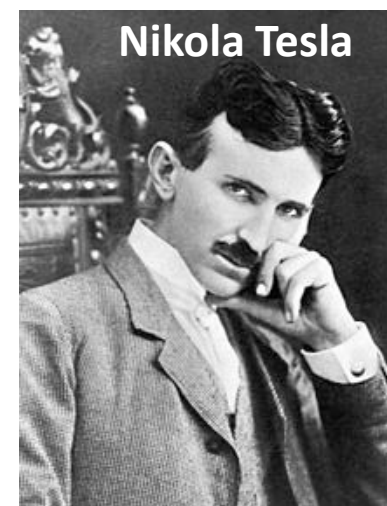
$\nu_0$  : Larmor (resonating) freq. of  $^1\text{H}$  nuclei of TMS

$\nu$  : Larmor (resonating) freq. of a particular  $^1\text{H}$  nuclei in a compound

**Chemical Shift: Difference between the resonant frequency of a hydrogen nuclei of a compound with that of hydrogen nuclei in TMS OR a measure of the degree to which a nucleus in a molecule is shielded**

- The chemical shift: Resonating frequency is telling us the strength of the magnetic field that the nucleus feels.

$B_0$ (Tesla)	1.41	2.35	7.05	9.39	11.74	14.09
MHz ( $\nu$ )	60	100	300	400	500	600



❖ If the spectrum is run at a magnetic field strength that generate precessional frequencies of 300 MHz (300 million cycles per sec, 7.05 Tesla), 1 ppm is equal to 300 Hz (300 cycles per second ). At 600MHz, 1 ppm = 600 Hz. Chemical shifts reported in ppm are independent of the field strength.

•  $\delta$  (ppm units) = shift from TMS in Hz / radiofrequency in MHz

For example: Cl-CH<sub>2</sub>-O-CH<sub>3</sub> shows two absorptions peak for <sup>1</sup>H.

• On a 90 MHz NMR, <sup>1</sup>H resonances are at 90,000,300 Hz and at 90,000,480 Hz (the instrument is tuned so that TMS absorbs at exactly 90,000,000 Hz)

- $\delta = 300 \text{ Hz} / 90 \text{ MHz} = 3.3 \text{ ppm}$
- $\delta = 480 \text{ Hz} / 90 \text{ MHz} = 5.3 \text{ ppm}$

• Note that on a higher-field instrument (e.g., 500 MHz), the chemical shifts would be the same although the absolute differences (in Hz) would be larger e.g., the proton resonances would be at 500,001,650 Hz (3.3 ppm) and 500,002,650 Hz (5.3 ppm). (Now  $\delta$  value is independent to the applied magnetic field.)

- Higher fields afford higher resolution:
  - better separation of absorptions
  - resonances typically look sharper at higher fields

## Nuclear Shielding and chemical Shifts



Q. In a particular experiment, the reference signal (TMS) occurs at exactly 100 MHz. The signal for a sample proton (X) is observed at 100 000 579.

(i) What is the absolute shift expressed in Hz?

Absolute shift = resonance frequency of proton X – operating frequency of instrument

$$= 100\,000\,579 - 100\,000\,000 = 579 \text{ Hz.}$$

(ii) What is the absolute chemical shift expressed in ppm.

Relative shift = chemical shift = (absolute shift/operating frequency)  $\times 10^6$

$$= (579/100\,000\,000 \text{ Hz}) \times 10^6 = 5.79 \text{ ppm}$$

Q. A signal for acetone ( $\text{CH}_3\text{COCH}_3$ ) is observed at 200 000 440 Hz and 400 000 880 Hz at 200MHz and 400 MHz NMR spectrometer respectively. What is the absolute chemical shift ( $\delta$ ) in ppm?

(i) Absolute shift = resonance frequency of proton X – operating frequency of instrument (200 MHz)

$$= 200\,000\,440 - 200\,000\,000 = 440 \text{ Hz.}$$

Relative shift = chemical shift = (absolute shift/operating frequency)  $\times 10^6$

$$= (440/200\,000\,000 \text{ Hz}) \times 10^6 = 2.2 \text{ ppm}$$

(ii) Similarly at 400 MHz,  $\delta = 2.2 \text{ ppm}$

Now, these are independent of the strength of an operating magnetic field.