CHEM F111 : General Chemistry
Semester II: AY 2017-18
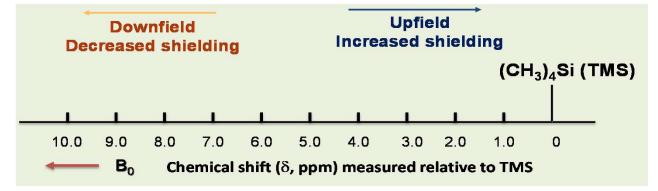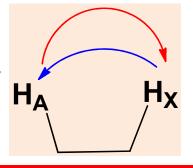### Lecture 20 (28-02-2018)

- **No. of peaks** in ^{1}H NMR spectrum equals the no. of distinct sets of "equivalent" protons.
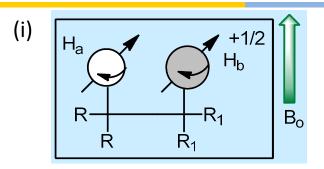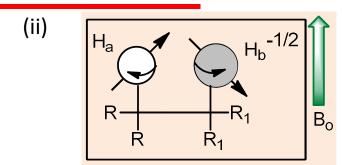

- $\sigma_{neighbour}$ **effect of neighboring environment: Anisotropic effect**

- **Intensity of a peak** is directly proportional to the no. of equiv. protons responsible for the peak (its given by area under peak).

- **Splitting of peaks:** The peaks in ^{1}H NMR spectrum are splitted into fine structures due to spin-spin coupling.

- **If a proton has n neighbors (protons attached to adjacent carbons), it will split into n+1 lines. Only nonequivalent protons couple.**

Effect of neighboring protons: Spin-spin coupling:

(i)

H_a H_b $+1/2$

R—R$_1$
R   R$_1$

B_o

(ii)
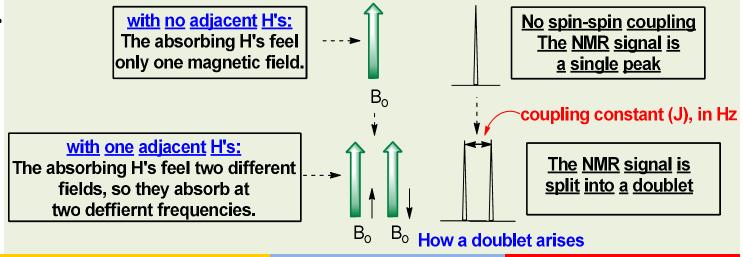
H_a H_b $-1/2$

R—R$_1$
R   R$_1$

B_o

- **The neighboring C-H is half the time aligned with the magnetic field and half the time aligned against the magnetic field.**
- **Due to this, the magnetic field of the nuclei whose peak is observed is perturbed slightly by the tiny fields of its neighboring ^1H nuclei**
- **H_a either feel a deshielding or a shielding effect from their neighbor (C-H$_b$), depending on whether its spin is aligned with or against the applied magnetic field.**

with no adjacent H's:
The absorbing H's feel only one magnetic field.

B_o

No spin-spin coupling
The NMR signal is a single peak

coupling constant (J), in Hz

with one adjacent H's:
The absorbing H's feel two different fields, so they absorb at two deffiernt frequencies.

B_o B_o

The NMR signal is split into a doublet
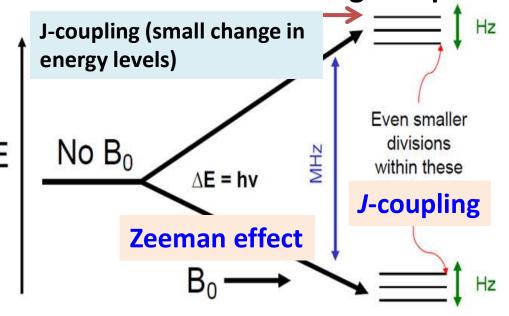
How a doublet arises

> (i) Chemical shift of proton H_a (deshielded- proton H_b has spin aligned with applied field)
>
> (ii) Chemical shift of proton H_a (shielded- proton H_b has spin opposed with applied field)
>
> Chemical shift of proton H_a if proton H_b is absent

- **This interaction is known as coupling and causes peaks to be split into a number of lines.**
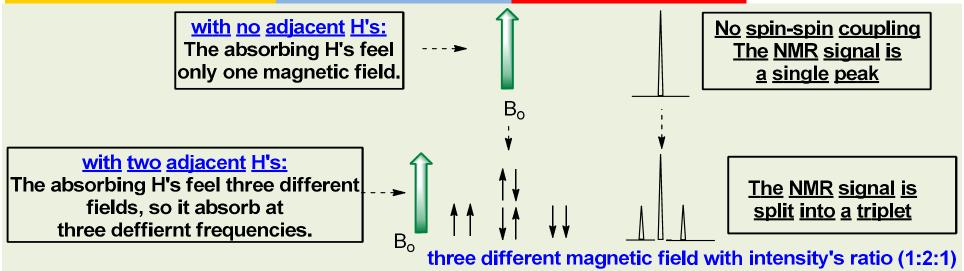- **When ^1H nuclei on one carbon is excited, the ^1H nuclei on neighboring carbons can be in either the lower or the higher spin state, with nearly equal probabilities.**
- **The spin state of one nucleus can create a slightly different B_{eff} in a Neighboring nucleus that gives us splitting of peaks.**
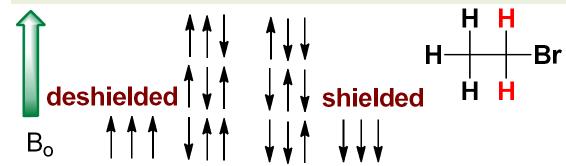
J-coupling (small change in energy levels)

E

No B_0

$\Delta E = hv$

MHz

$B_0 \longrightarrow$

Zeeman effect

Hz

Even smaller divisions within these

J-coupling

Hz

Spin-spin coupling: For example CH_3CH_2Br

with no adjacent H's:
The absorbing H's feel only one magnetic field.

B_o

No spin-spin coupling
The NMR signal is a single peak

with two adjacent H's:
The absorbing H's feel three different fields, so it absorb at three deffiernt frequencies.

B_o

The NMR signal is split into a triplet

three different magnetic field with intensity's ratio (1:2:1)

1. Both aligned with field
2. One aligned with the field and one against it (2 combinations); and
3. Both aligned against the field

• The two X nuclei may have the $2^2 = 4$ spin arrangements. The middle two arrangements are responsible for the coincident resonance of H_a.
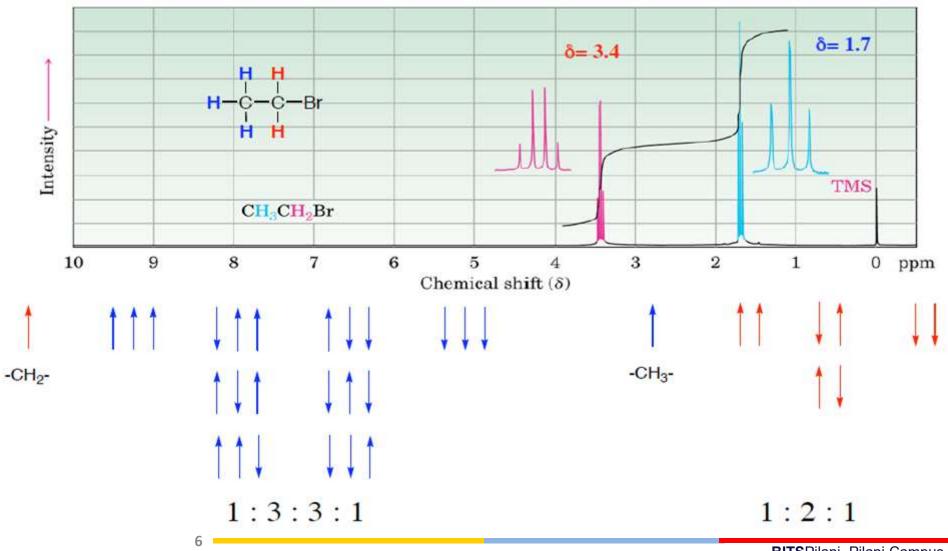
deshielded   shielded

B_o

H   H
H—┼——┼—Br
H   H

There are $2^3 = 8$ arrangements of the spins of the three H nuclei, and their effects on the H nucleus gives rise to four groups of resonances.

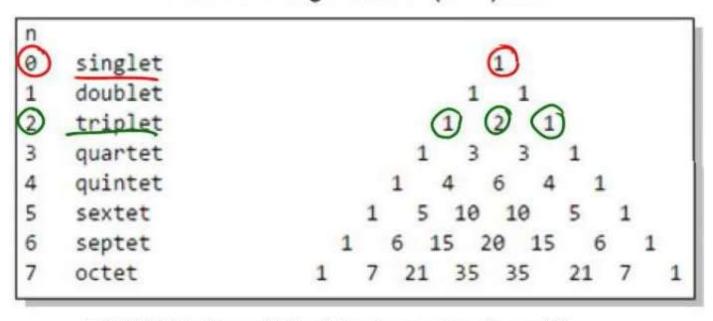**four different magnetic field with intensity's ratio (1:3:3:1)**

GENERAL RULE: If a proton has n neighbors (protons attached to adjacent carbons), it will split into n+1 lines. Only nonequivalent protons couple.
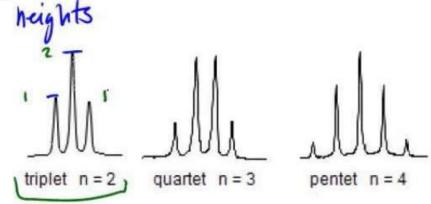
Multiplets when (n+1) rule works: Pascal's triangle

Pascal's Triangle with the (n + 1) Rule

n		
0	singlet	1
1	doublet	1 1
2	triplet	1 2 1
3	quartet	1 3 3 1
4	quintet	1 4 6 4 1
5	sextet	1 5 10 10 5 1
6	septet	1 6 15 20 15 6 1
7	octet	1 7 21 35 35 21 7 1

EXAMPLE: How will the following protons be split?

heights

2

1

r

triplet n = 2   quartet n = 3   pentet n = 4

All the *J*-values are equal for chemically equal protons

Spin-spin coupling constant (*J*)
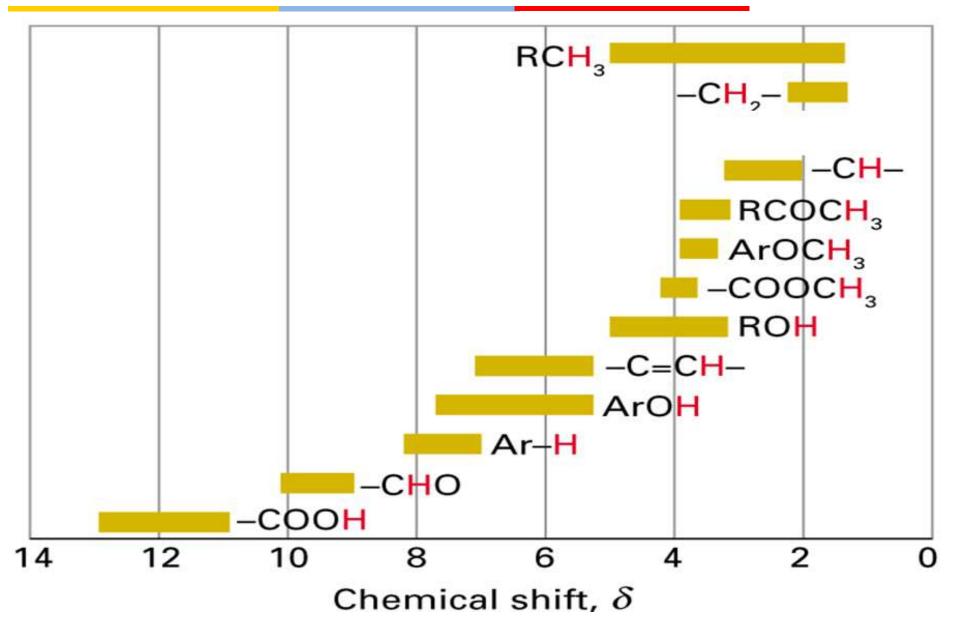
$^1J_{CH}$ means the coupling ^{13}C-^1H ➡ **Not observed**

H_X ⟋ H_Y
$^1J \, _{^{13}C\text{-}H_Y}$

$^2J_{CH}$ means the coupling ^{13}C- C-^1H ➡ **Not observed**

H_X ⟋ H_Y
$^2J \, _{^{13}C\text{-}H_Y}$

^3J is low but detectable ➡

H_X ⟋ H_Y
$^3J_{HH}$

• **The separation of the lines of a multiplet is *J*, the coupling constant, measured in Hz. *J* is independent of magnetic field (B).**

•**all peaks in the spin-coupled multiplet are separated by the same amount of *J*.**

•**coupling is strong for nearest neighbors H-C-C-H, and small for more distant neighbors**

•**equivalent Hs don't split one another (i.e., ethane is a singlet, not 2 quartets)**

•**Equivalent Hydrogens have same chemical Shifts and Intensity of a peak is directly proportional to the no. of equiv. protons responsible for the peak (its given by area under peak).**

1. Number of signals: number of equivalent hydrogens in the molecule.

2. Position of signals (δ, chemical shift): indicate chemical environments for these equivalent hydrogens.

3. Relative areas under signals (integration or intensities): indicate the number of H's of each type.

4. Splitting pattern: indicate the number of neighboring hydrogen nuclei.

CH_3CHO 2 peaks; d (1:1, 3H), q (1:3:3:1, 1H);   [3:1]

$CH_3COCH_2CH_3$ 3 peaks; s (3H), q (1:3:3:1, 2H), t (1:2:1, 3H);   [3:2:3]

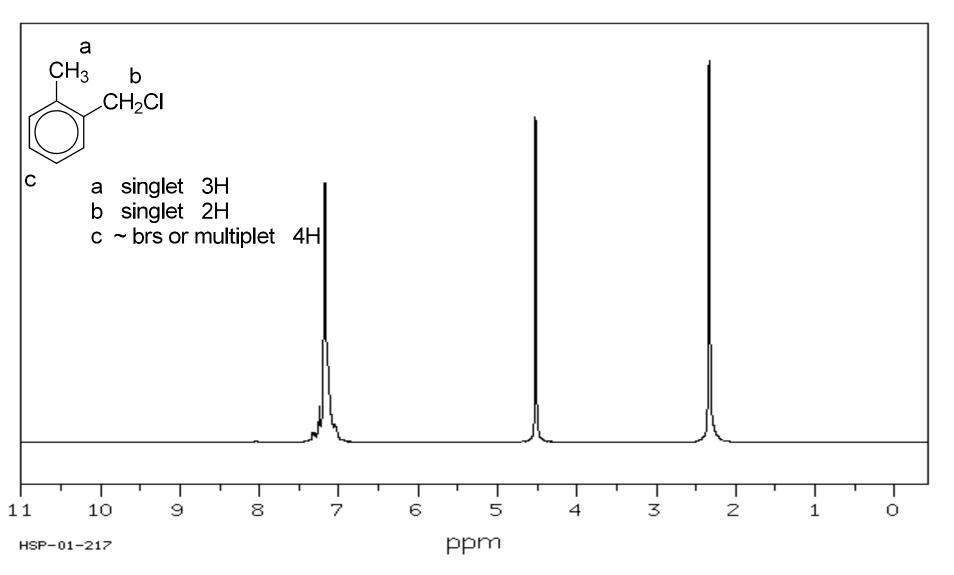CH_3COOCH_3 2 peaks, s (3H), s (3H);   [1:1]

$CH_3CH_2CHClCH_3$ 4 peaks, t (1:2:1, 3H), m (1:4:6:4:1, 2H), m (1:5:10:10:5:1, 1H), d (1:1, 3H);   [3:2:1:3]
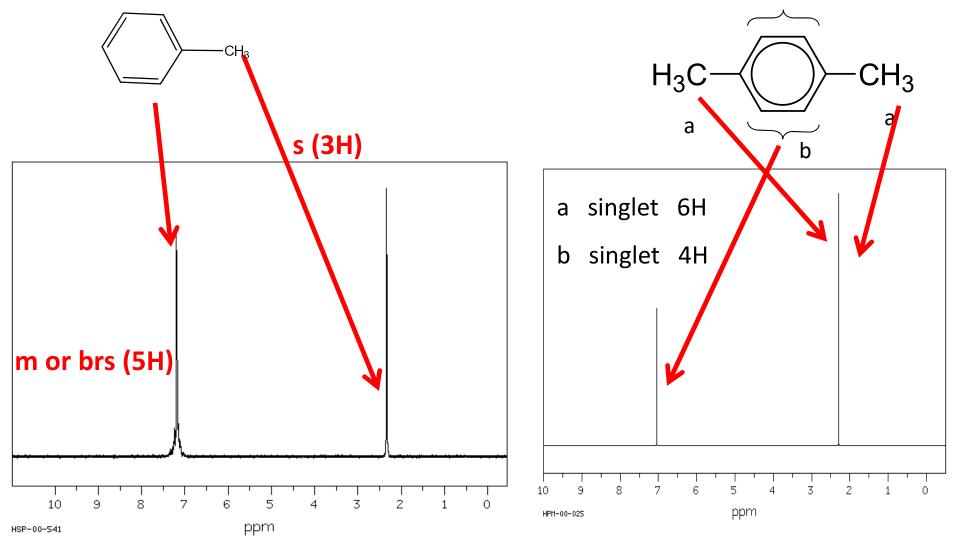
C_6H_6 1 peak (s, 6H)

o-methylbenzyl chloride

a CH₃

b CH₂Cl

c

a singlet 3H
b singlet 2H
c ~ brs or multiplet 4H

11 10 9 8 7 6 5 4 3 2 1 0

ppm

HSP-01-217

innovate   achieve   lead

s (3H)

a   singlet   6H

b   singlet   4H

m or brs (5H)

HSP-00-541

ppm

HPM-00-025   ppm

m: multiplet or brs: broad singlet

Carbon-13 NMR spectroscopy

CARBON-13 NMR:

Carbon-12 nucleus is spin inactive, I = 0 (NMR inactive)
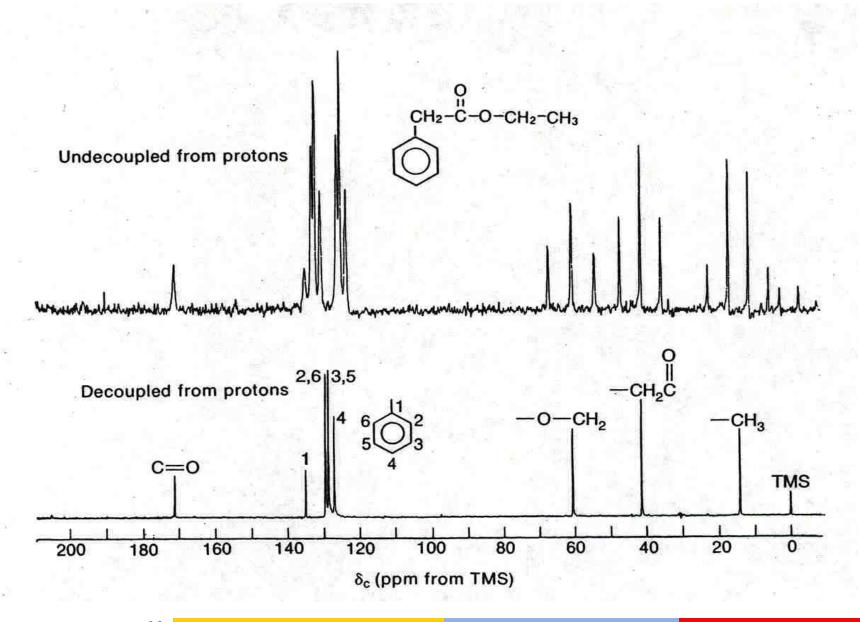
Carbon 13 nucleus is spin active , I = ½ (NMR active)

Solvent	^{1}H-NMR shift (multiplicity)	^{13}C NMR shift (multiplicity)
Chloroform-d (CDCl$_3$)	7.24 (singlet)	77.0 (triplet)

- **Carbon-13 NMR is usually recorded under conditions of proton decoupling.**
- **However, coupling with protons detectable. (Very strong: J ~ 100-200 Hz).**
- **Thus, all the ^{13}C-^{1}H coupling are decoupled by irradiation (saturation) of all the protons and only a single signal is observed for each of the chemically different carbons.**

^{13}C-NMR spectroscopy

Interesting facts associated with ^{13}C NMR

- For ^{13}C, γ_N= 6.7X10^7 T^{-1}s^{-1} (4 times less than for ^{1}H)

- Resonant frequency or field strength required for ^{13}C-NMR has to be 4 times less than in case of ^{1}H NMR.

- Isotopic abundance is 1.11% (for 1H = 99.98%)

- ^{13}C-NMR signals are about 5672 times weaker than in ^{1}H NMR.

- Spin-spin coupling of between C-atoms not observed.

- ^{13}C experiments require higher concentration and more scans/time.

- Only 02 Carbon nuclei is in excess per 2 million nuclei on a 1.41 T magnetic field strength (This number is 09 nuclei for H nucleus).
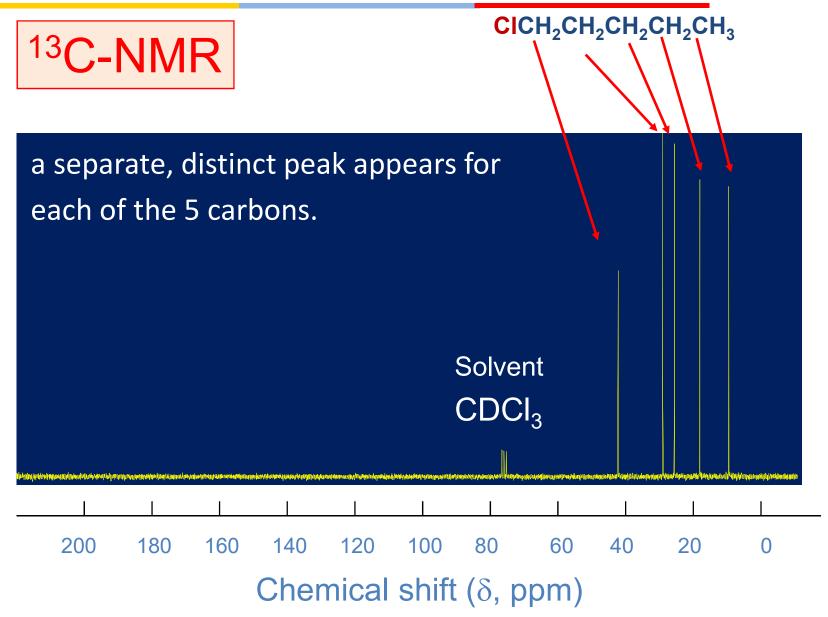
Even though, C-13 NMR spectroscopy is possible and very useful in organic chemistry for structure elucidation.
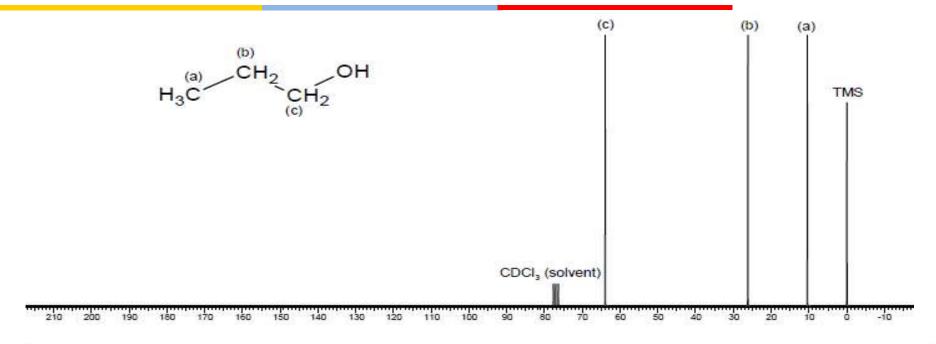
BITSPilani, Pilani Campus
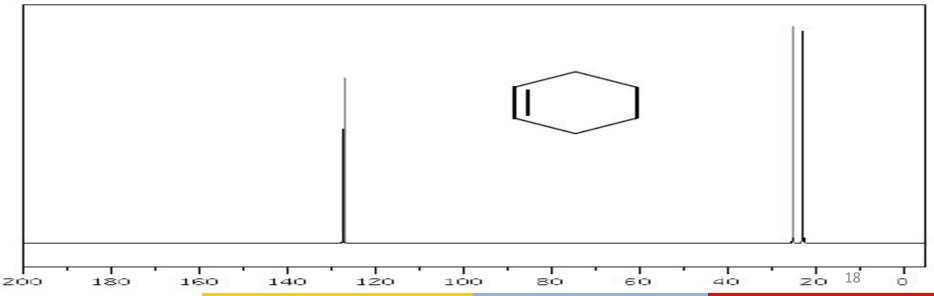
^{13}C-NMR provides information on:

- **Number of chemically different carbons:** The number of distinct kinds of carbons atoms present equals the number of peaks in a proton decoupled ^{13}C spectra.
- The All carbon peaks appears as singlets when decoupled from protons.
- **Chemical shift information:** The chemical environment of the carbon
- chemical shift (δ_c) is given in ppm, the usual range = 0-250 ppm with the zero being the methyl carbon in TMS.
- ^{13}C are shielded and deshielded (chemical shift) due to the same factors as for ^{1}H-NMR.
  - Electron withdrawing ability of the nearby group
  - Hybridization
  - Electron current effects

$ClCH_2CH_2CH_2CH_2CH_3$

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

Solvent
$CDCl_3$

Chemical shift (δ, ppm)

200 180 160 140 120 100 80 60 40 20 0

(c)   (b)   (a)

(b)
(a) CH₂ OH
H₃C   CH₂
(c)

TMS

CDCl₃ (solvent)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

200 180 160 140 120 100 80 60 40 20 18 0

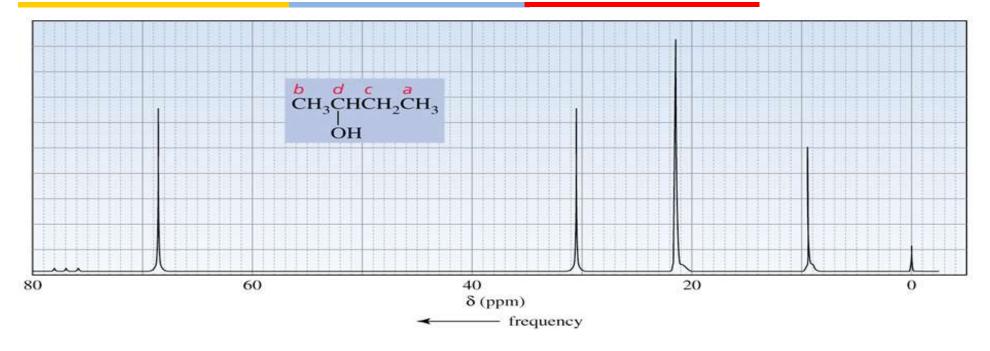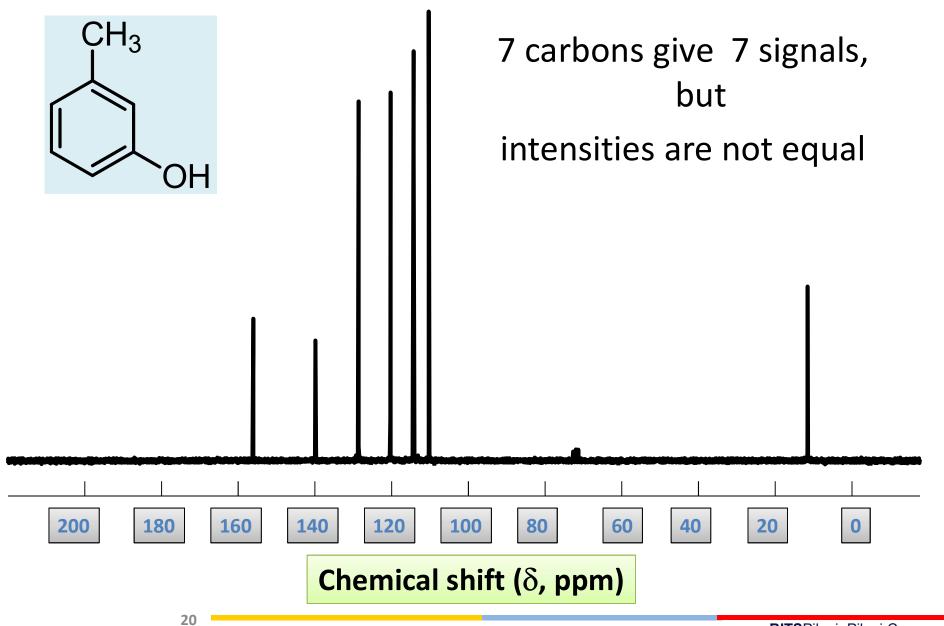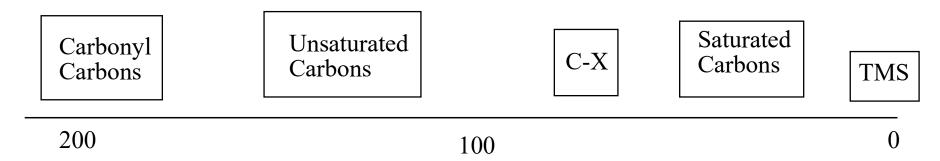The NMR spectrum of $CH_3CHCH_2CH_3$ with OH group, labeled b, d, c, a.

- Interestingly, ^1H-NMR spectrum does not give any signals for groups such as internal acetylene, tetrasubstitutued olefins, CN, CO and quarternary carbons.
- Whereas, the groups like acetylene carbons, CN, CO, quarternary carbons (no protons) are easily detected by the Carbon-13 NMR.
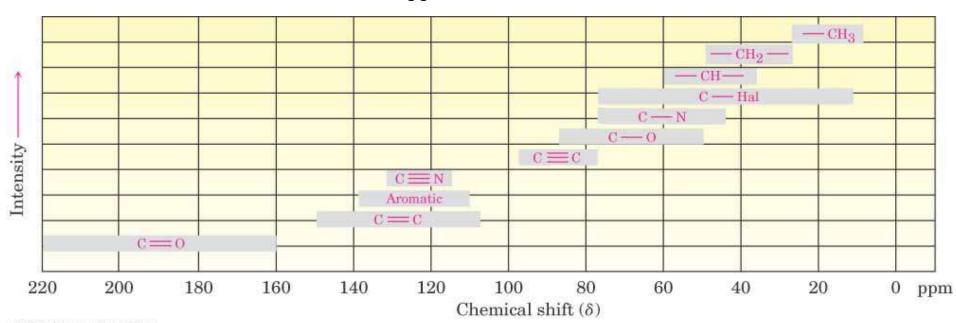
7 carbons give 7 signals, but intensities are not equal

Chemical shift (δ, ppm)

| Carbonyl Carbons | | Unsaturated Carbons | | | C-X | | Saturated Carbons | | TMS |

200   100   0

ppm

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^{1}H and ^{13}C-NMR technique

- **Information from ^{1}H and ^{13}C-NMR**

1. **Number of signals**   **(chemically different nucleus)**

2. **Chemical shift of signals**   **(shielded or deshielded w.r.t reference)**

3. **Intensity of signals**   **(population difference, number of nuclei)**

4. **Spin-spin splitting of signals (interaction with nearby nucleus, only for 1H)**