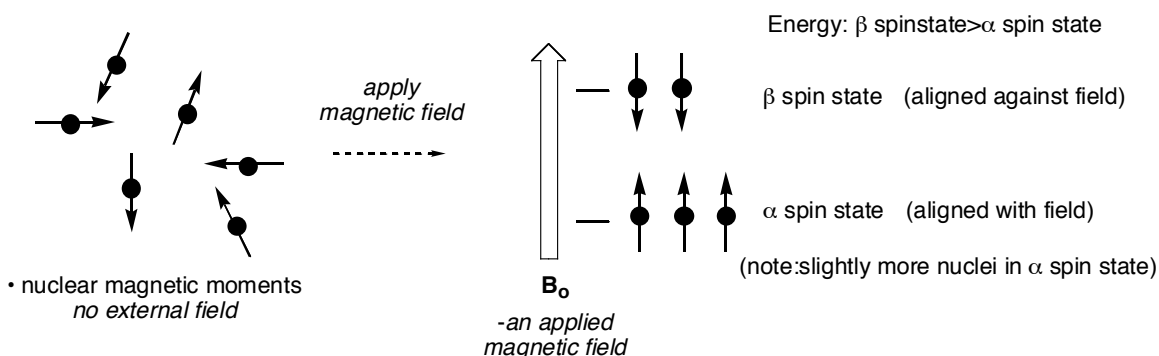# Chem 203: ^{1}H (Proton) Nuclear Magnetic Resonance (NMR) Spectroscopy

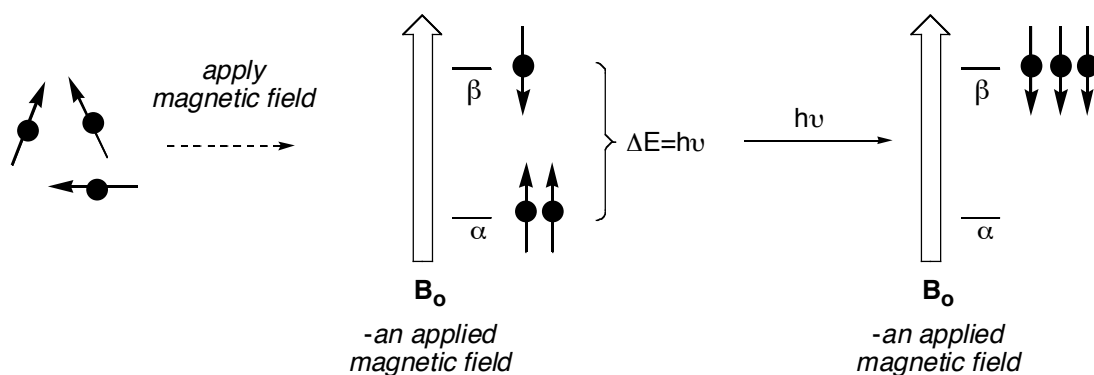*• the most powerful tool for structure determination*

a) basis for NMR spectroscopy is *nuclear spin*

b) all nuclei have charge and mass. Those with *odd* atomic numbers or mass possess nuclear spin   e.g. ^{1}H, ^{13}C, ^{19}F, ^{31}P   these element's nuclei possess spin, have angular momentum or magnetic moments

c) when nuclei possessing spin are placed in a magnetic field, their magnetic moments align with or against the field

Energy: β spinstate>α spin state

β spin state   (aligned against field)

α spin state   (aligned with field)

(note:slightly more nuclei in α spin state)

• nuclear magnetic moments
    no external field

B$_o$
*-an applied
magnetic field*

d) **resonance** (or spin-flipping) takes place when the sample is irradiated with energy just sufficient to convert a nucleus with an α-spin state to a β-spin state

β

$\Delta E = h\upsilon$

α

hυ

β

α

B$_o$
*-an applied
magnetic field*

B$_o$
*-an applied
magnetic field*

The energy difference ΔE depends on the strength of the applied field, **B$_o$** (also called H$_o$) and characteristics of nuclei.

e) for ^{1}H, ^{13}C, ^{19}F, ^{31}P

constant characteristic
of nuclei

Planck's constant

the strength of the magnetic field
*felt by the nucleus (not **B$_o$**!)*

$$\Delta E = h\upsilon \quad = \quad \frac{h\ \delta\ \mathbf{B}}{2\pi}$$

B (magnetic field felt by nucleus) is NOT equal to **B$_o$**

actually **B**=**B$_o$**—**b$_{local}$** ← *a small induced field opposed to the magnetic field; a function of the
electron density around the nucleus*

The magnetic field felt by the ^{1}H nucleus depends on the electron density around the nucleus. Electrons around the nucleus set up tiny local magnetic fields of their own. These fields act in opposition to the applied field and *shield* the nuclei from it. Therefore, *non-equivalent* protons in an organic compound resonate at *different positions* in a ^{1}H NMR spectrum.

chemical shift = a measure of the position of the resonating frequency of a given ^{1}H nucleus relative to that of the ^{1}H nucleus of a standard compound, tetramethylsilane (TMS)

resonance frequency of proton i (Hz)

$$\delta_i = \frac{\upsilon_i - \upsilon_{TMS}}{\upsilon_o}$$ resonance frequency of TMS (Hz)

given in ppm (parts per million)

operating frequency of spectrometer (MHz)

$CH_3-Si-CH_3$ with CH_3 above and CH_3 below

| 10 | 8 | 6.5 | 4 | 2.5 | 1.5 | 0 |

δ

less shielded   *more shielded*
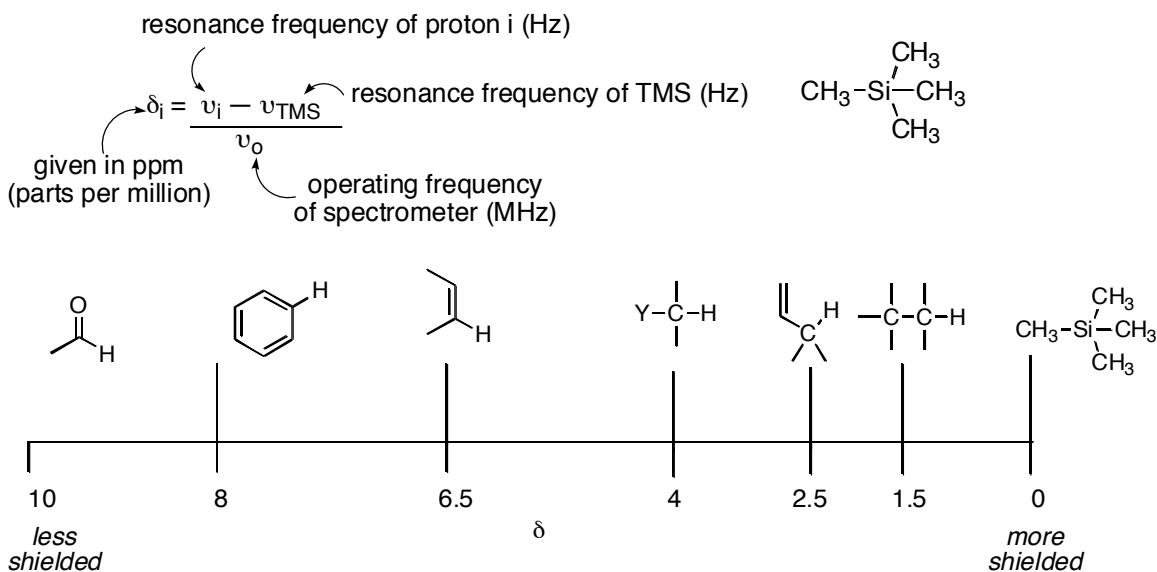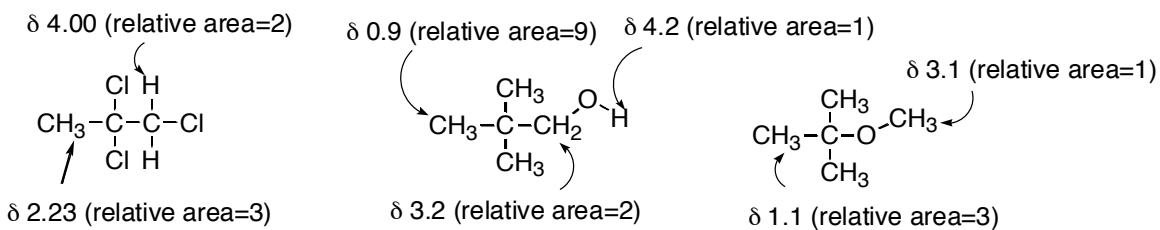
f) relative peak areas
- area under each signal is proportional to the number of protons giving rise to that signal. **Integration** of this area provides the **relative** number of protons in each signal.

g) structure and chemical shift
- different protons in different molecular environments experience different degrees of "shielding" and therefore resonate at difference field strengths (B_o) at constant υ.

less shielding→less electron density → resonate at lower field strengths (higher δ values)

more shielding→higher electron density → resonate at higher field strength (lower δ values)

δ 4.00 (relative area=2)   δ 0.9 (relative area=9)   δ 4.2 (relative area=1)

δ 3.1 (relative area=1)

δ 2.23 (relative area=3)   δ 3.2 (relative area=2)   δ 1.1 (relative area=3)

"equivalent" protons: replacement of H with X gives same compound (or enantiomer)

h) spin-spin coupling

• provides very useful structural information

• the actual magnetic field (B) experienced by one proton is modified by the actual spin-state (α or β; and the attendant fields $\pm$ b$_{local}$) of neighbouring protons. The result is *spin-spin coupling*
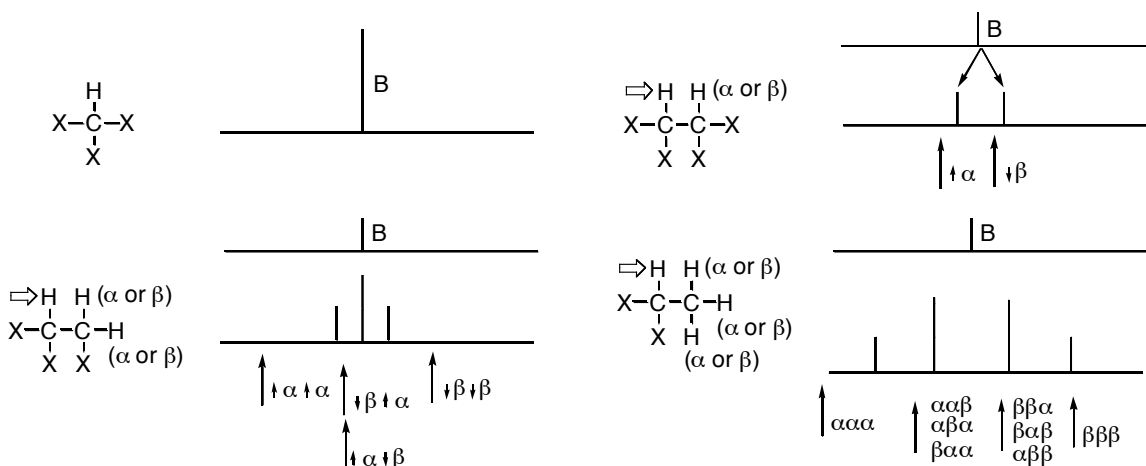
In general, if one is looking at the signal of H$_x$

# of adjacent protons	total # of peaks in signal of Hx	area ratio of the peaks
0	1 (singlet, s)	1
1	2 (doublet, d)	1:1
2	3 (triplet, t)	1:2:1
3	4 (quartet, q)	1:3:3:1
4	5 (quintet)	1:4:6:4:1
5	6 (sextet, hextet)	1:5:10:10:5:1
6	7 (septet, heptet)	1:6:15:20:15:6:1

This is the (n+1) rule.

The amount (size) of coupling (*J*) between two (groups of) protons is equal. The size is dependent on a number of variables, and varies from 0-20 Hz (typically ~7 Hz).

Important points:

• protons that *exchange* with D_2O are typically O-H or N-H groups
• compounds with ≥4 (four) degrees of unsaturation *may* contain an aromatic ring (a six membered ring with 3 double bonds in it). Look for NMR signals between δ 6.7 and 8.5

How to solve spectroscopy problems:

C_3H_7Cl δ: 4.05 (septet, ratio: 1); 1.40 (d, ratio: 6)

$C_6H_{11}Br_3$ δ: 6.35 (d, ratio: 1); 4.45 (d, ratio: 1); 1.20 (s, ratio: 9)

$C_4H_8O_3$ δ: 10.2 (s, ratio: 1, exchanges with D_2O); 4.15 (s, ratio: 2); 3.65 (q, ratio: 2), 1.3 (t, ratio: 3)