# Spectroscopy

① NMR Nuclear Magnetic Resonance

- Neucleus Spin State
- Radio frequencies
- Information on chemical enviroment of the observed neucleus

③ IR Infrared Spectroscopy

- Bond Vibrational frequencies
- InfraRed light
- Information on functional groups

② MS Mass Spectometry

- Time of flight of Charged particle
- Ionization using different techniques
- Ions travel through magnetic field
- Information on mass/Charge Ratio of particles or Molecules

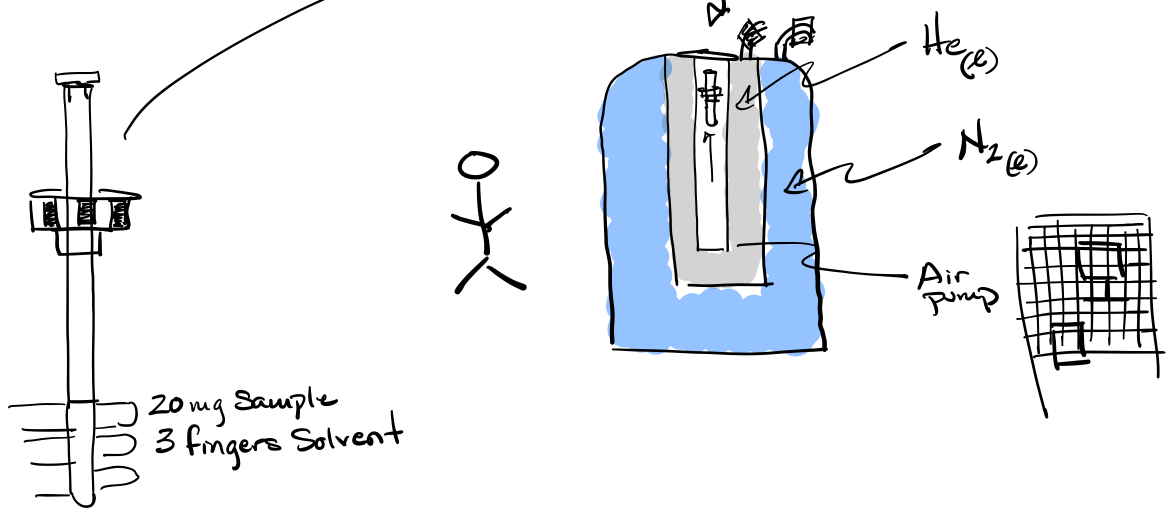
$M/Z$ ratio | $m$ = mass, $Z$ = Charge

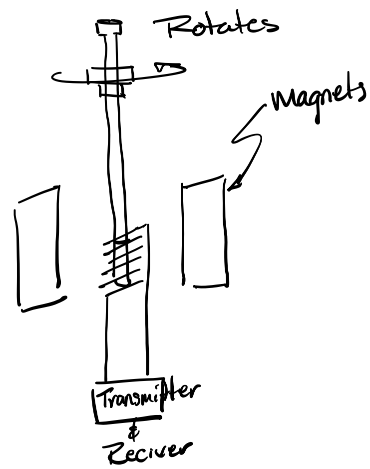
* Molecular Ion mass $M^{\cdot +}$

⟹ Molecular Weight of Molecule

⟹ Molecular formula

# NMR

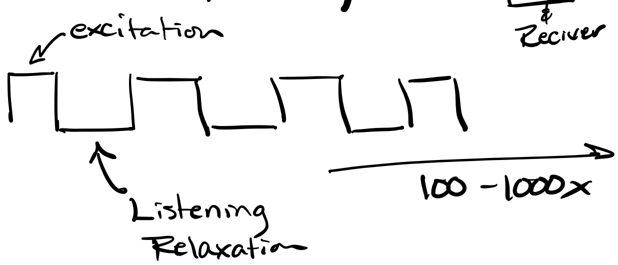



① Rotate sample

② Shimming
- Magnetic field homogeneous

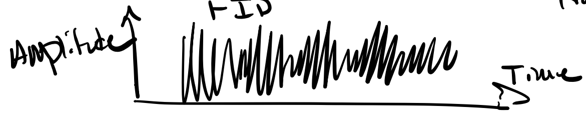
③ Acquisition
- Radio transmittions
- Radio Receiving

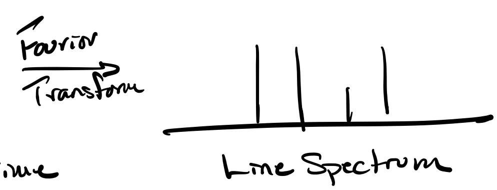



④ Data work up

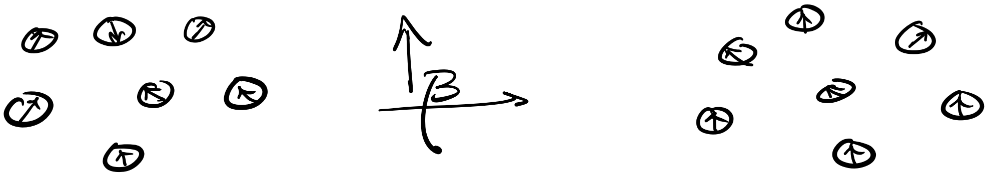
Free Induction Decay

FID

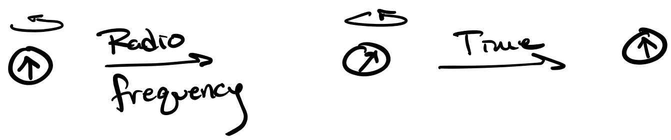


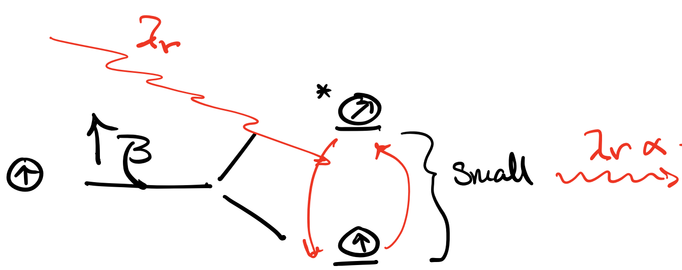



Individual Atom nucli




$>50\%$ are in ground state




$h\nu \propto$ to energy of transition

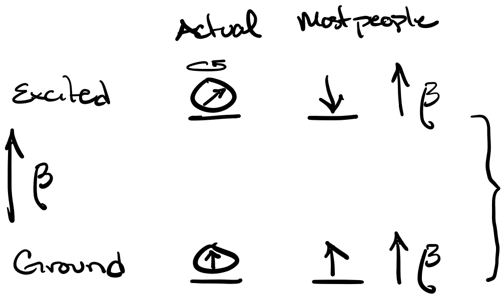
Only Some nucli are NMR Active

$I$ = Spin of nucleus

$I$ = odd #'s $\frac{1}{2}$, $\frac{2}{3}$ NMR Active

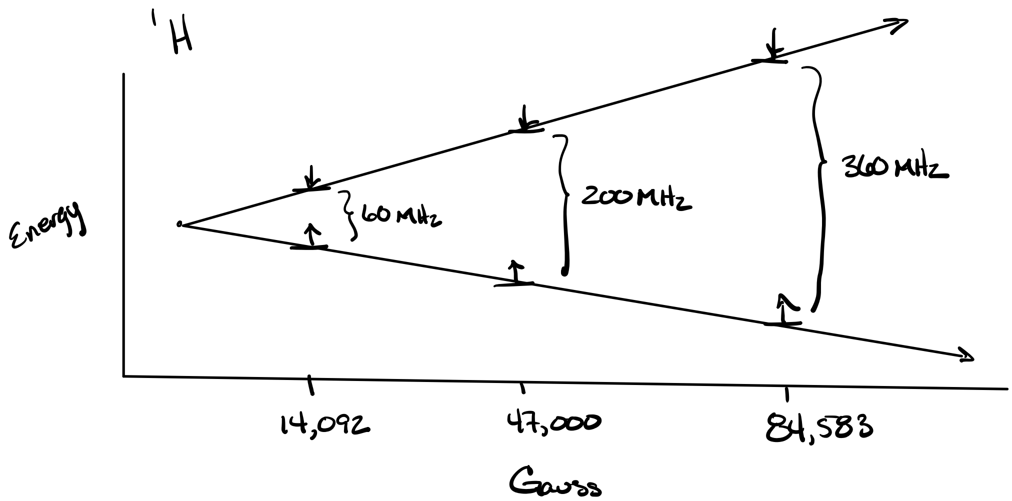
$I$ = even #'s 1, 2 NMR Inactive

| | $^{1}H$ | $^{2}H$ | $^{12}C$ | $^{13}C$ | $^{14}N$ | $^{15}N$ | $^{10}B$ | $^{11}B$ |
|---|---|---|---|---|---|---|---|---|
| $I$ | $\frac{1}{2}$ | 1 | 1 | $\frac{1}{2}$ | 1 | $\frac{1}{2}$ | $\frac{3}{2}$ | |
| %RAb | 99.985% | 0.015% | 98.9% | 1.1% | 99.6 | 0.366 | 19.9% | 80.1% |
| | fast | | | slow | | slow | | |




$\Delta E$ for Hydrogen $^1H$ 200 MHz

$^1H$ = 200,000,000 cycles/sec




NMR Instruments are rated by the $\Delta E$ between excited & ground state for $^1H$ NMR, 60 MHz, 200 MHz, 360 MHz, 500 MHz, 1 GHz

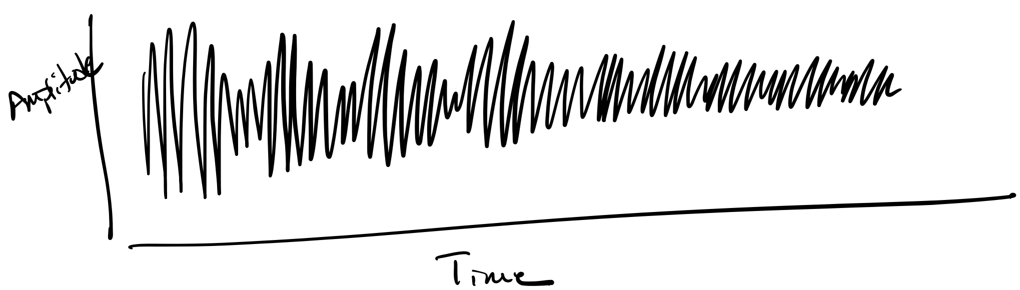
- Higher $\beta$ = Larger energy difference between excided & ground state

- The bigger the difference, the more atoms in ground state

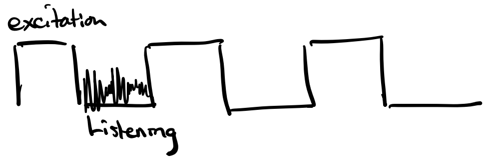
- more atoms excited
- more signal, fewer acquisition & less sample
  - less time doing experiment
  - more detail from experiment

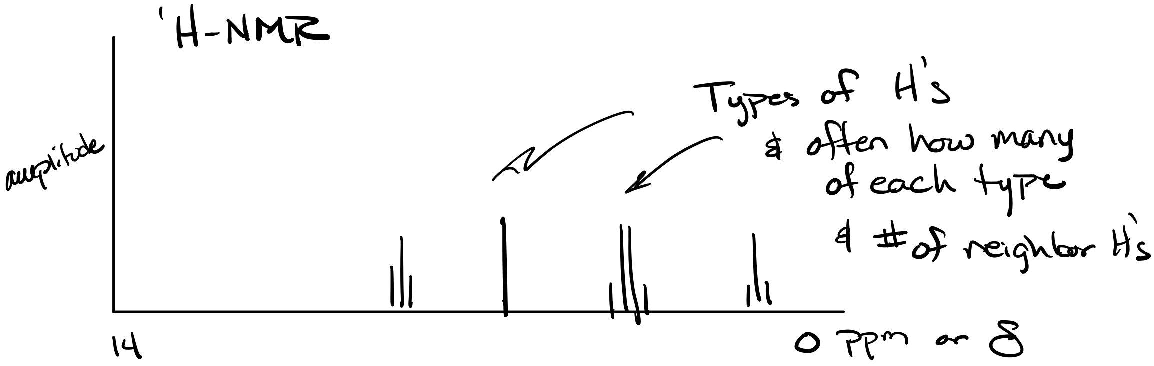
| | | | $^1H$ | $^{13}C$ |
|---|---|---|---|---|
| 60 MHz<br>90 MHz | fixed magnet<br>no cryogenics needed | \$120,000 | 30min | 2days |
| 200 MHz<br>250 MHz | | | 15 min | 1day |
| ↓ | | | | |
| 500 MHz | | \$1,000,000 | 2min | 30min |
| ↓ | | | | |
| 1GHz | ? | | | |

Signal




Free Induction decay






ppm = parts per million

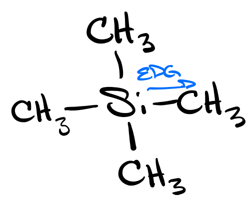
δ = Chemical shift in parts per million

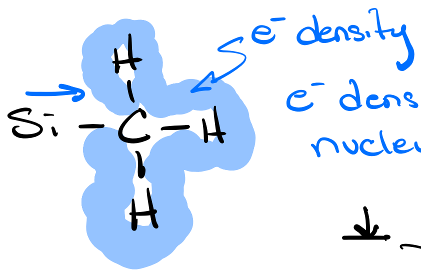
$$\delta = \frac{\nu_{sample} - \nu_{Reference\ (TMS)}}{\nu_{applied}} \times 10^{6} = \text{ppm}$$

small Hz

super large MHz

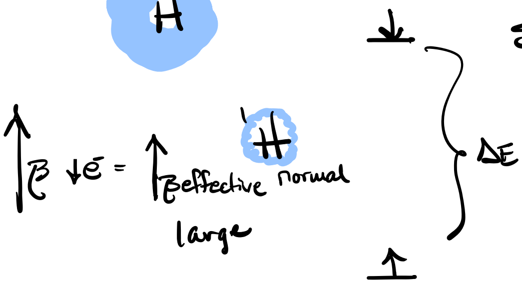
Reference Compound TMS

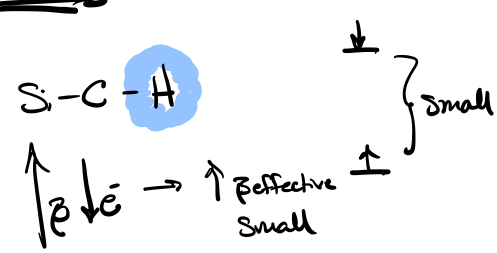
Tetramethylsilane  0 ppm

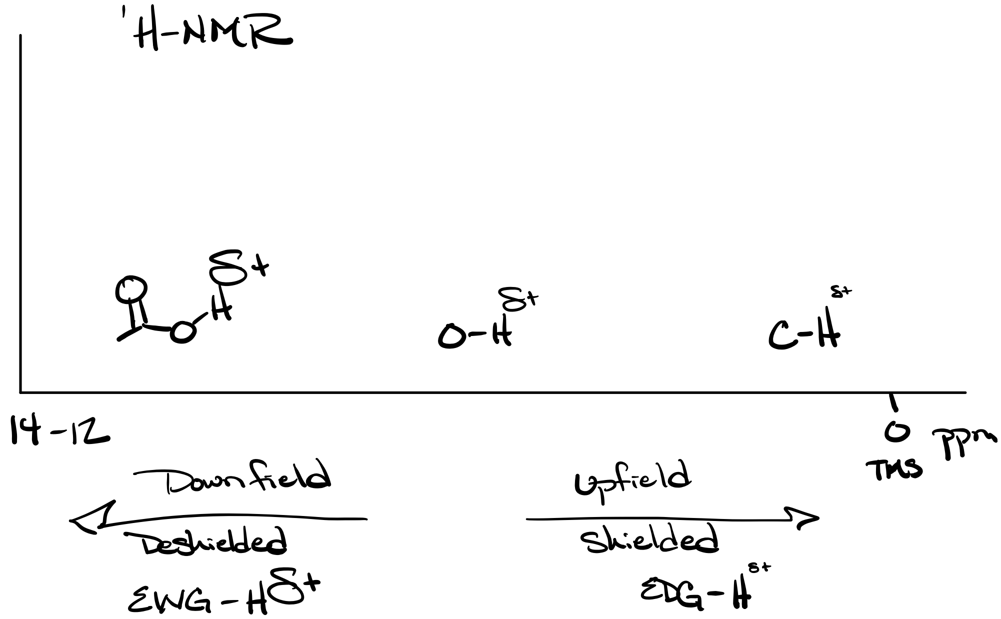




e⁻ density shields the nucleus from the B field

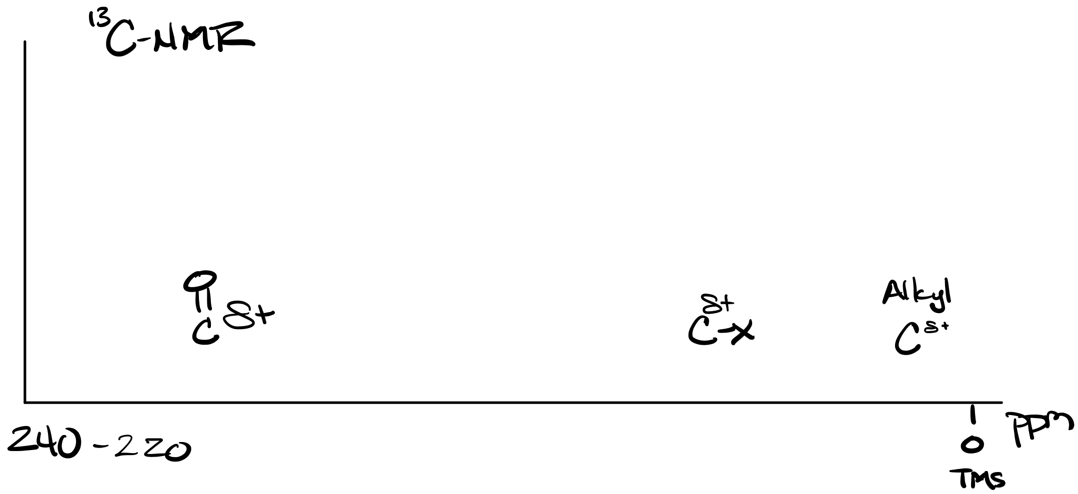
<u>Shielding</u>



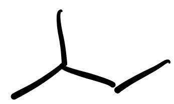



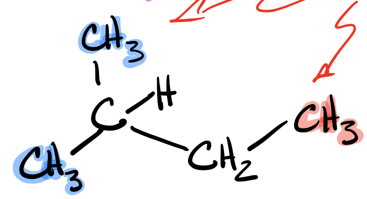



Chemical Environment

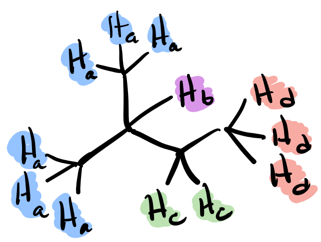


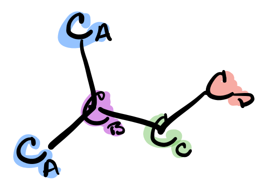
# Chemical Enviroment





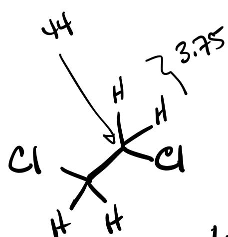

Both methyls
but in different
Chemical Environments
the "see" different
things

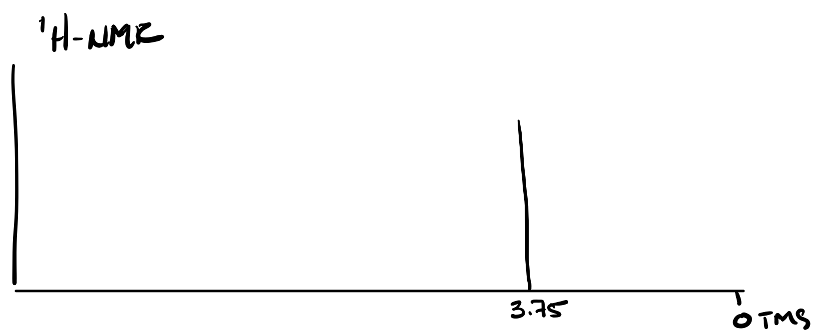


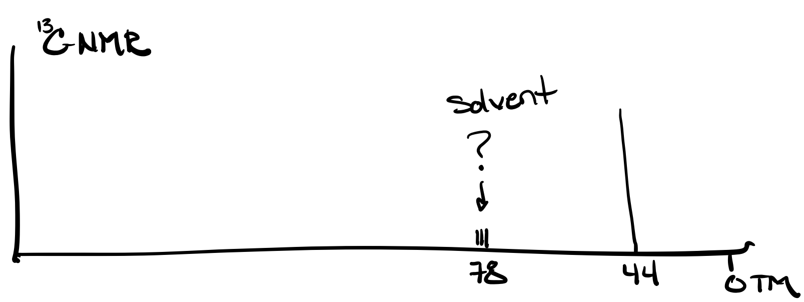




4 H environments

4 C environments



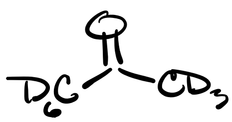
## NMR Solvents

$CDCl_3$ deuterated Chloroform

78ppm

$D = {}^2H$

$D_2O$




$CD_3OD$