

Nuclear Magnetic Resonance (NMR) - Theory

p 1) Nuclear magnetism - NMR requires paramagnetic nuclei
NMR active

Review: paramagnetic objects pulled toward magnetic fields
unpaired e⁻ spins $\Rightarrow S = \frac{\# \text{ of unpaired } e^-}{2}$

n & p have weaker magnetic spins (< 0.001 spin of e⁻)
↑ too weak to afford bulk magnetism

n & p isolated have spin ↑ or ↓

nuclei - spins pair up. Nuclear spin $I = \frac{\# \text{ of unpaired spins}}{2}$

Isotopic properties: mass, I, A, Z, etc

metastable isotope $\xrightarrow{\text{gamma decay}}$ more stable isotope (different I)

^{99m}Tc $\xrightarrow{\gamma = 143 \text{ keV}}$ ⁹⁹Tc
'Cardiolite' I = 1/2 I = 9/2

NMR \rightarrow almost always used w/ non-radioactive isotopes \Rightarrow MRI

Nuclei with A = odd are always NMR active. I > 0
¹H = proton (I = 1/2) I = 1/2, 3/2, 5/2, ...

Nuclei with A = even $\xrightarrow{\quad}$ Z = even
Z = odd (rare) even n, even p
NMR active, I = 1, 2, 3, ... I = 0 (diamagnetic)
¹⁴N - 99.6% of N - NMR is weak & broad NMR inactive
²H = D (deuterium) - 0.02% \Rightarrow enriched to 99.99%
NMR solvents: CDCl₃, acetone-d₆, D₂O ¹²C, ¹⁶O, ³²S
reasons: don't give ¹H NMR signal
: lock signal - keeps field strength constant

p2) Theory of NMR for $I = 1/2$ nuclei
} most studied by NMR

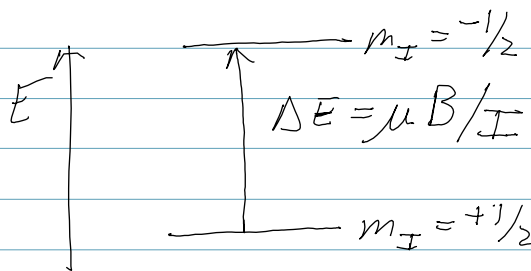
5 most studied isotopes
 ($I = 1/2$)

		Magnetic moment (μ)	ΔE	radio frequency for spin flips
^1H (proton)	99.98%	$2.79 \mu_N$	$3.31 \times 10^{-25} \text{ J}$	500 MHz
^{19}F	100%	$2.63 \mu_N$	$3.12 \times 10^{-25} \text{ J}$	471 MHz
^{31}P	100%	$1.13 \mu_N$	$1.34 \times 10^{-25} \text{ J}$	202 MHz
^{13}C	1.1%	$0.702 \mu_N$	$0.833 \times 10^{-25} \text{ J}$	126 MHz
^{15}N	0.4%	$-0.283 \mu_N$	$-0.336 \times 10^{-25} \text{ J}$	51 MHz

$1 \mu_N = 5.051 \times 10^{-27} \text{ J T}$ } Tesla = units of magnetic field

Nucleus in magnetic field:

B = magnetic field strength
 (units = T)



our spectrometer: $B = 11.75 \text{ T}$

* - for ^{15}N , $m_I = -1/2$ is lower E than $m_I = +1/2$

Spin flips in NMR caused by radio waves

$E = h\nu \Rightarrow \nu = \frac{\Delta E}{h}$ ← energy gap = 500,000,000 s^{-1} for ^1H
 = 500 MHz

"Resonance" - frequency and field matched to allow spin flips

freq is specific to 9 sig figs. Last 4 or 5 digits depend on chemical environment. (1)

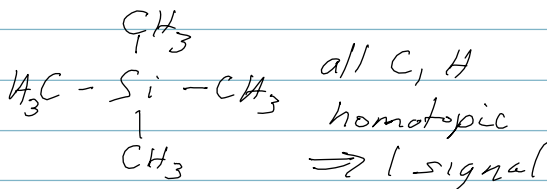
p 3) Two designs of NMR spectrometers

¹H spectrum of H₂O in acetone-d₆

Goal of NMR: determine $\frac{\text{freq.}}{\text{field}}$ ratio of all atoms of element
 relative values, rel. to ref. compd.

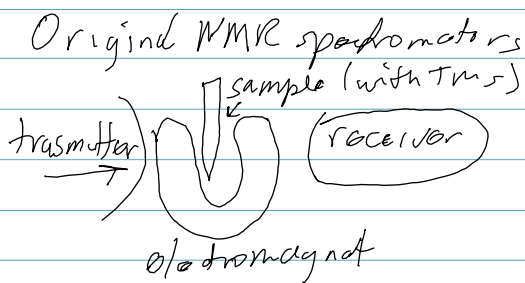
for ¹H & ¹³C, ref. compd is tetramethylsilane (TMS), (CH₃)₄Si

Define chemical shift of X as



$$\delta = \frac{\left(\frac{\text{freq.}}{\text{field}}\right)_X - \left(\frac{\text{freq.}}{\text{field}}\right)_{\text{TMS}}}{\left(\frac{\text{freq.}}{\text{field}}\right)_{\text{TMS}}} \times 10^6 \text{ ppm}$$

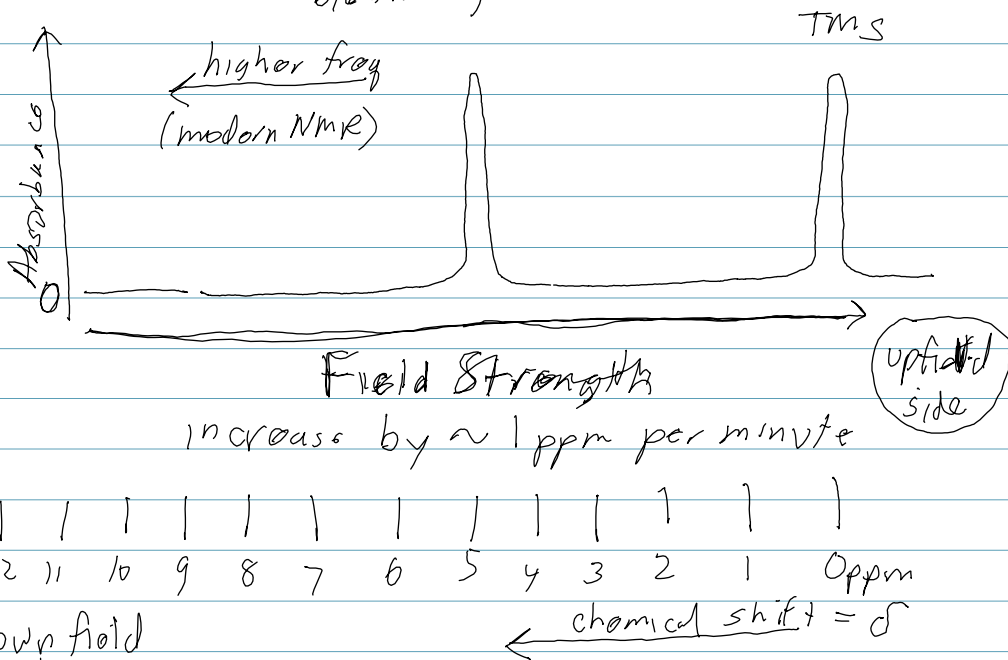
Small fraction
0.00000...



Modern NMR spectrometers

- 1) pulse very strong multiple frequencies
- 2) excite nuclei
- 3) detect frequencies given off (FT)
- 4) analyze with Fourier transform techniques

Field is constant



"upfrequency shift"? No.