

NMR I

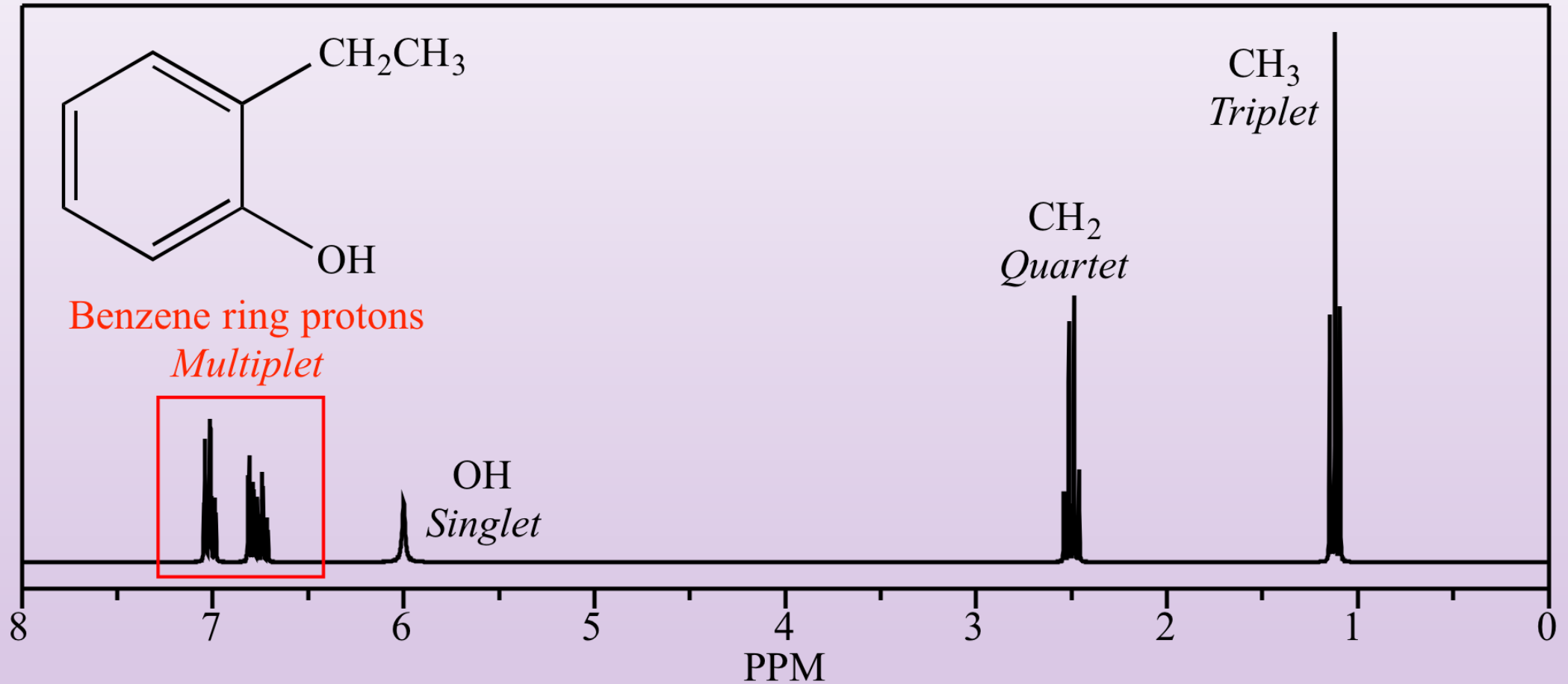
Keto-Enol Tautomerization

Alec Beaton

CHE 357

Spring 2020

Background: NMR



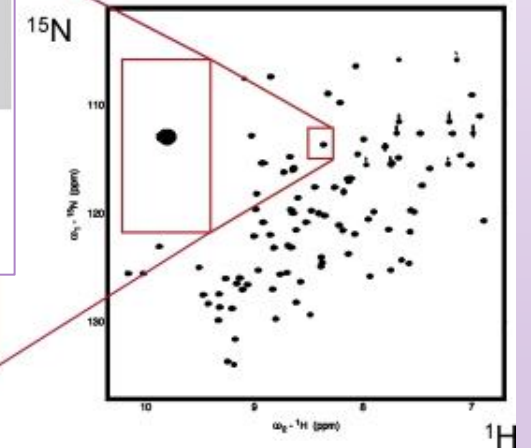
Background: NMR



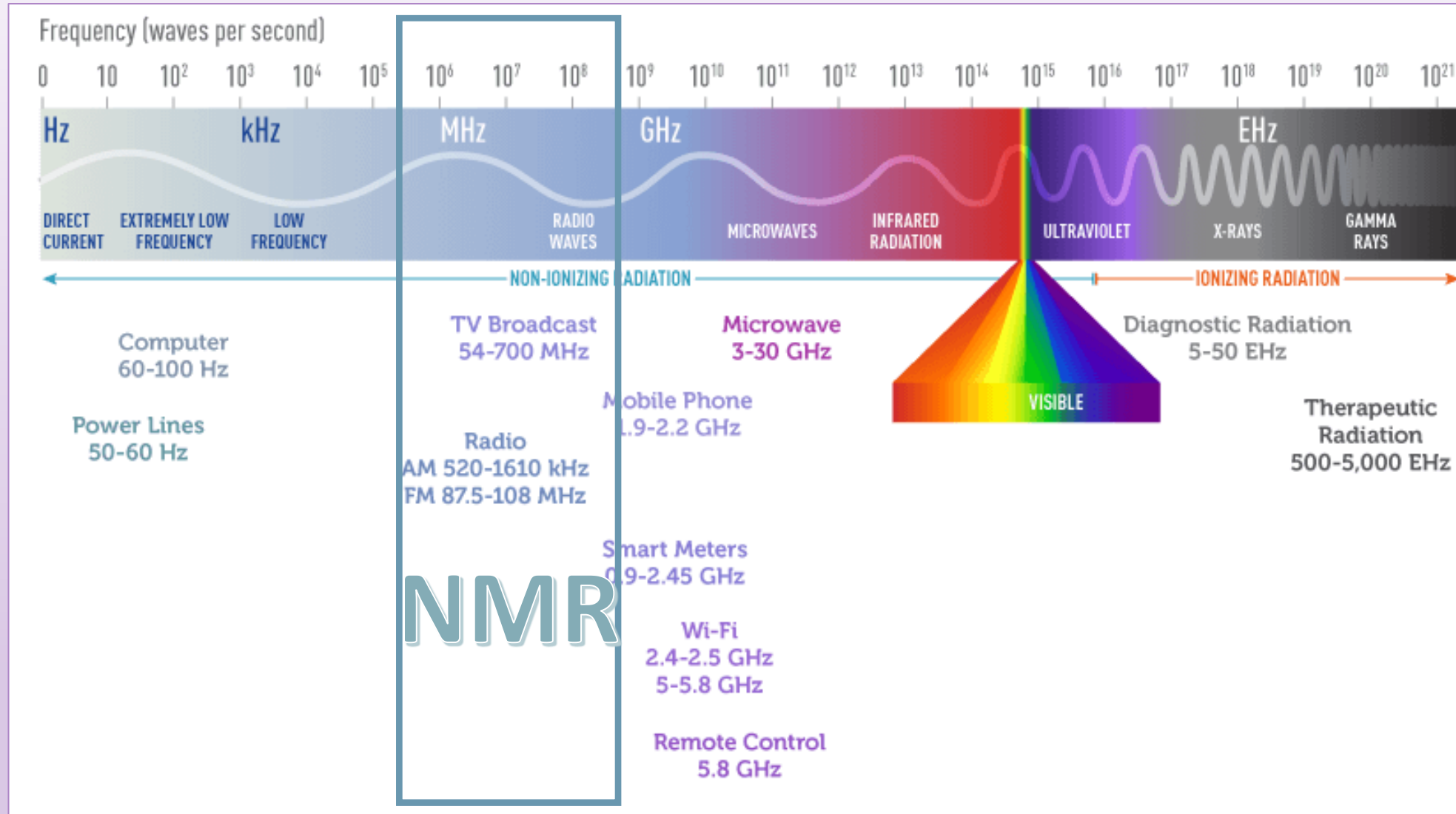
today

tomorrow?

miniaturization



Background: NMR



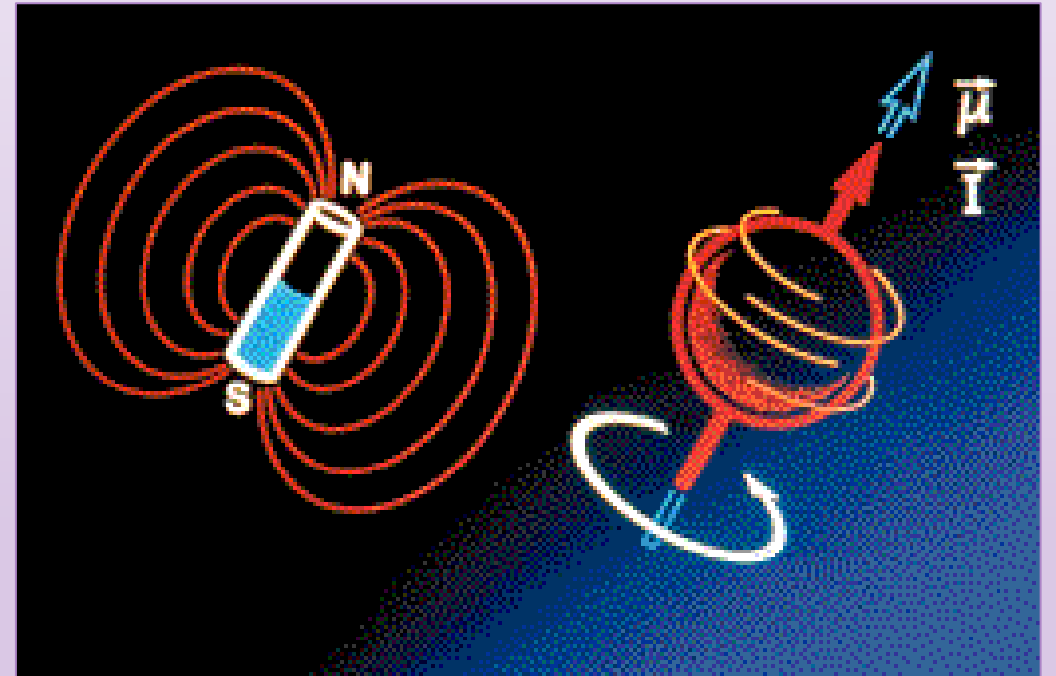
Background: The nucleus

Gyromagnetic
ratio

Nuclear magnetic
moment

$$\gamma = \frac{\mu}{I\hbar}$$

Nuclear spin angular
momentum



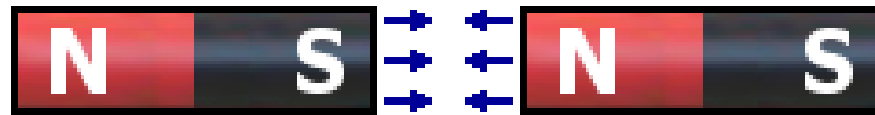
We typically only consider nuclei with $I = \frac{1}{2}$ (^1H , ^{13}C , ^{31}P)

No data for synthetic elements ≥ 103

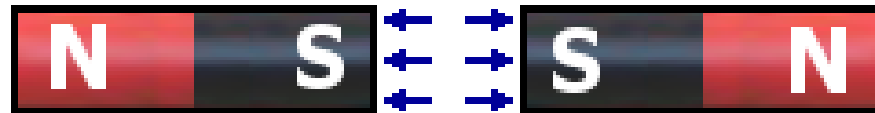
Theory

Magnets interact

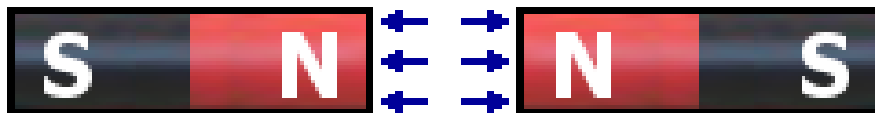
ATTRACTION



REPULSION



OR



Theory

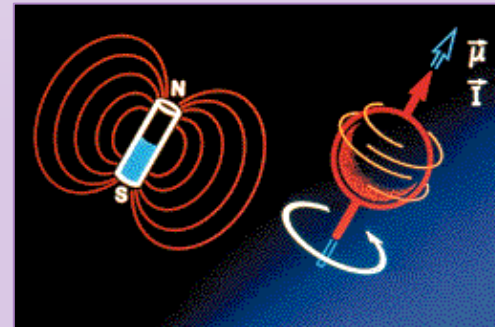
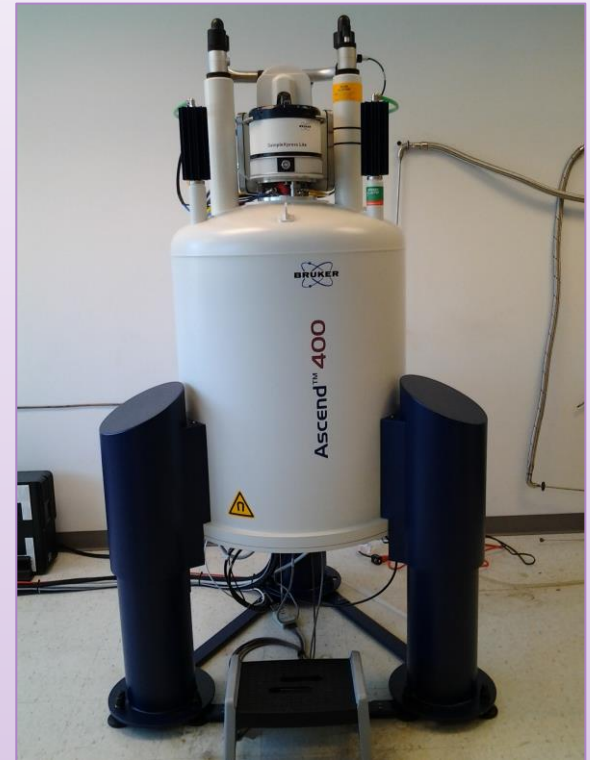
Magnets interact

Static
magnetic field

$$\frac{d}{dt} I \hbar = \mu \times B_0$$

Torque (rate of
change of angular
momentum)

Nuclear magnetic
moment



Theory

Magnets interact

$$\frac{d}{dt} I \hbar = \mu \times B_0$$

Through simple algebra,
we find that...

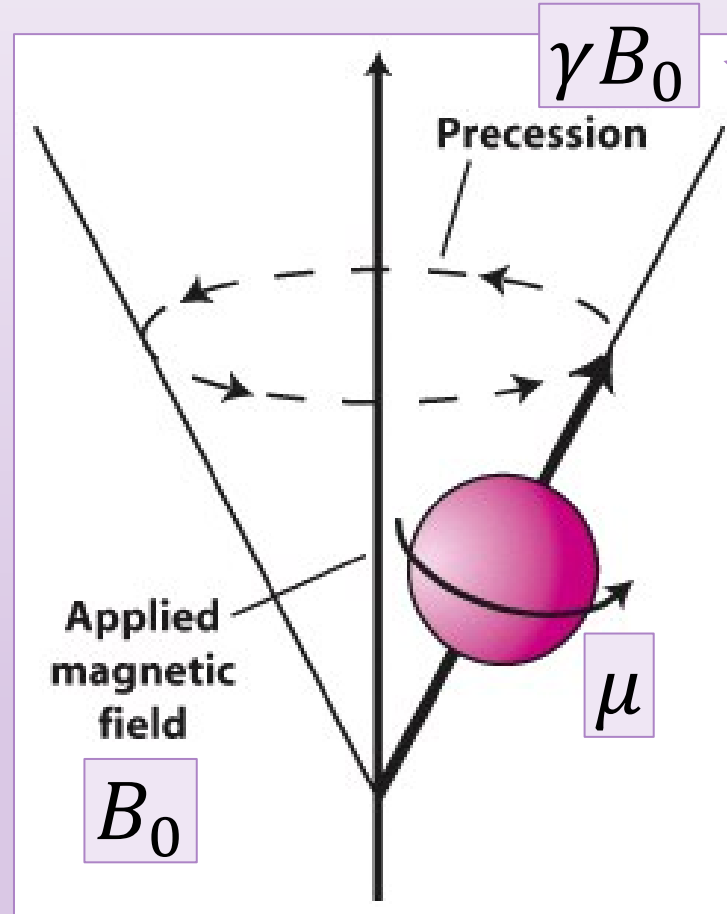
$$\frac{d}{dt} \mu = \mu \times \gamma B_0$$

The change in μ is always perpendicular to the plane defined by μ and B_0 -- i.e., μ precesses about B_0 ,
changing direction but not magnitude

Theory

Magnets interact

$$\frac{d}{dt}\mu = \mu \times \gamma B_0$$

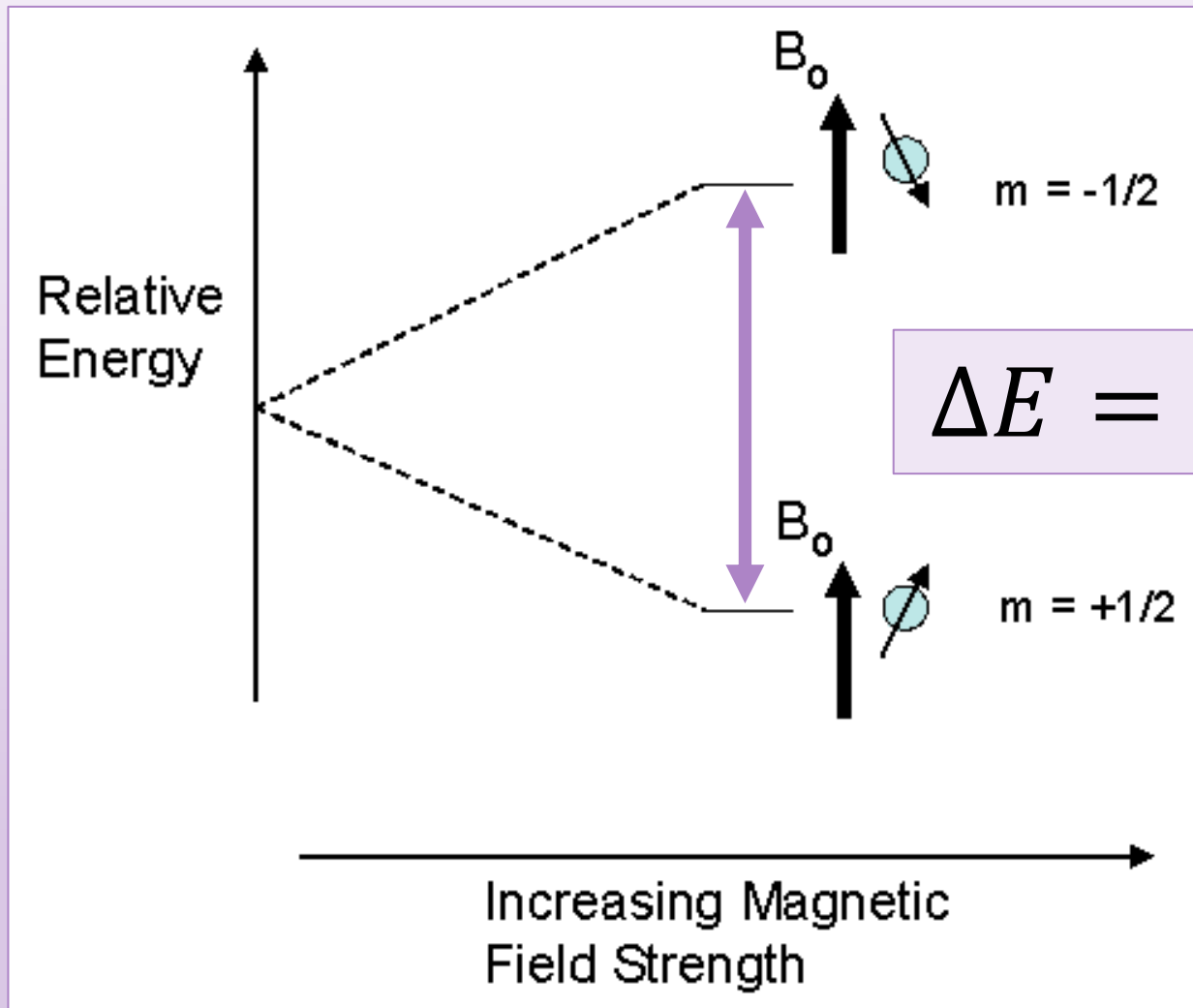


Larmor
Precession

$$\omega_0 = \gamma B_0$$

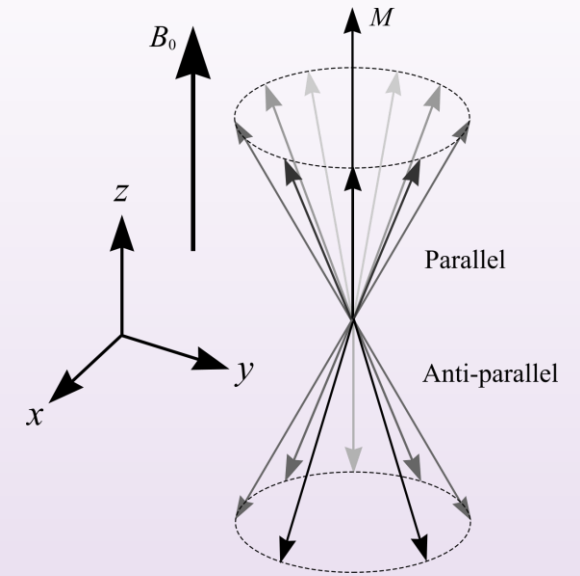
Theory

For $I = \frac{1}{2}$, $2I+1$ states exist
(i.e., two states exist)



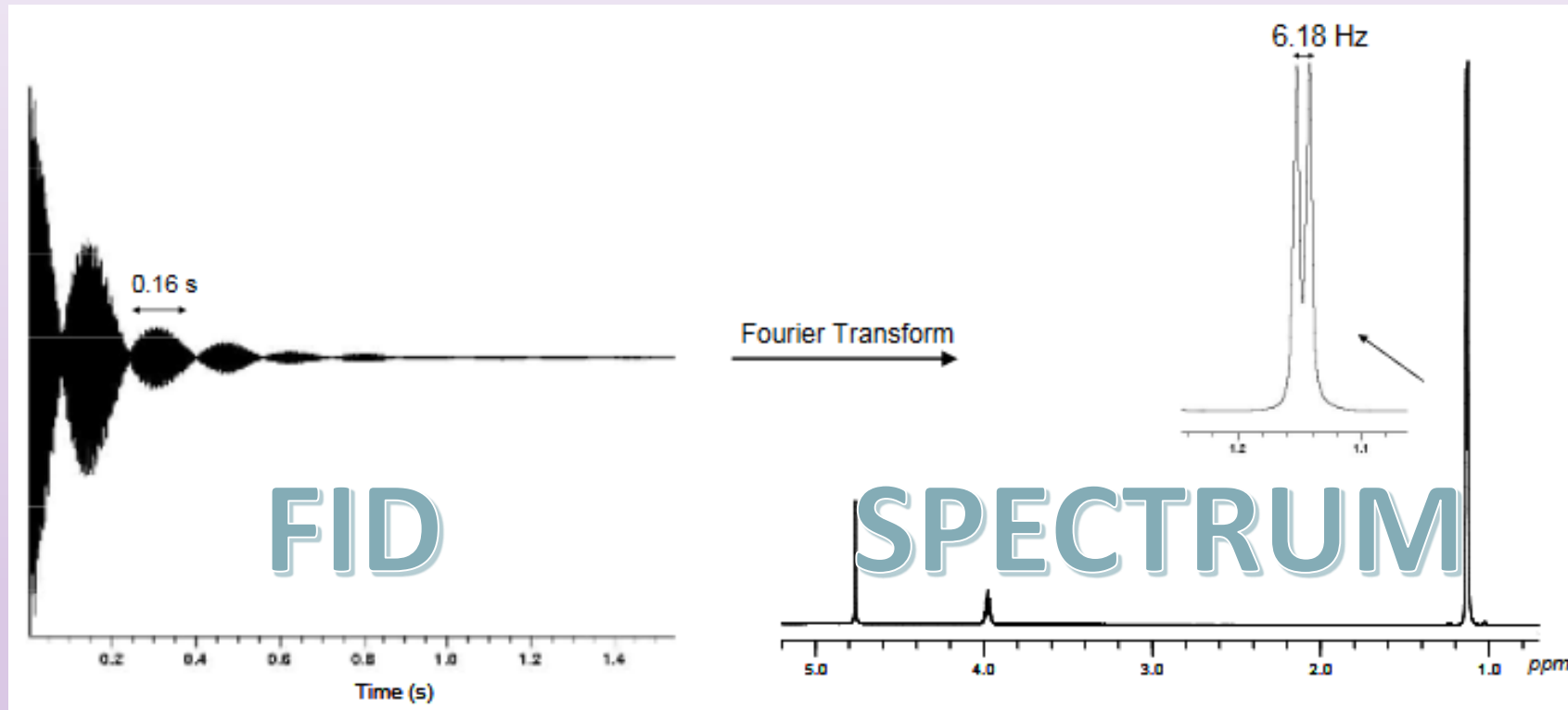
$$\Delta E = \hbar\omega_0 = \hbar\gamma B_0 = h\nu_0$$

The 400 MHz NMR has a magnetic field $B_0 = 9.4 \text{ T}$ – which we find using γ for the ^1H nucleus



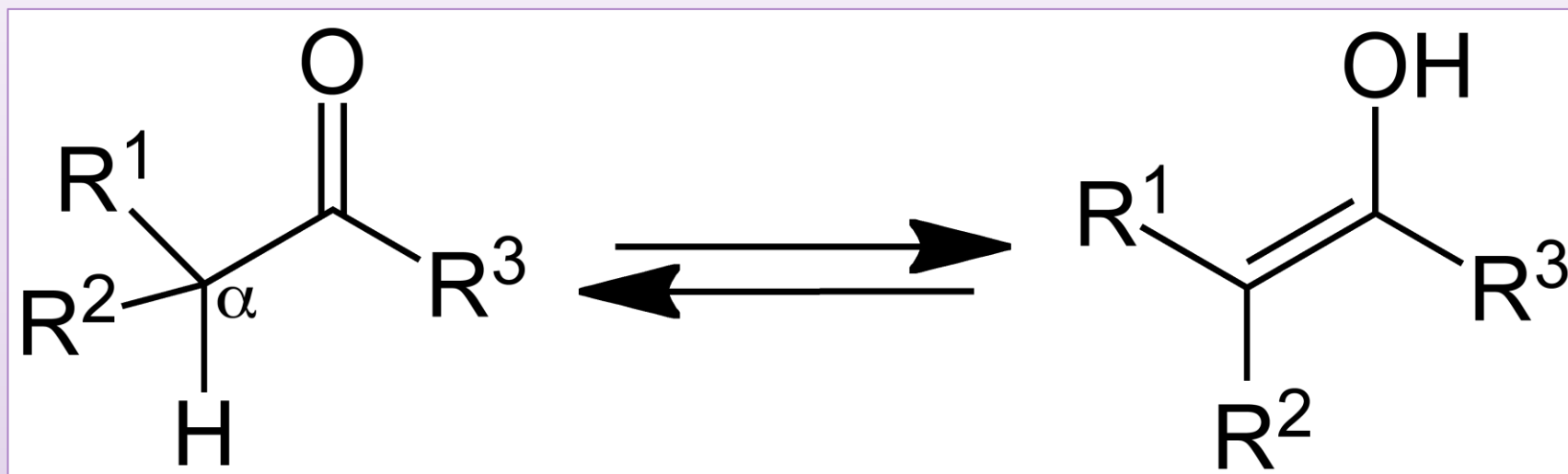
Theory

We apply an rf pulse to excite the spins – we are able to detect them in this state as they return to equilibrium, generating the Free Induction Decay (FID)



More on this next week

Experiment

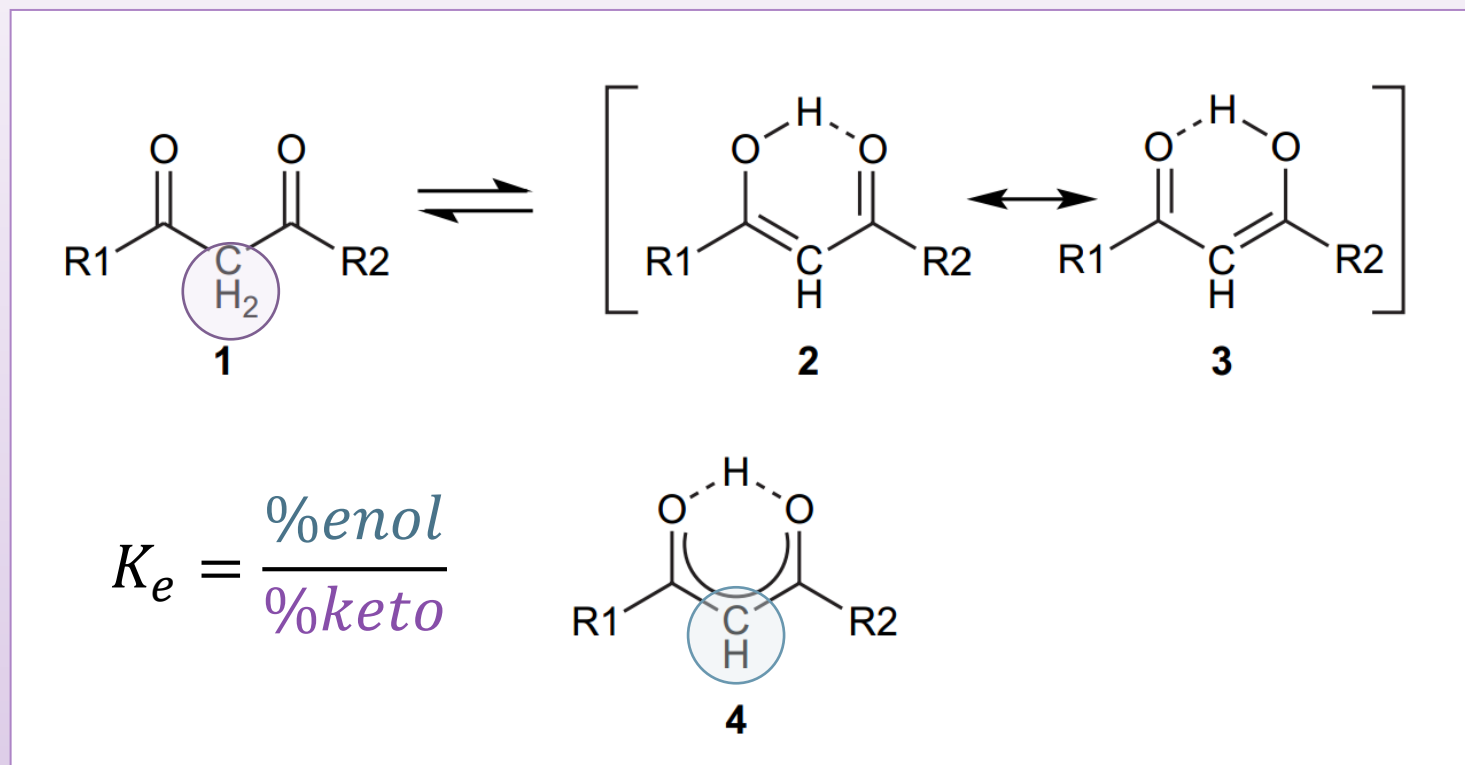


KETONE

ENOL

How do environmental factors, such as **solvent**, **temperature**, and **concentration** affect this equilibrium?

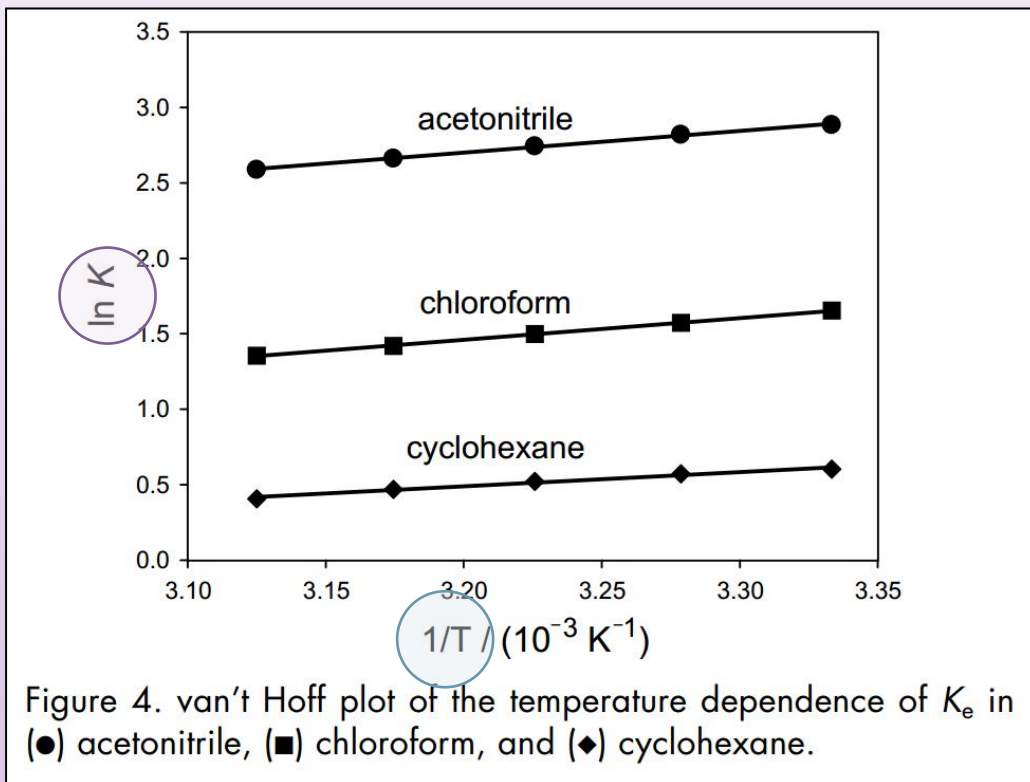
Experiment



We assess this by comparing the **proton resonances** of the respective forms

Experiment

For the variable temperature experiments, we will generate van't Hoff plots to determine thermodynamic quantities by linear fits



$$\ln(K_e) = \left(\frac{\Delta H}{R} \right) \left(\frac{1}{T} \right) + \left(\frac{\Delta S}{R} \right)$$

Experiment

We will meet in LSB 215 to prepare some NMR samples – then run the proton NMR experiments together, followed by processing of the data.

Please be sure to refer to the handout posted on Blackboard for details of what I expect in your reports.

A note on the mole fraction calculation:

We prepare 600 μL (or 0.6 mL) samples. Using this final volume, find the volume of acetone- d_6 and acac needed to prepare approx. 0.1 and 0.2 mf solutions (you will need the densities for each)

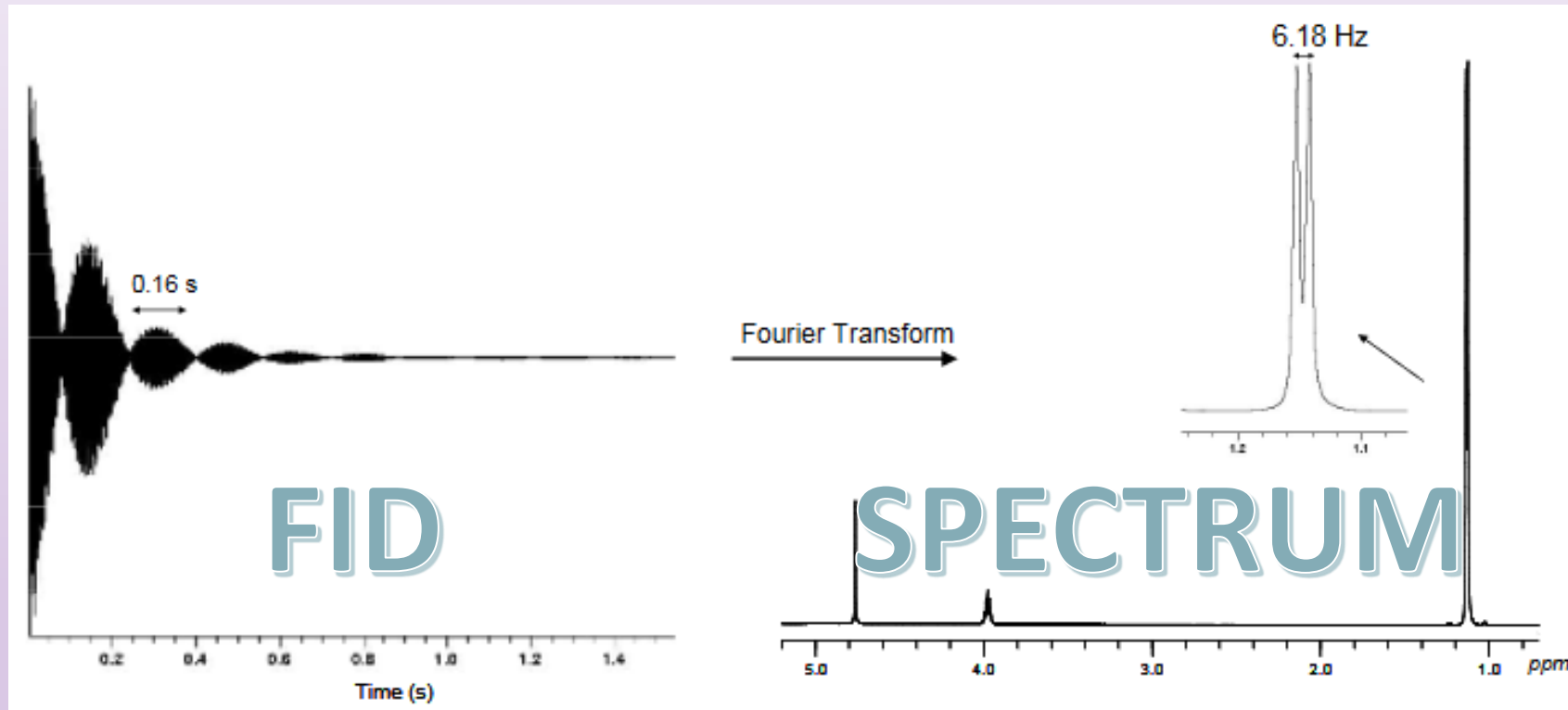
NMR II

Lineshape Analysis of Reversible Hydrolysis Reaction

Alec Beaton
CHE 357
Spring 2020

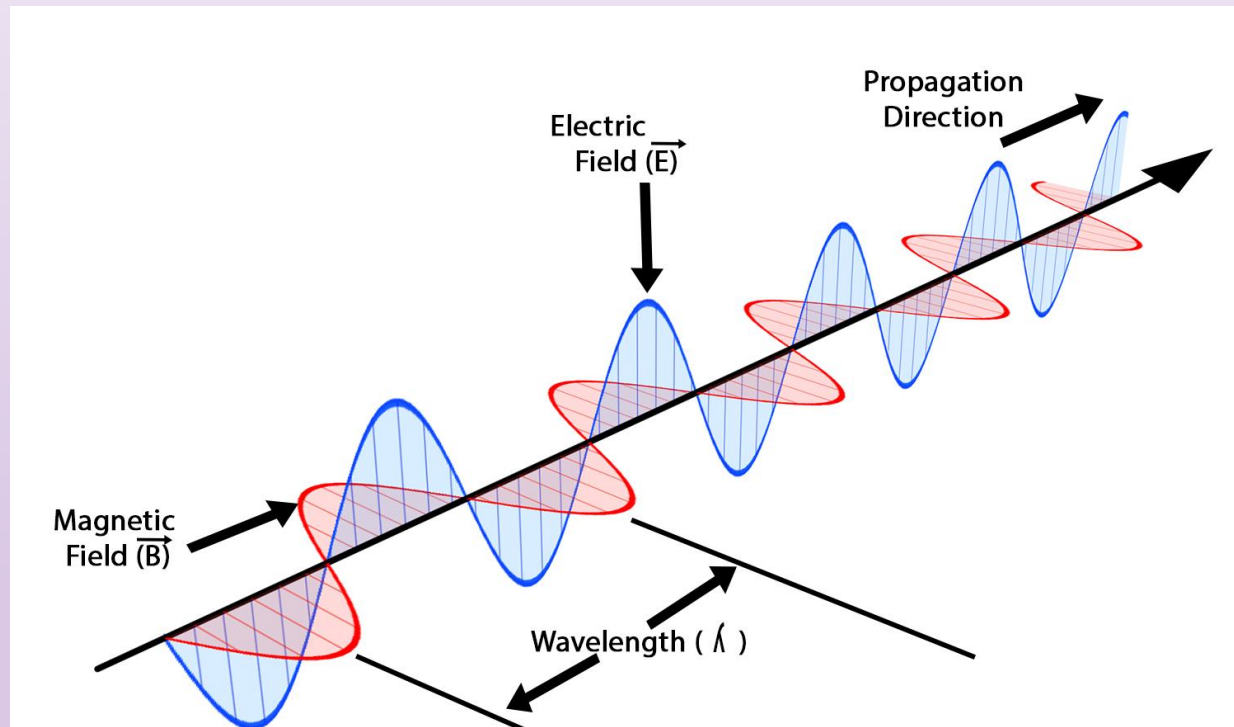
Theory

We apply an rf pulse to excite the spins – we are able to detect them in this state as they return to equilibrium, generating the Free Induction Decay (FID)

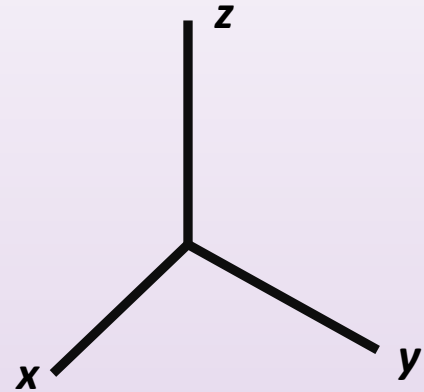


Theory: Free Induction Decay

We call the rf pulse B_1 (remember the static field is called B_0) -- this causes the spins to tip



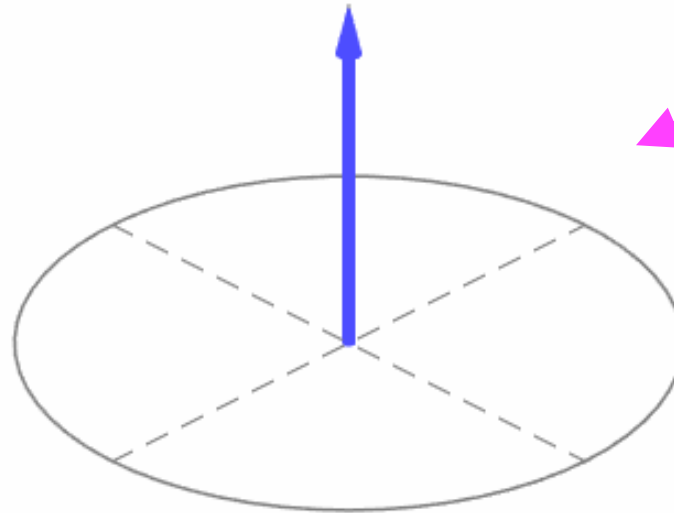
Theory: Free Induction Decay



We call the rf pulse B_1 (remember the static field is called B_0) -- this causes the spins to tip

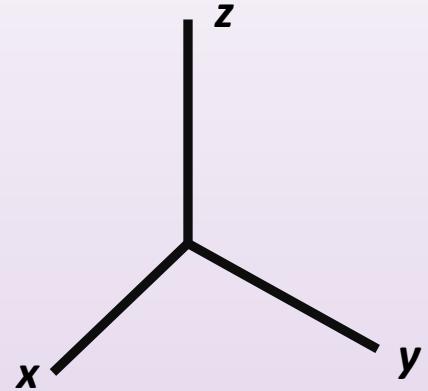
Blue = effective magnetic field (combined effect of B_0 and B_1)

Pink = nuclear spin magnetization



Pink spins always precess at Larmor frequency

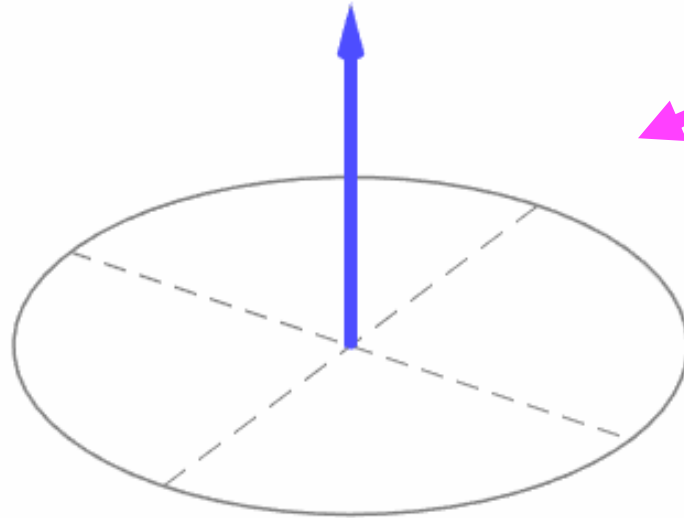
Theory: Free Induction Decay



Switch from the *laboratory frame* to the *rotating frame*

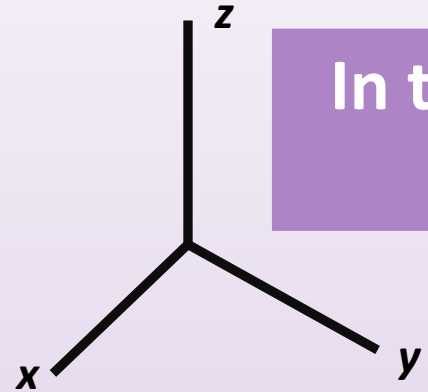
Blue = effective magnetic field (combined effect of B_0 and B_1)

Pink = nuclear spin magnetization



Thus let our coordinate axes also rotate at the Larmor frequency

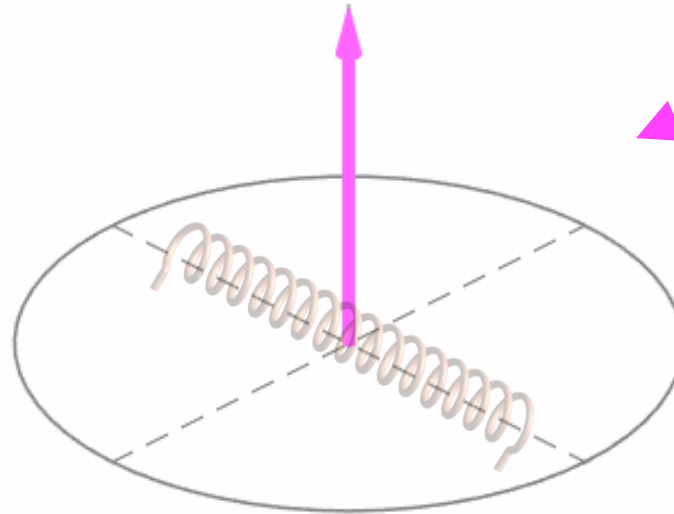
Theory: Free Induction Decay



In the *rotating frame*, the “tip” of nuclear spins is much easier to visualize (i.e., the effect of B_1 is easier to see)

Blue = B_1 (rf pulse), in rotating frame

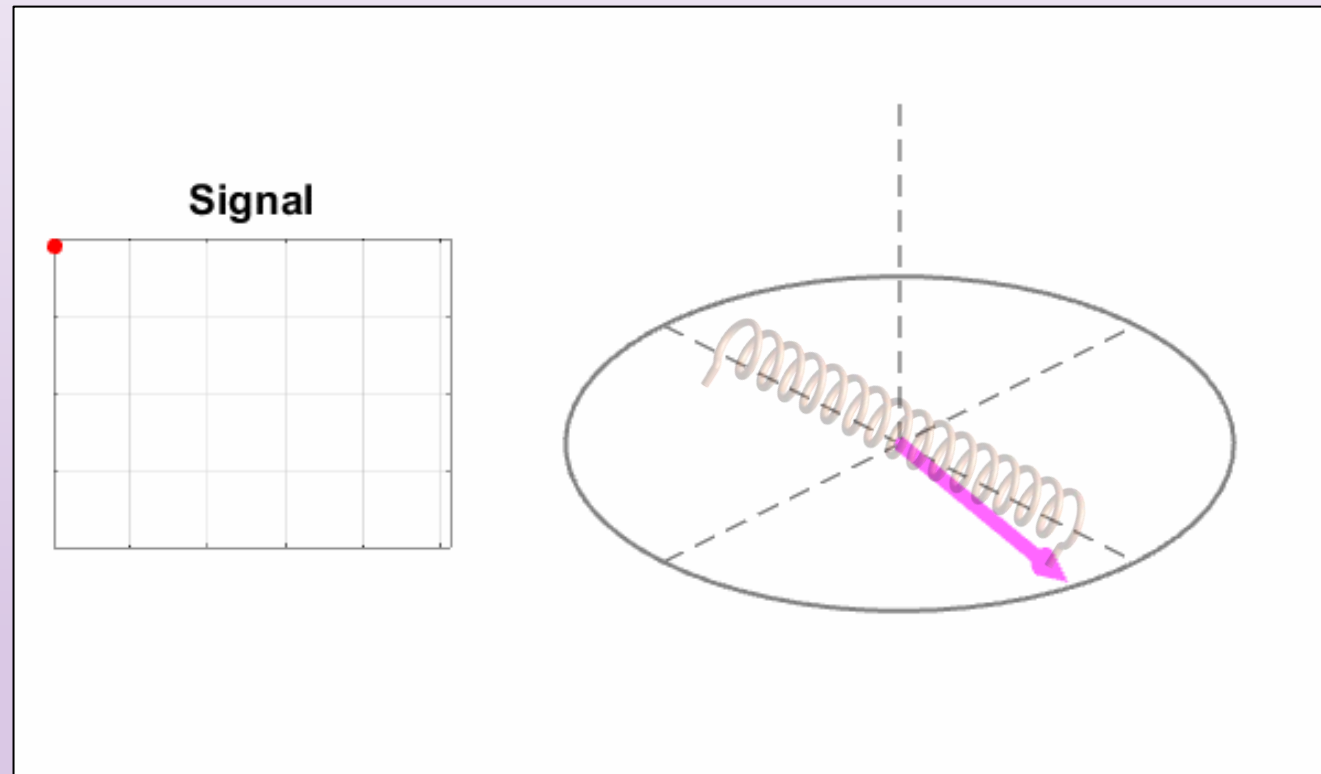
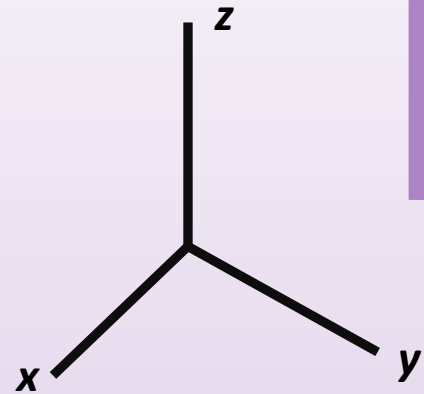
Pink = nuclear spin magnetization



See very clean “tip” of the magnetization into the XY (or transverse) plane

Theory: Free Induction Decay

As the spins return to equilibrium (along the z-axis), they induce a current in the coil, and we detect signal (**FID**)

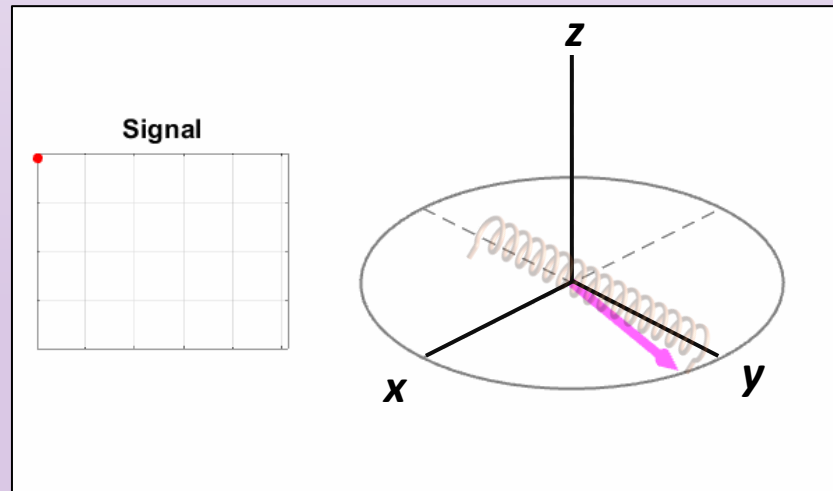


Theory: Free Induction Decay

The FID is an oscillatory decaying exponential

$$s(t) = e^{\frac{-t}{T_2}}$$

T_2 (spin-spin or *transverse relaxation*) describes the decay of signal
 T_1 (spin-lattice or *longitudinal relaxation*) describes signal return to equilibrium



Theory: Fourier Transformation

Fourier Transformation of the FID provides the familiar NMR spectrum

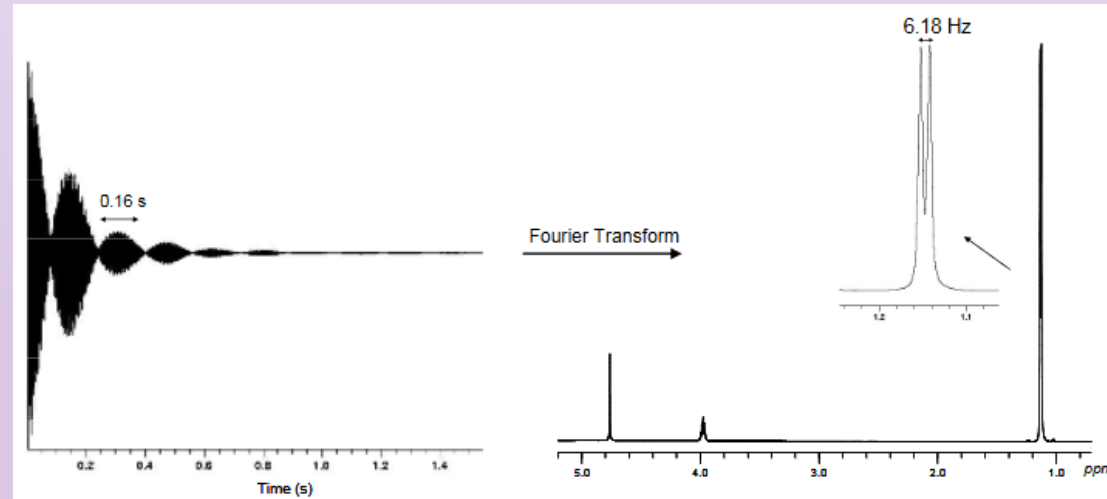
$$S(\nu) = \int_{-\infty}^{+\infty} e^{-i\nu 2\pi t} s(t) dt$$

SPECTRUM

Signal in the frequency domain

FID

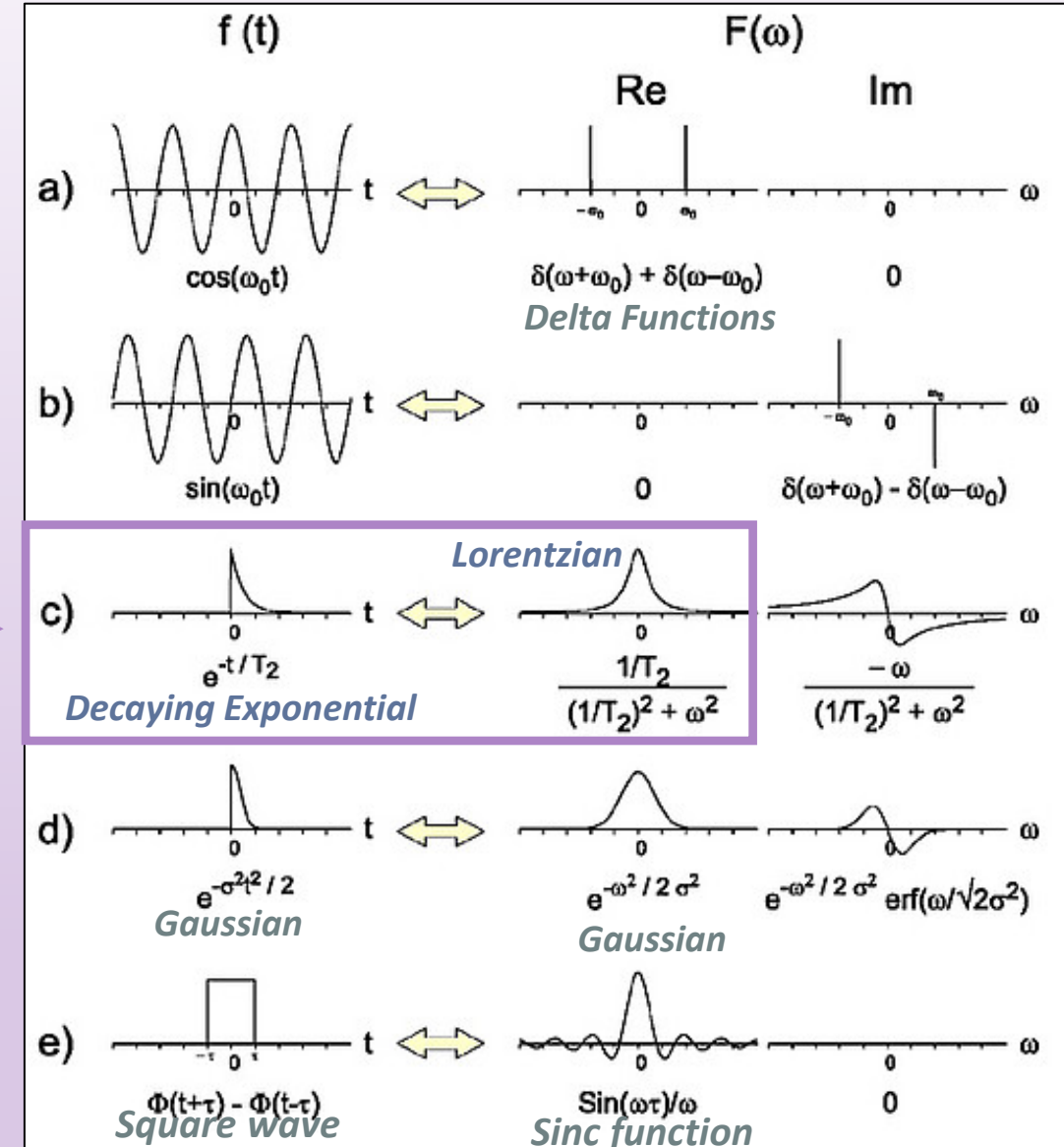
Signal in the time domain



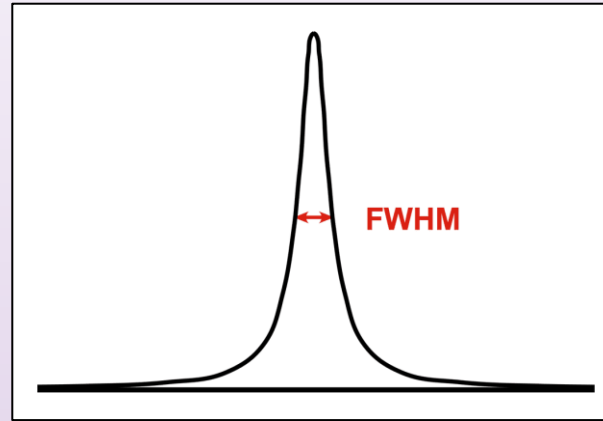
Theory: Fourier Transformation

There are several **Fourier Transform pairs**, but in NMR we only care about c

NMR



Theory: Fourier Transformation



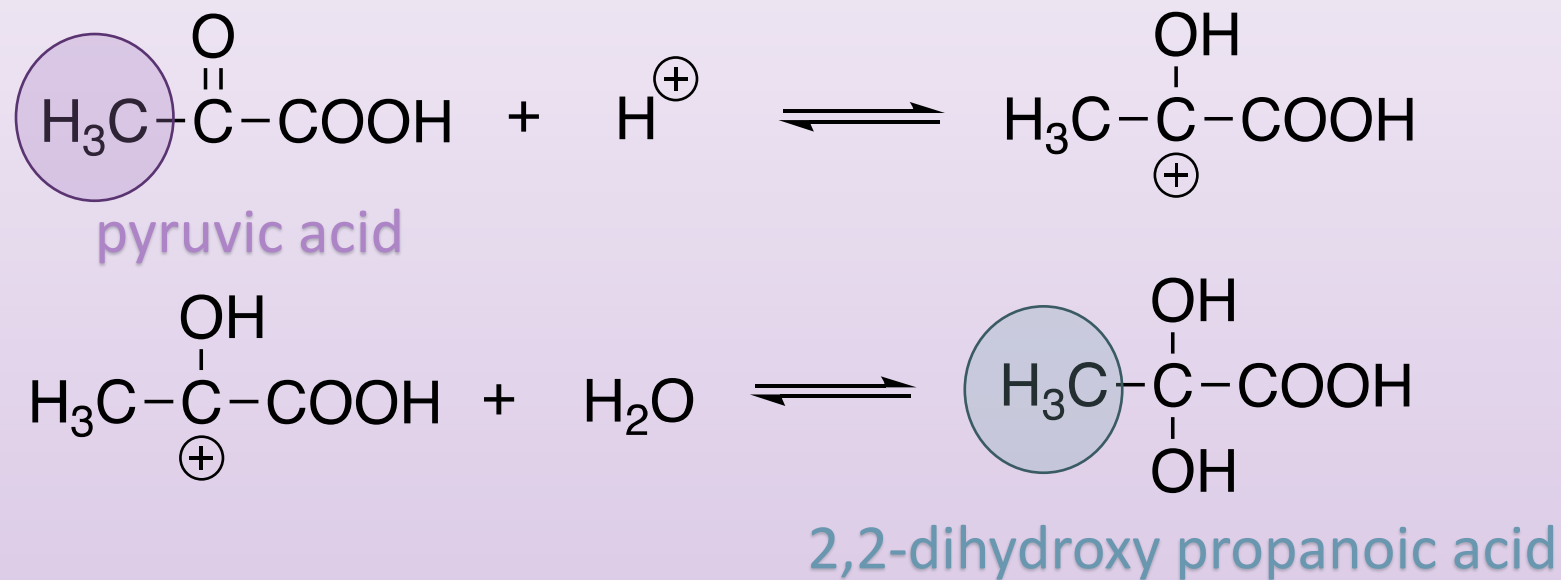
The width of a Lorentzian line, often called the **full width half maximum (FWHM)** or **W** is determined by T_2^* and chemical exchange

$$W = \frac{1}{\pi T_2^*} + \frac{1}{\tau} = \frac{1}{\pi T_2^*} + k$$

T_2^* contains the natural T_2 of the sample, as well as the extent of imperfections in B_0 (i.e., imperfections in the magnetic field)

Experiment

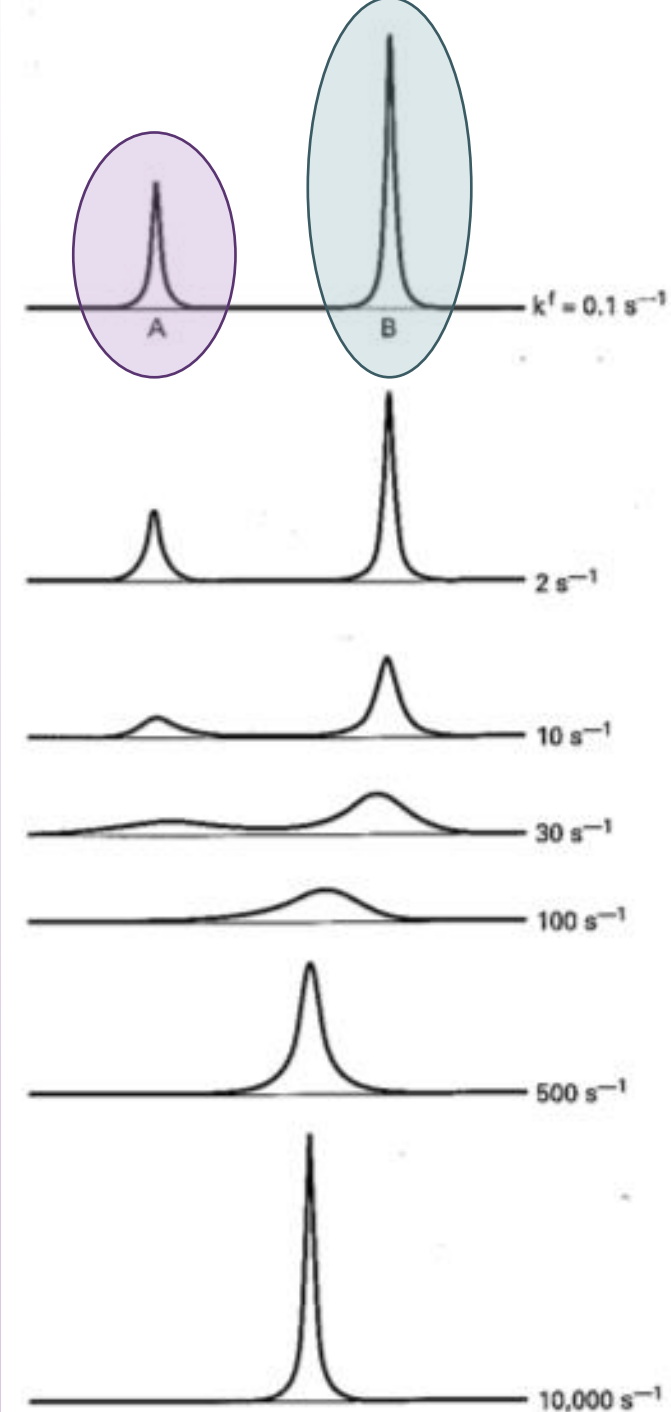
In the presence of chemical exchange, two proton resonances broaden into one



$$k_f = k_0^f + k_H^f[H^+]$$

$$k_r = k_0^r + k_H^r[H^+]$$

$$K_{eq} = \frac{k_H^f}{k_H^r}$$



Experiment

- We will study the effect of $[H^+]$ on the hydrolysis equilibrium:
 - Collect NMR spectra at varied concentrations of acid
 - Process NMR spectra to determine FWHM for peaks of interest at different concentrations
 - By plotting linewidth as a function of concentration, rate constants can be determined (for forward and reverse reactions)
 - Equilibrium constant can be calculated
- Additional considerations:
 - Assess the linear fit of FWHM vs $[H^+]$
 - Chemical shift variations as function of $[H^+]$

Experiment

We will meet in LSB 301 to run the NMR spectra in the basement, then return to LSB 301 to process spectra together

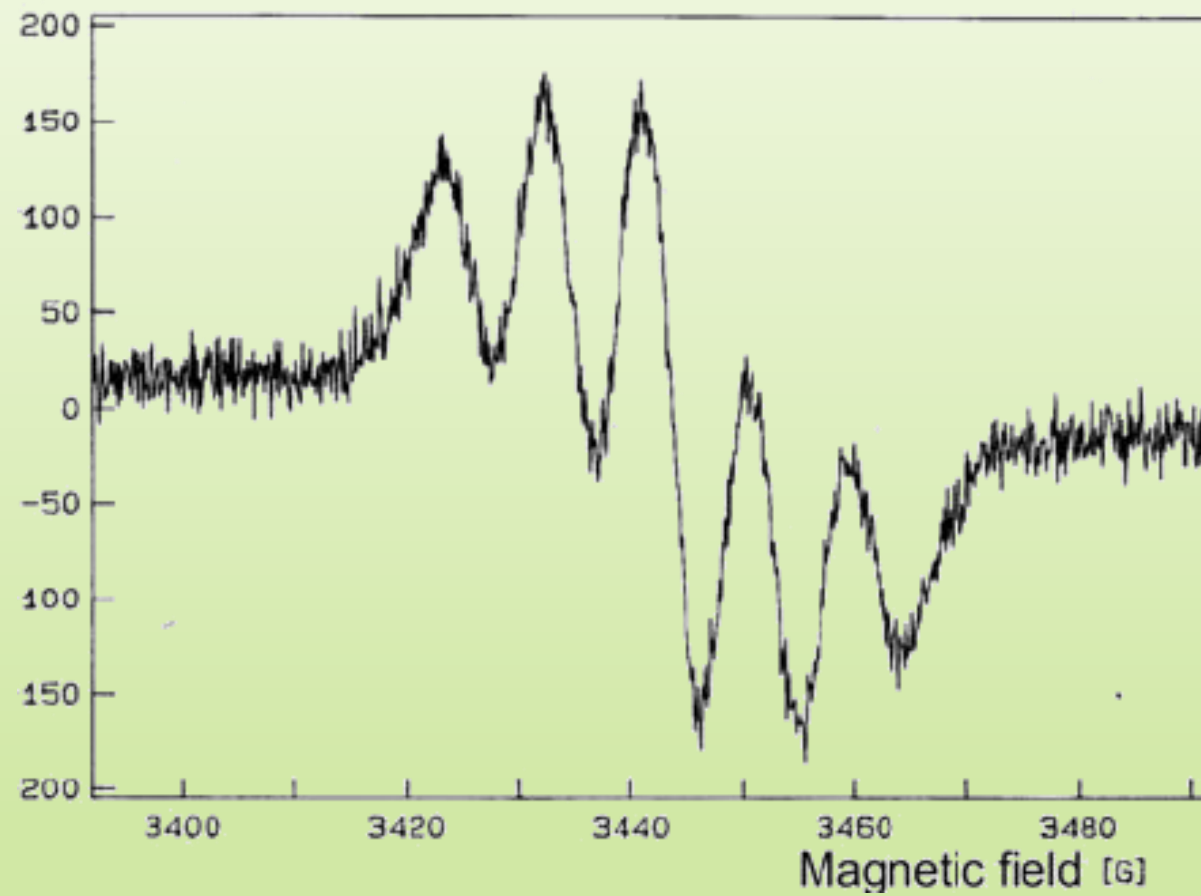
Please be sure to refer to the handout posted on Blackboard for details of what I expect in your reports

ESR

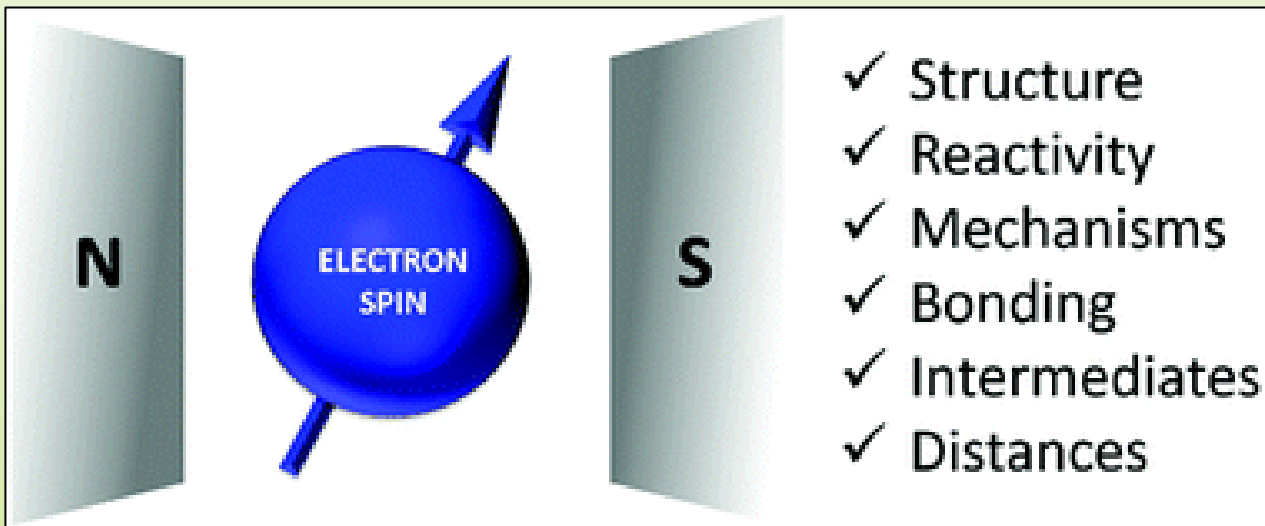
Introduction to Electron Spin Resonance Spectroscopy

Alec Beaton
CHE 357
Spring 2020

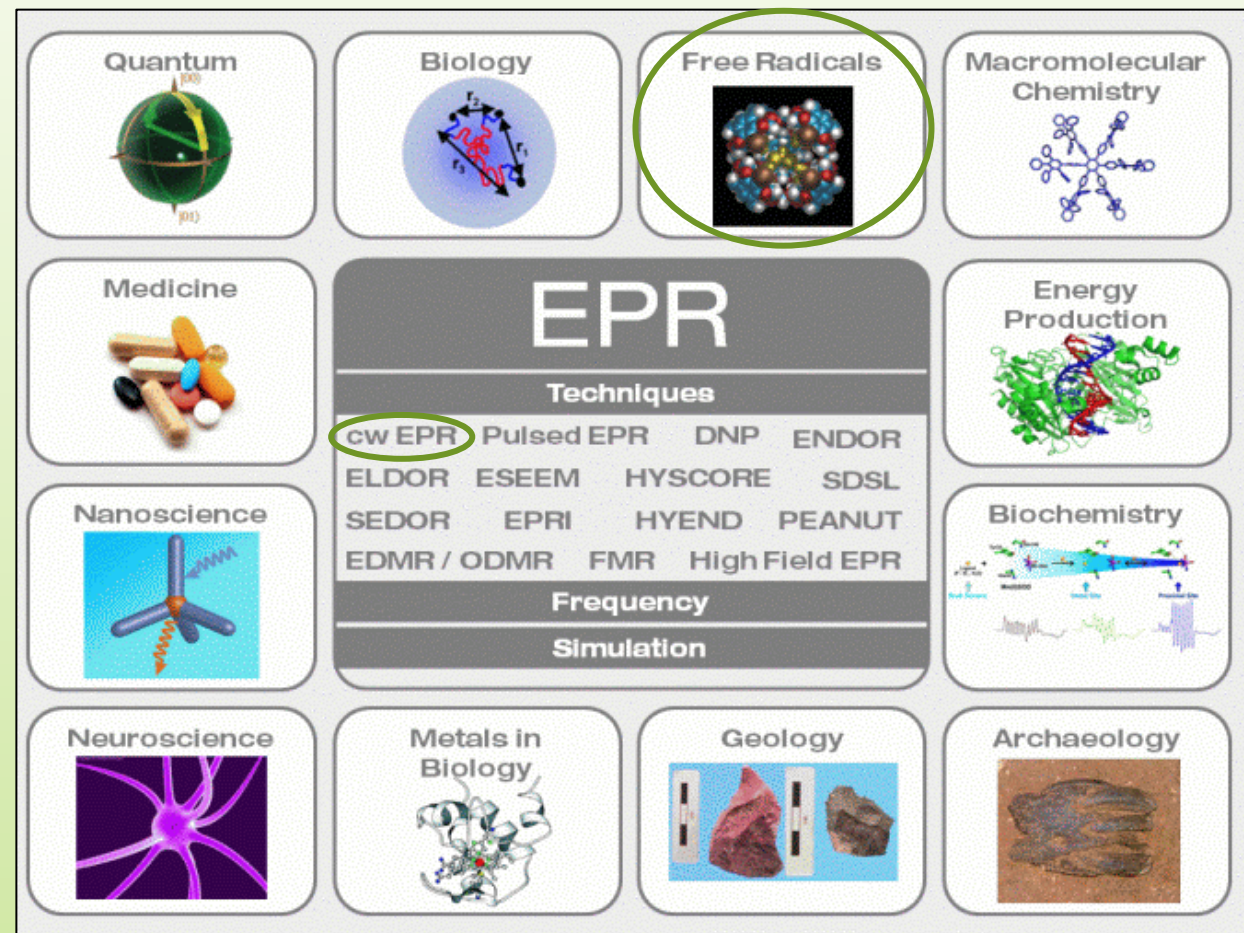
Background



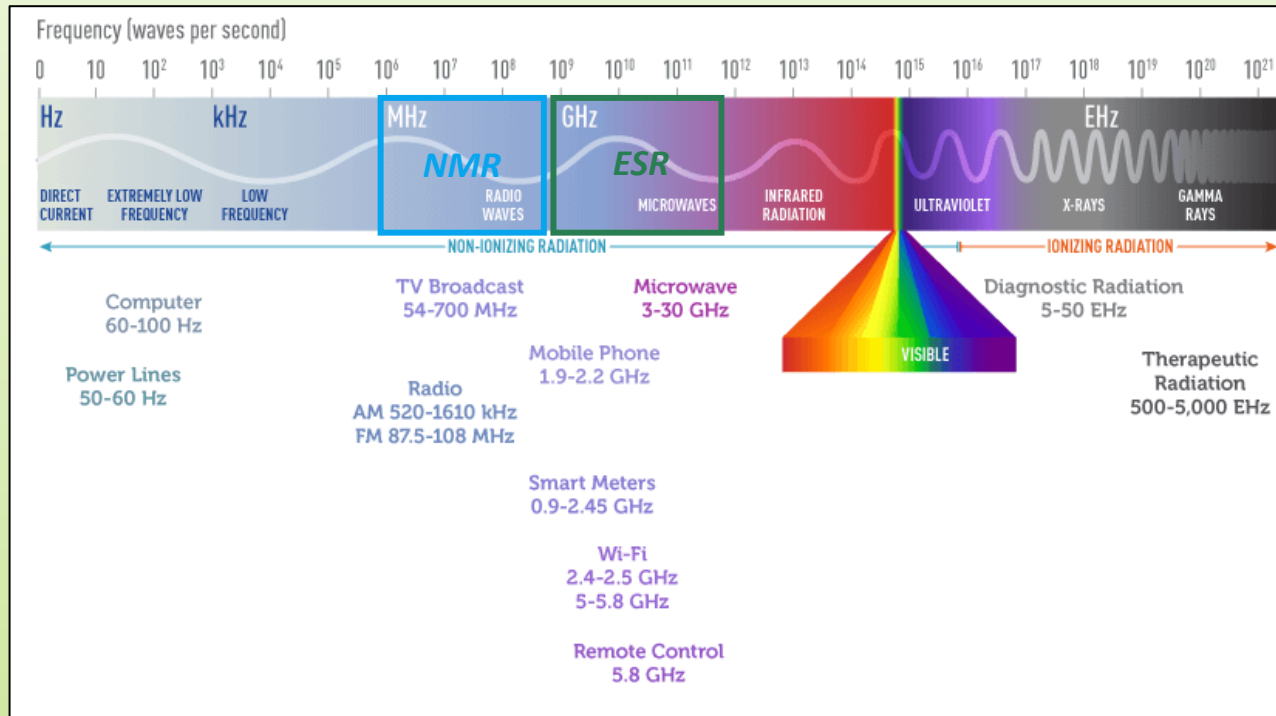
Background



Roessler, M.M. et al. *Chemical Society Reviews*, 2018.



Background



science.jrank.org



Background



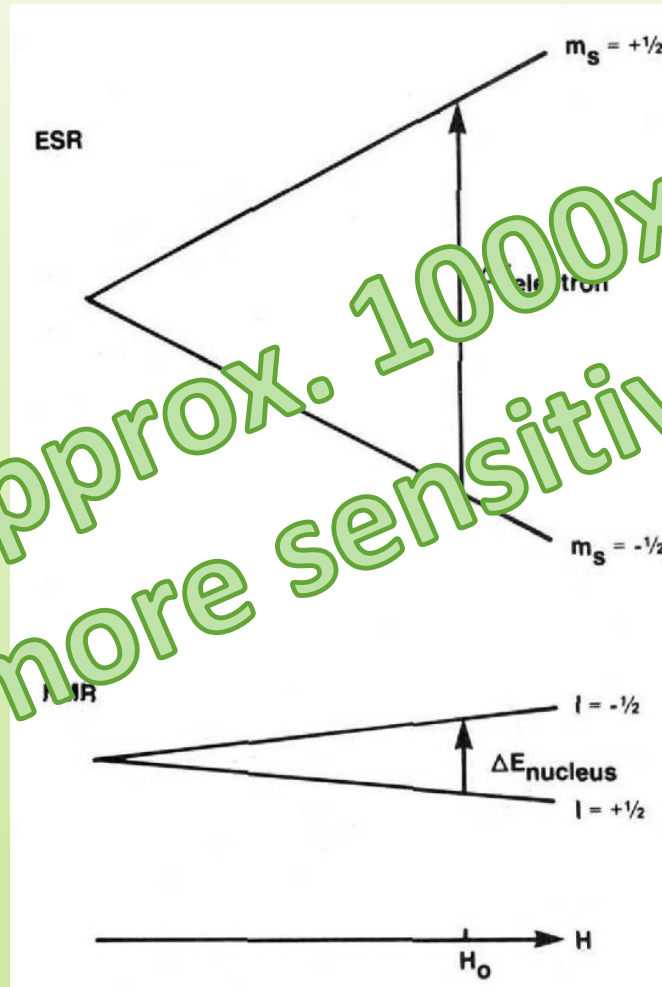
Traditional NMR

- “Characterize nuclei” (*nuclear spin*)
- Pulses of radio frequency (MHz)
- Fixed, continuous magnetic field
- Detects signal in time domain - FT into **frequency** domain (*absorptive line shape*)
- Spectrum as function of frequency (ppm, chemical shift)

$$\nu = \frac{\gamma_H B_0}{2\pi}$$

- Less sensitive

NMR vs ESR



Traditional ESR

- “Characterize electrons” (*electron spin*)
- Fixed, continuous microwave frequency (GHz)
- Vary the magnetic field
- Detects change in signal intensity with change in magnetic field (*derivative line shape*)
- Spectrum as function of magnetic field (*G, g-factor*)

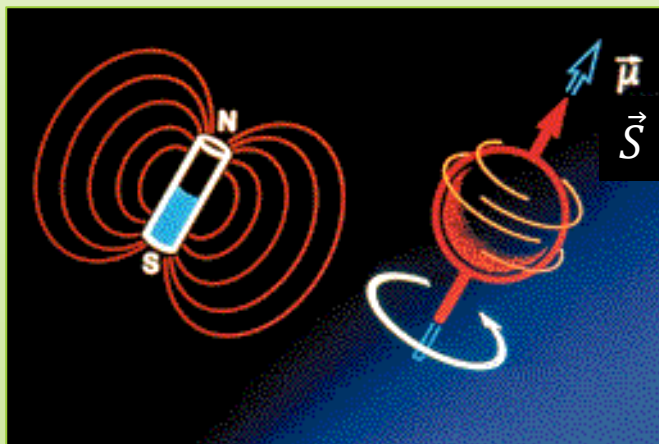
$$\nu = g\beta B_0 = \frac{\gamma_e B_0}{2\pi}$$

- More sensitive

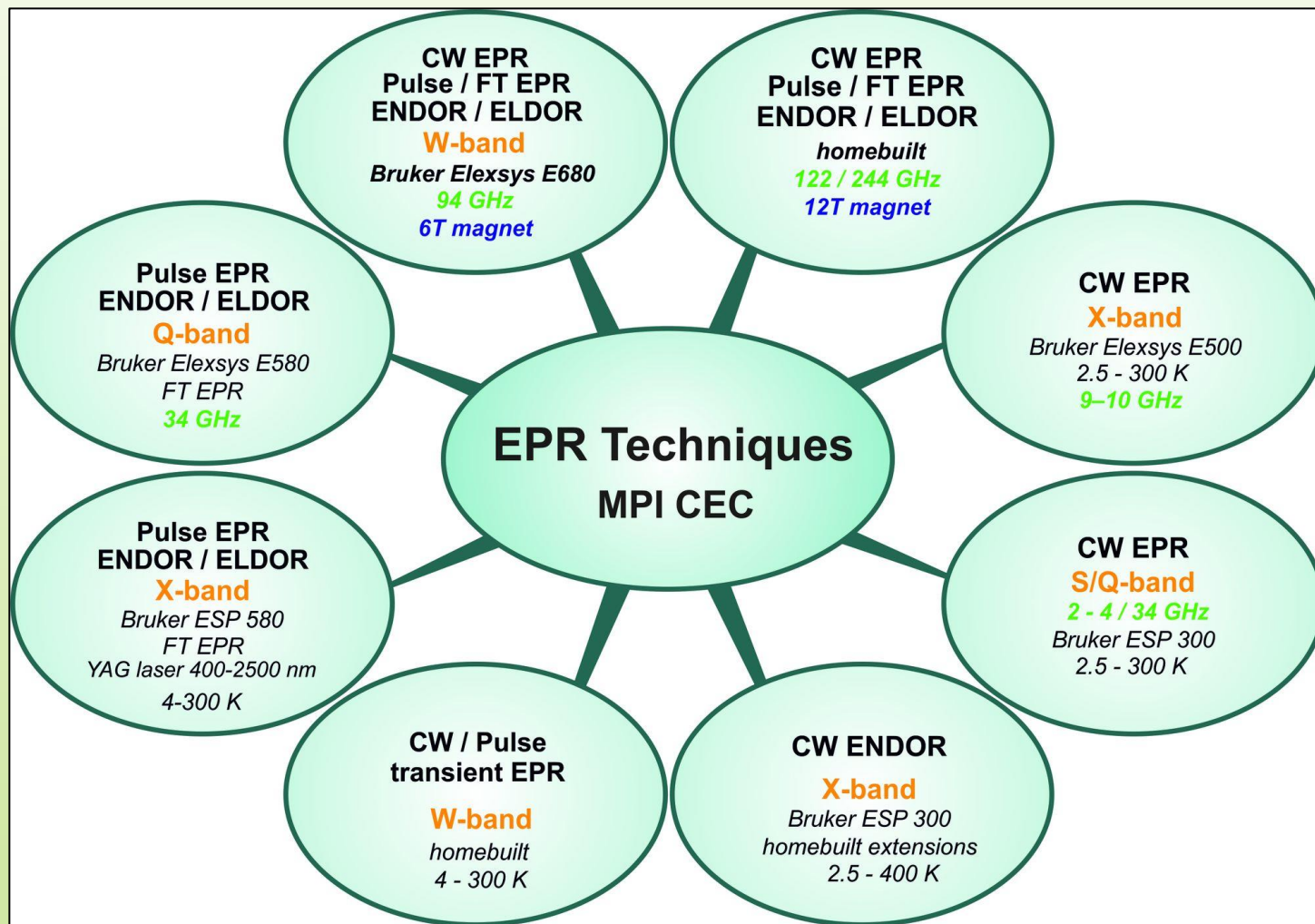
Theory

SPIN HAMILTONIAN

$$\hat{H} = \underbrace{\beta_B (\vec{B}_0 \cdot \vec{g} \cdot \hat{\vec{S}})}_{\text{ZEEMAN}} + \underbrace{\hat{\vec{S}} \cdot \vec{D} \cdot \hat{\vec{S}}}_{\text{ELECTRON-ELECTRON SPIN/SPIN INTERACTION}} + \underbrace{\hat{\vec{S}} \cdot \vec{A} \cdot \hat{\vec{I}}}_{\text{ELECTRON-NUCLEUS SPIN/SPIN INTERACTION}}$$



Instrumentation



$$\omega_0 = \gamma B_0$$

Band Designation	Band Range	Typical EPR Frequency ν (GHz)	Typical EPR Field B (mT)
L	0.390–1.550	1.5	54
S	1.550–3.900	3.0	110
C	3.900–6.200	6.0	220
X	6.200–10.900	9.5	340
K	10.900–36.000	23	820
Q	36.000–46.000	36	1300
V	46.000–56.000	50	1800
W	56.000–100.000	95	3400

1H NMR Frequency (MHz)	Field Strength (T)
300	7
400	9.4
800	18.8

Instrumentation

Microwave Source
(Bridge)

Resonator

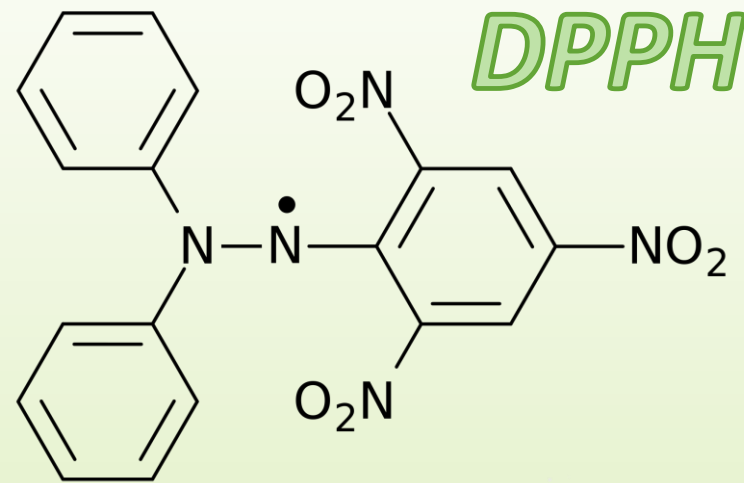
Power
Supply



Magnet

© BRUKER

ESR Spectra



Nuclear Spins for Main Elemental Isotopes that Undergo NMR

1A	2A	3A	4A	5A	6A	7A	8A
1H	4Be	9B	6C	7N	8O	9F	2He
3Li	9Be	10B	12C	14N	16O	19F	10Ne
11Na	12Mg	13Al	14Si	15P	16S	17Cl	18Ar
19K	20Ca	21Sc	22Ti	23V	24Cr	25Mn	26Fe
37Rb	38Sr	39Y	40Zr	41Nb	42Mo	43Tc	44Ru
55Cs	56Ba	57La	58Ce	59Pr	60Nd	61Pm	62Sm
87Fr	88Ra	89Ac	90Th	91Pa	92U	93Np	94Pu
101Lr	102No	103Lr	104No	105Lr	106No	107Lr	108No

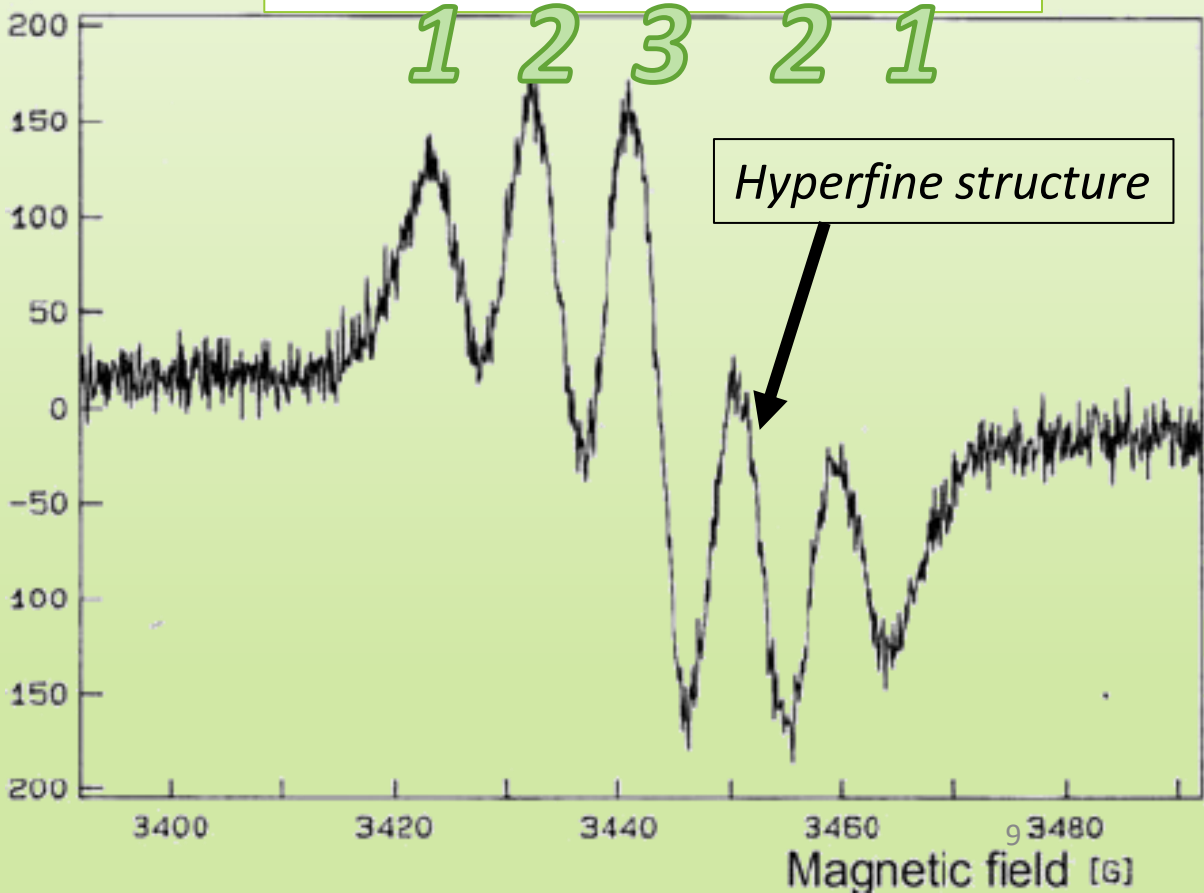
Nuclear Spin

- 1/2
- 3/2
- 5/2
- 7/2
- 9/2
- 5
- 8

No data for synthetic elements ≥ 103

Determination of Hyperfine Structure Intensity Ratios for Two Equally Coupled $I = 1$ Nuclei (e.g., Nitrogen) Such As the Ones Found in DPPH

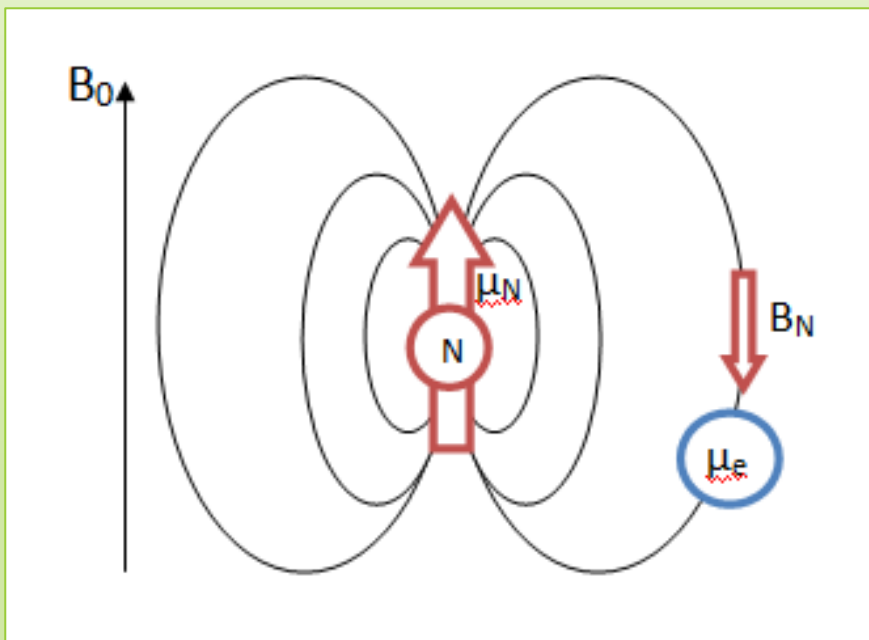
Spin Configurations	m_1	m_2	$M = m_1 + m_2$	Intensity Ratio
↑ ↑	1	1	2	1
↑ →	1	0	1	2
→ ↑	0	1	1	2
↑ ↓	1	-1	0	3
→ →	0	0	0	3
↓ ↓	-1	-1	-2	1
→ ↓	0	-1	-1	2
↓ →	-1	0	-1	2
↓ ↓	-1	-1	-2	1



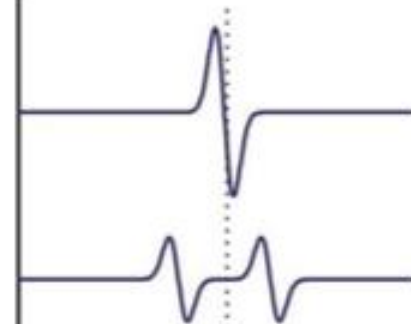
ESR Spectra

Hyperfine Interaction

$$2I + 1$$



A



$$S = 1/2$$

A



$$S = 1/2 \quad I = 1/2 \text{ (1 nucleus)}$$



$$S = 1/2 \quad I = 1$$

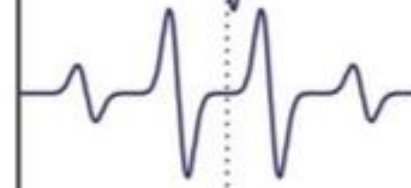


$$S = 1/2 \quad I = 3/2$$

B

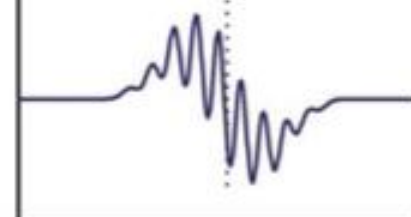


$$S = 1/2 \quad I = 1/2 \text{ (2 nuclei)}$$



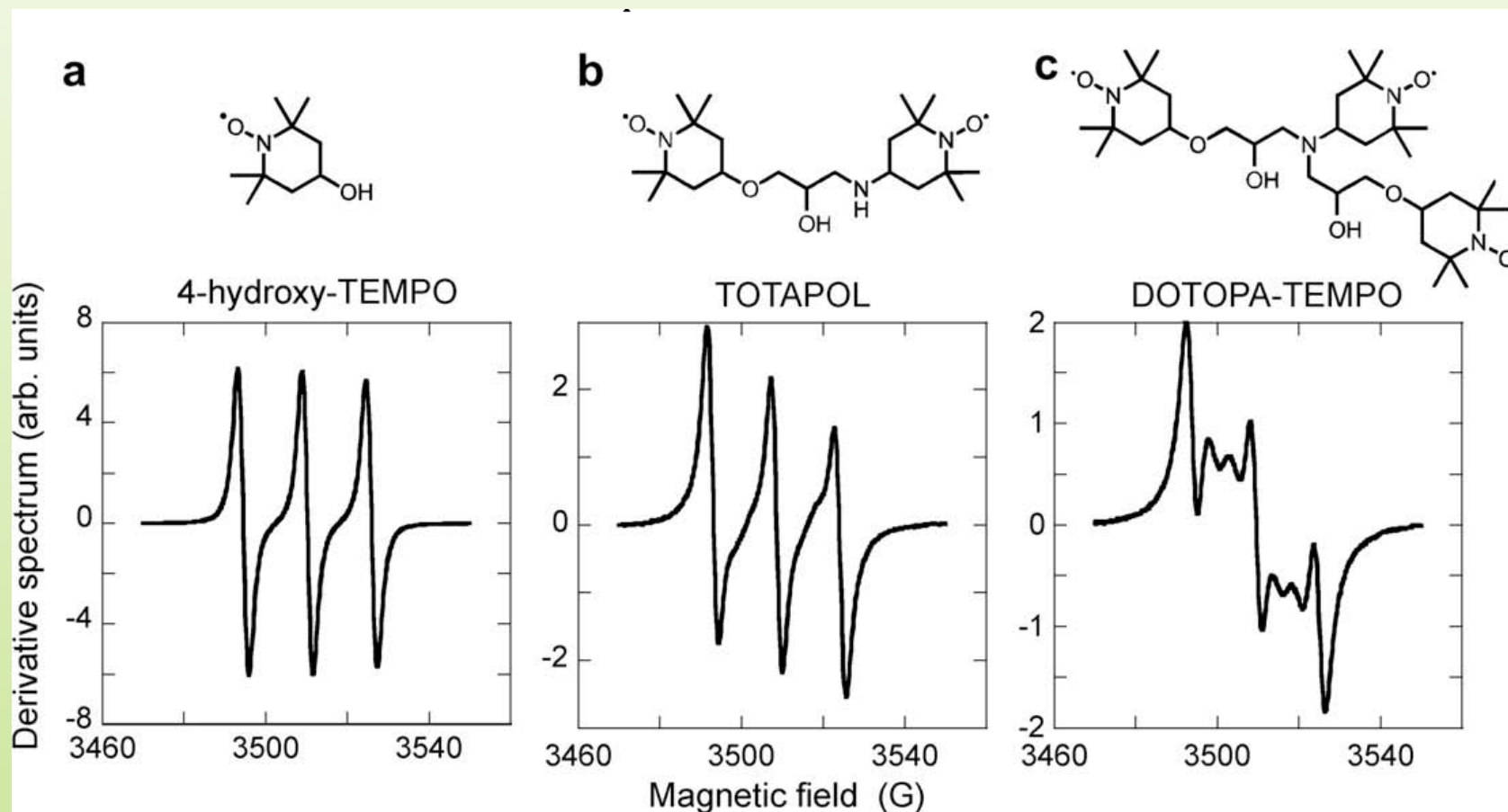
$$S = 1/2 \quad I = 1/2 \text{ (3 nuclei)}$$

C



$$S = 1/2 \quad I = 1 \text{ (4 nuclei)}$$

ESR Spectra



*Simulating
EPR Spectra*

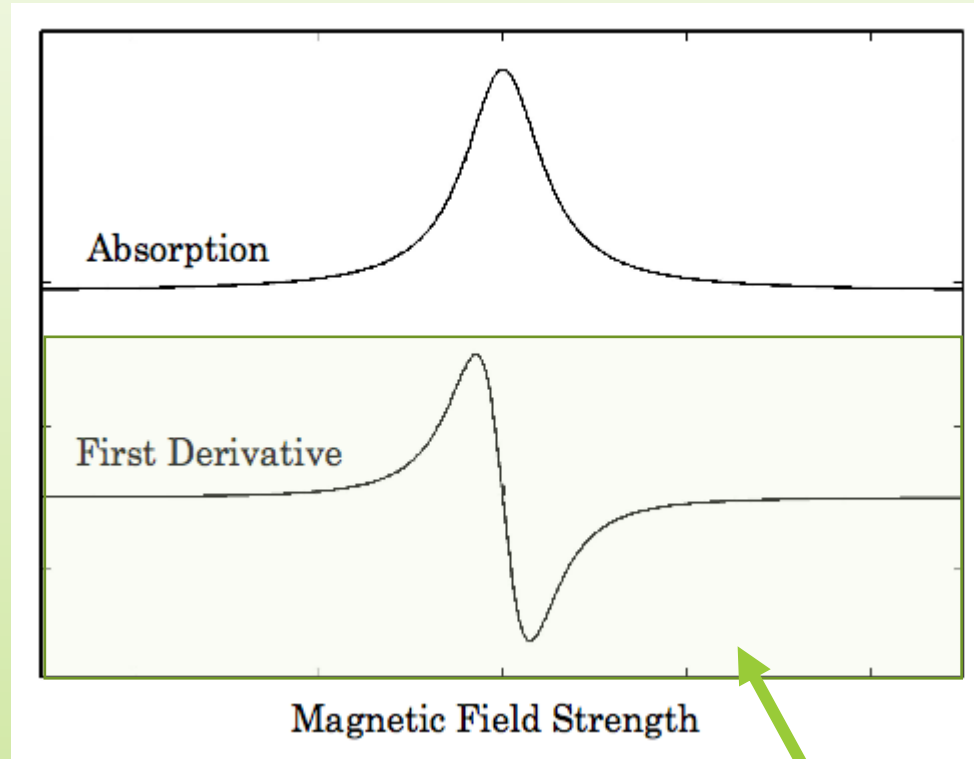


TopSpin

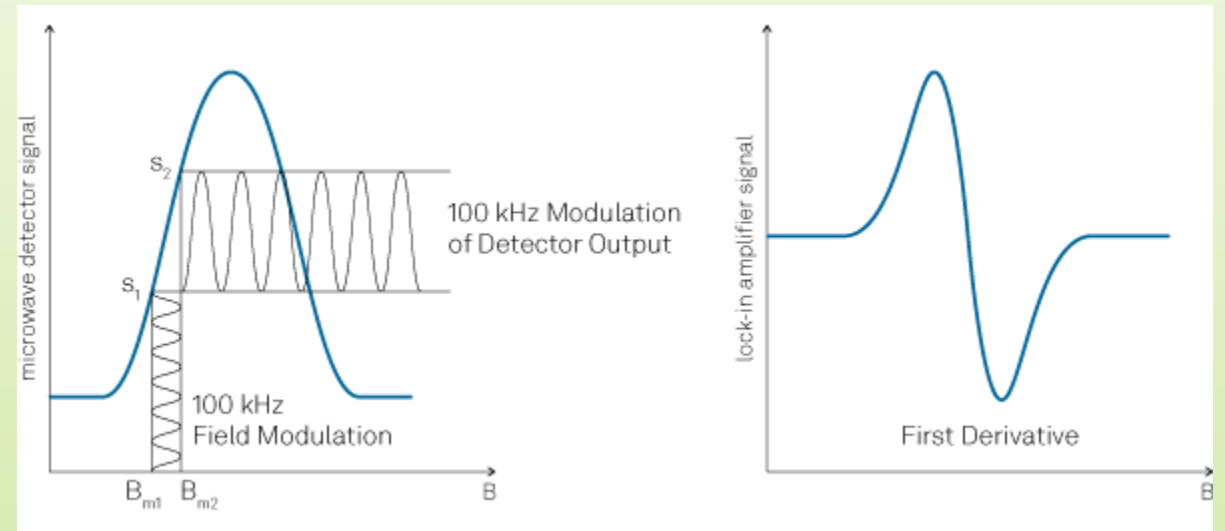


ORCA

ESR Spectra



*We detect this in
CW ESR*



Report

***Please be sure to refer to the handout
posted on Blackboard for details of
what I expect in your reports***