The Structure of Glass - Lectures 10 and 11: Nuclear Magnetic Resonance Spectroscopy of Glass Structure: Theory and Background

Be able to recognize the four magnetic interactions affecting the NMR resonance signal

Be able to recognize the main components of the NMR spectrometer

Be able to identify dipolar versus quadrupolar nucleii and recognize the expected differences in their NMR absorption spectra

Application of 29Si MASS-NMR – Identification of Si sites in Alkali Silicate Glasses

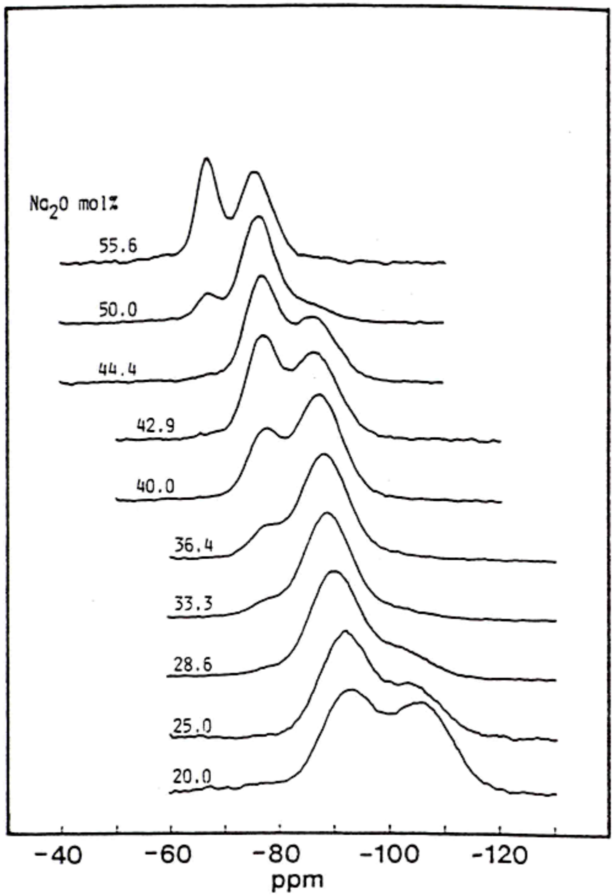


Fig. 1. ^{29}Si MAS-NMR spectra of sodium silicate glasses.

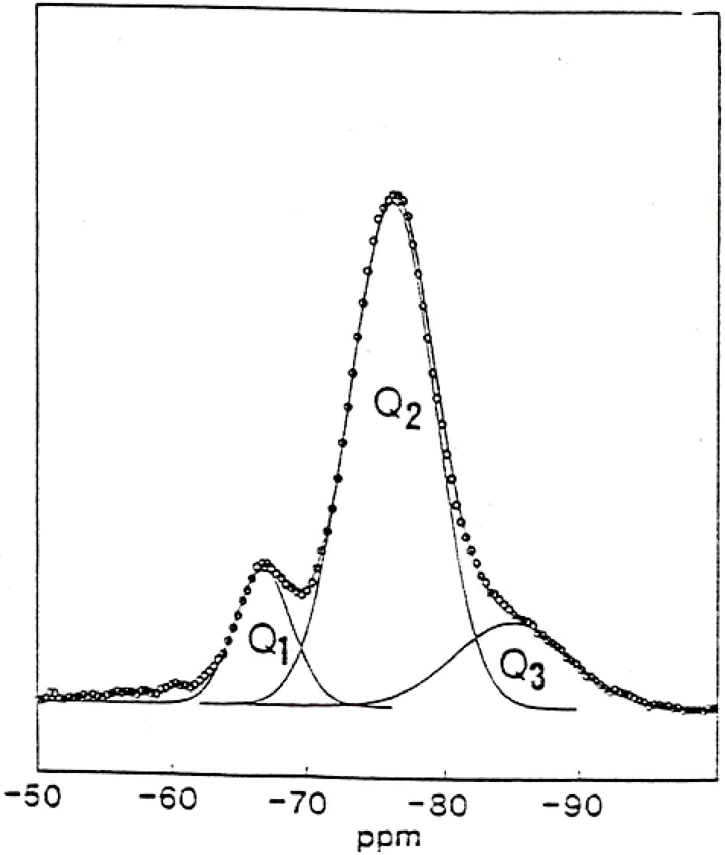
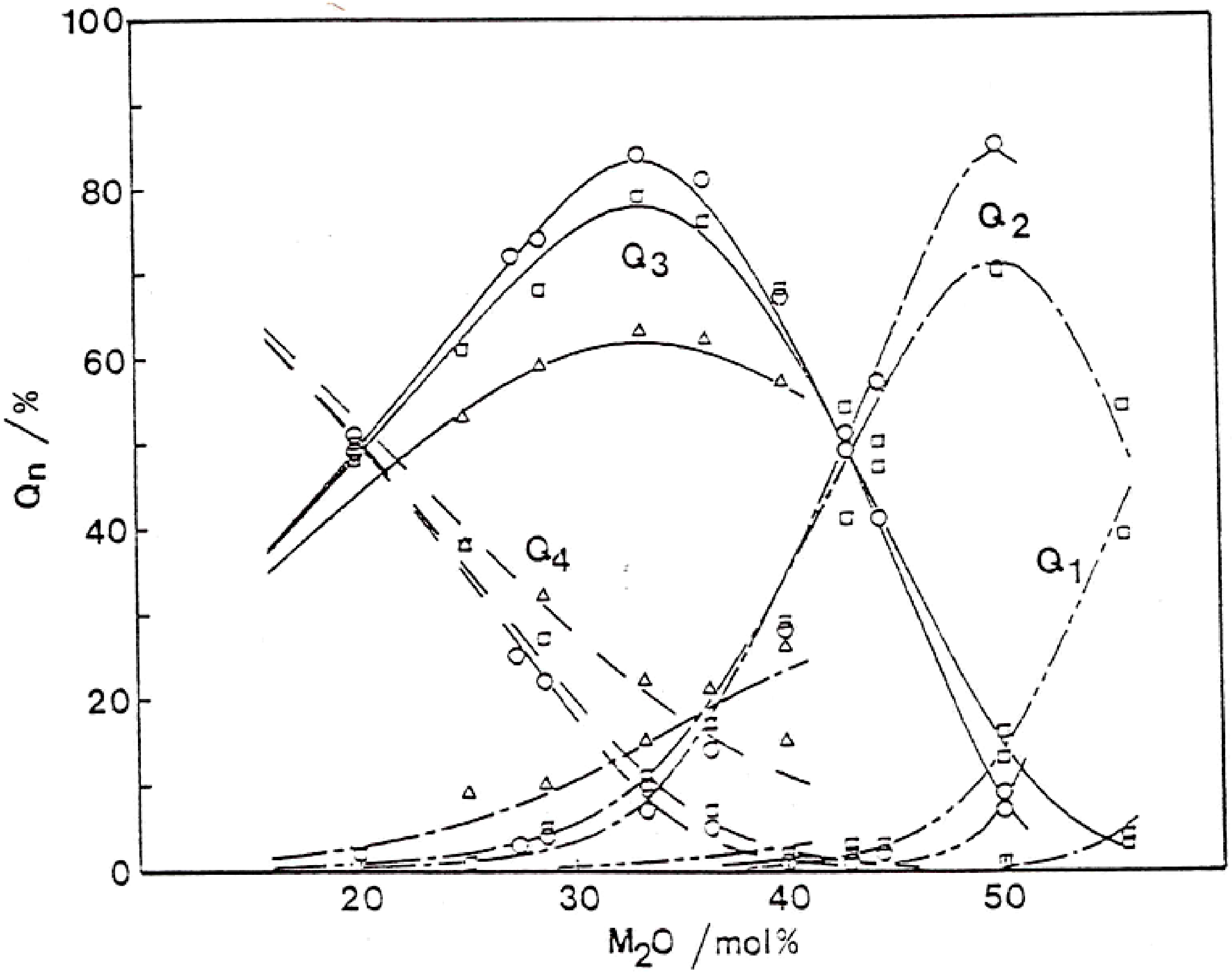


Fig. 3. ^{29}Si MAS-NMR spectrum of sodium metasilicate glass.

Maekawa, et al. **The structural groups of alkali silicate glasses determined from silicon-29 MAS- NMR.** Journal of Non-Crystalline Solids (1991), 127(1), 53-64.

Application of 29Si MASS-NMR – Identification of Si sites in Alkali Silicate Glasses



Maekawa, et al. **The structural groups of alkali silicate glasses determined from silicon-29 MAS- NMR.** Journal of Non-Crystalline Solids (1991), 127(1), 53-64.

Magnetic Fields

- Magnetic fields have direction and magnitude
- The direction controls the effect of the magnetic field
- The magnitude controls the extent of the effect of the magnetic field

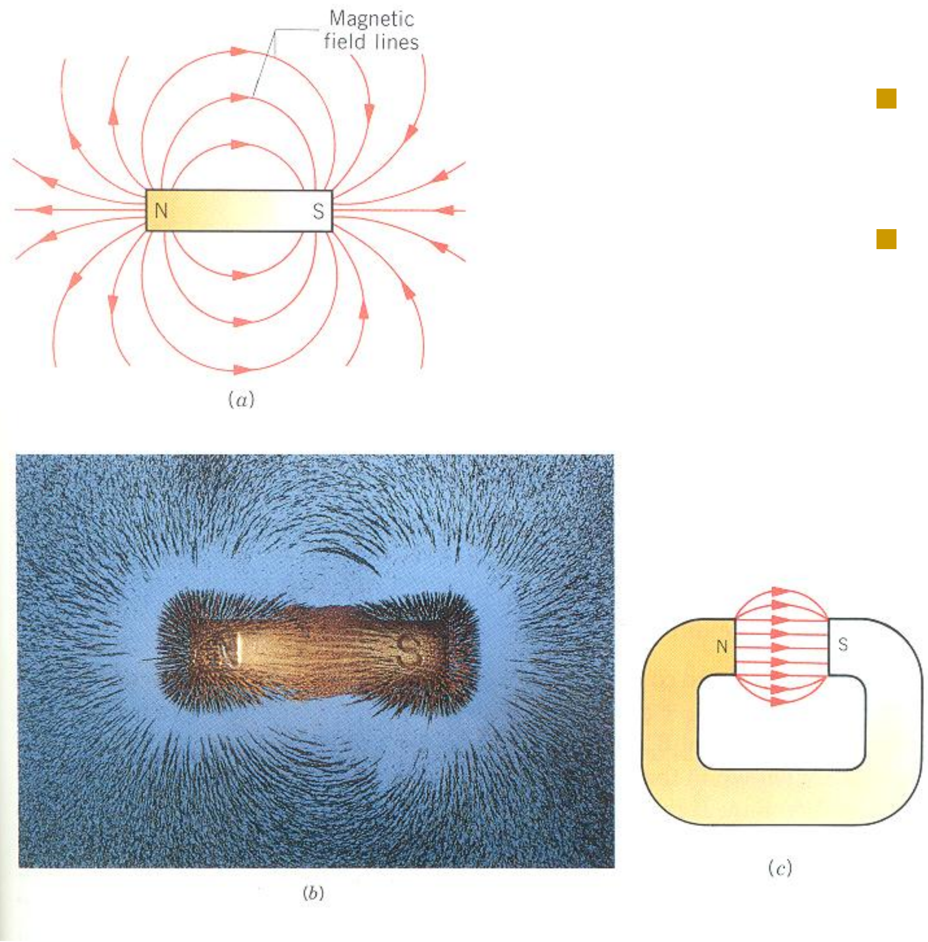
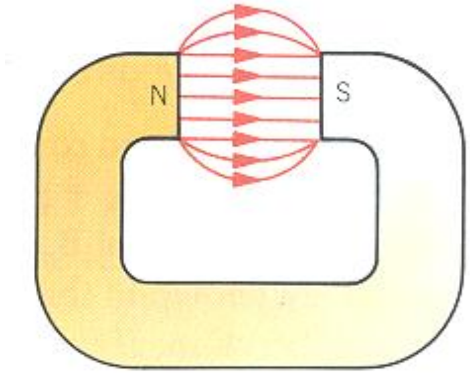


Figure 21.4 (*a*) The magnetic field lines and (*b*) the pattern of iron filings in the vicinity of a bar magnet. (*c*) The magnetic field lines in the gap of a horseshoe magnet.

Physics, 3rd Edition, Cutnell and Johnson, Wiley

Nearly constant magnetic fields



- By carefully adjusting the geometry of the field lines
- A nearly constant magnetic field can be obtained
  - Smaller carefully controlled geometries create more constant (more homogenous) magnetic field lines
  - Larger less carefully controlled geometries create less constant (more inhomogeneous) field lines
- Homogenous field lines are important for NMR spectroscopy

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Magnetic Flux

- The magnetic flux, B, is proportional to the number of magnetic field lines passing through a surface
- The larger the number of field lines, the larger the flux
- The larger the flux the greater the magnetic force

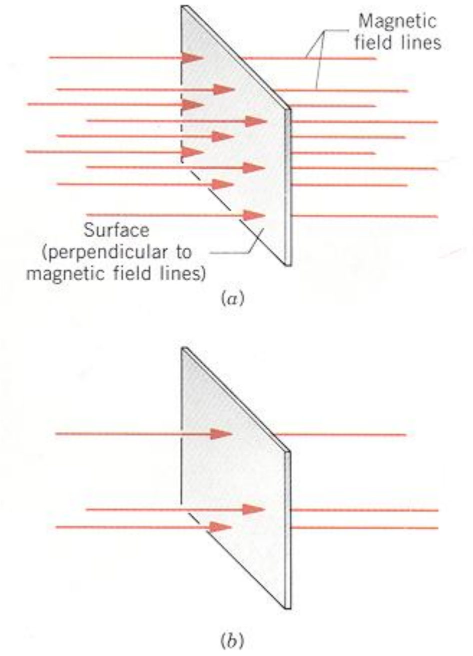

Figure 22.11 The magnitude of the magnetic field in (*a*) is three times greater than that in (*b*), because the number of magnetic field lines crossing the surfaces is in the ratio of 3 : 1.

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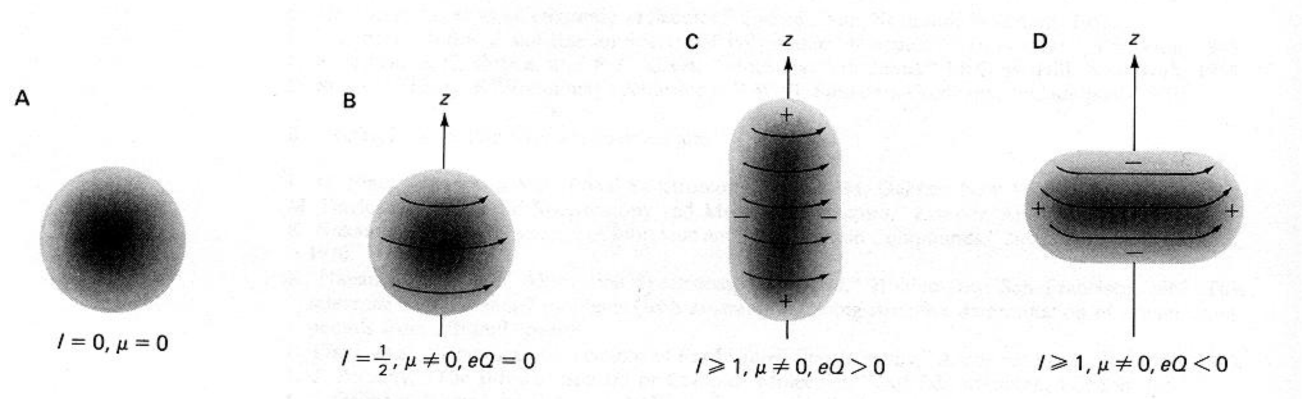
The NMR experiment – The magnetic moment

- All nucleii have a spin quantum number I
  - I = 0, ½, 1, 3/2, 2, 5/2….
- Spin quantum number I imparts a magnetic moment
  - Spherical magnetic moment, eQ = 0, dipolar nucleii
  - Aspherical magnetic moment, eQ ≠ 0, quadrupolar nucleii
- Nucleii with a non-zero magnetic moment can couple to an external magnetic field to generate nuclear magnetic energy levels



Drago, Physical Methods in Chemistry, Saunders

The NMR Experiment – The Nuclear Angular Momentum

- Angular momentum P depends upon the nuclear spin quantum number I

$$P = \sqrt{I(I+1)}h/2\pi$$

- Magnetic moment μ depends upon the nuclear angular momentum P

$$\mu = \gamma P$$

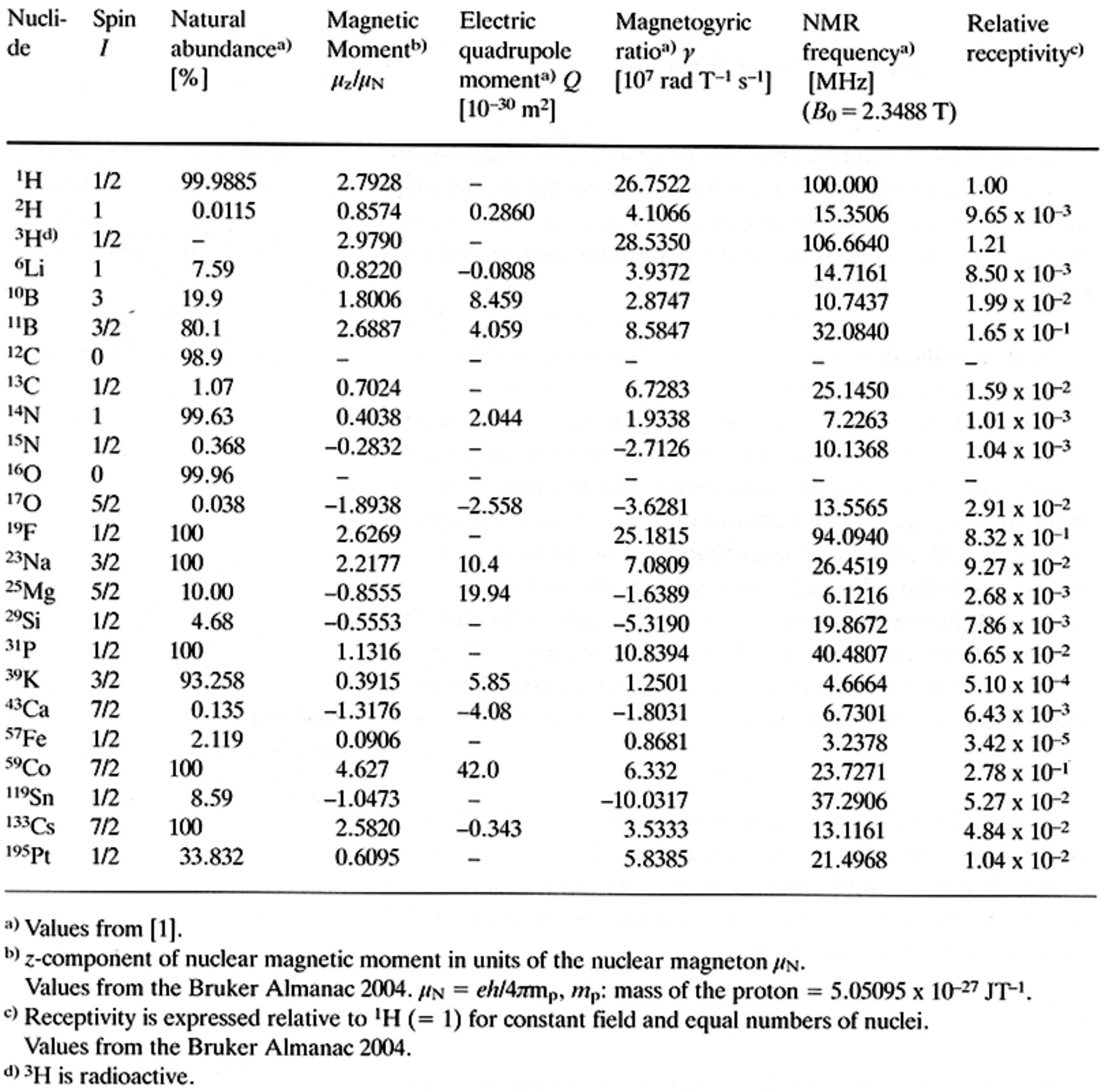
- Magnetic moment μ in turn depends upon the upon the nuclear spin quantum number I

$$\mu = \gamma\sqrt{I(I+1)}h/2\pi$$

The Four NMR interactions

- The interaction of the nuclear spin with its chemical surroundings changes the energy of the spin states and if we can sense these changes, we can gain chemical information about the environment around the active nuclei
- The Total NMR Interaction Hamiltonian: H_{total}
  - $H_{\text{total}} = H_{\text{zeeman}} + H_{\text{dipoloar}} + H_{\text{chemical shift}} + H_{\text{quadrupolar}}$
  - $E_{\text{total}} = E_{\text{zeeman}} + E_{\text{dipoloar}} + E_{\text{chemical shift}} + E_{\text{quadrupolar}}$
- Each interaction produces an energy splitting in the NMR signal
- The complicating factor is that these interactions all act at the same time and on the same nucleii
- NMR signals can get very complicated very quickly
  - Especially for Quadrupolar nulceii

Typical values for common nuclides



Nuclide	Spin I	Natural abundance a) [%]	Magnetic Moment b) μ_z/μ_N	Electric quadrupole moment a) Q [10^{-30} m^2]	Magnetogyric ratio a) γ [10^7 rad T^{-1} s^{-1}]	NMR frequency a) [MHz] ($B_0 = 2.3488$ T)	Relative receptivity c)
^{1}H	1/2	99.9885	2.7928	–	26.7522	100.000	1.00
^{2}H	1	0.0115	0.8574	0.2860	4.1066	15.3506	9.65×10^{-3}
^{3}H d)	1/2	–	2.9790	–	28.5350	106.6640	1.21
^{6}Li	1	7.59	0.8220	–0.0808	3.9372	14.7161	8.50×10^{-3}
^{10}B	3	19.9	1.8006	8.459	2.8747	10.7437	1.99×10^{-2}
^{11}B	3/2	80.1	2.6887	4.059	8.5847	32.0840	1.65×10^{-1}
^{12}C	0	98.9	–	–	–	–	–
^{13}C	1/2	1.07	0.7024	–	6.7283	25.1450	1.59×10^{-2}
^{14}N	1	99.63	0.4038	2.044	1.9338	7.2263	1.01×10^{-3}
^{15}N	1/2	0.368	–0.2832	–	–2.7126	10.1368	1.04×10^{-3}
^{16}O	0	99.96	–	–	–	–	–
^{17}O	5/2	0.038	–1.8938	–2.558	–3.6281	13.5565	2.91×10^{-2}
^{19}F	1/2	100	2.6269	–	25.1815	94.0940	8.32×10^{-1}
^{23}Na	3/2	100	2.2177	10.4	7.0809	26.4519	9.27×10^{-2}
^{25}Mg	5/2	10.00	–0.8555	19.94	–1.6389	6.1216	2.68×10^{-3}
^{29}Si	1/2	4.68	–0.5553	–	–5.3190	19.8672	7.86×10^{-3}
^{31}P	1/2	100	1.1316	–	10.8394	40.4807	6.65×10^{-2}
^{39}K	3/2	93.258	0.3915	5.85	1.2501	4.6664	5.10×10^{-4}
^{43}Ca	7/2	0.135	–1.3176	–4.08	–1.8031	6.7301	6.43×10^{-3}
^{57}Fe	1/2	2.119	0.0906	–	0.8681	3.2378	3.42×10^{-5}
^{59}Co	7/2	100	4.627	42.0	6.332	23.7271	2.78×10^{-1}
^{119}Sn	1/2	8.59	–1.0473	–	–10.0317	37.2906	5.27×10^{-2}
^{133}Cs	7/2	100	2.5820	–0.343	3.5333	13.1161	4.84×10^{-2}
^{195}Pt	1/2	33.832	0.6095	–	5.8385	21.4968	1.04×10^{-2}

a) Values from [1].

b) z-component of nuclear magnetic moment in units of the nuclear magneton μ_N.
Values from the Bruker Almanac 2004. $\mu_N = eh/4\pi m_p$, m_p: mass of the proton $= 5.05095 \times 10^{-27}$ JT^{-1}.

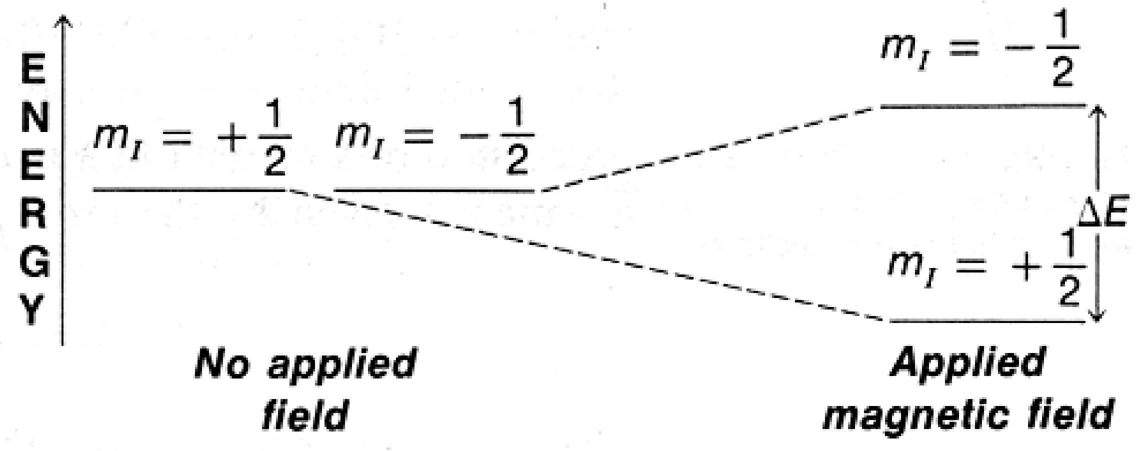
c) Receptivity is expressed relative to ^{1}H (= 1) for constant field and equal numbers of nuclei.
Values from the Bruker Almanac 2004.

d) ^{3}H is radioactive.

Freibolin, Basic one- and two-dimensional NMR spectroscopy, Wiley-VCH

The NMR Experiment – The Zeeman Interaction

- Spin quantum number I generates 2I + 1 “Zeeman” energy levels
  - The *Zeeman* Interaction
  - Spin angular momentum quantum number m creates
  - -I, (-I +1), (-I+2)….(I – 2), (I - 1), I … Zeeman Energy States
  - Dipolar nuclei, m = ½
  - For m = ½, the simplest “dipolar” nuclei, ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P…
  - ½, -½ Zeeman energy levels are created in a magnetic field



$$\Delta E_Z = \bar{\gamma} h B_o$$
$$= h\nu_o = h\nu_L$$

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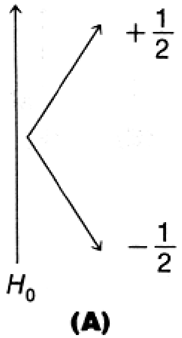
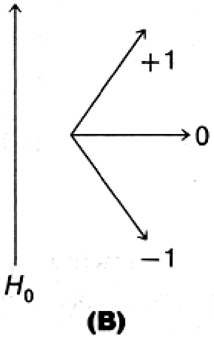
The Zeeman Interaction for Quadrupolar Nucleii

- For quadrupolar nuclei 2I + 1 Zeeman energy level are set up which in first order are evenly spaced in energy
- NMR absorption would in principle occur between any two states
- Example I = 1 , m = -1, 0, and 1
- Example I = 3/2 , m = -3/2, -1/2, ½, and 3/2

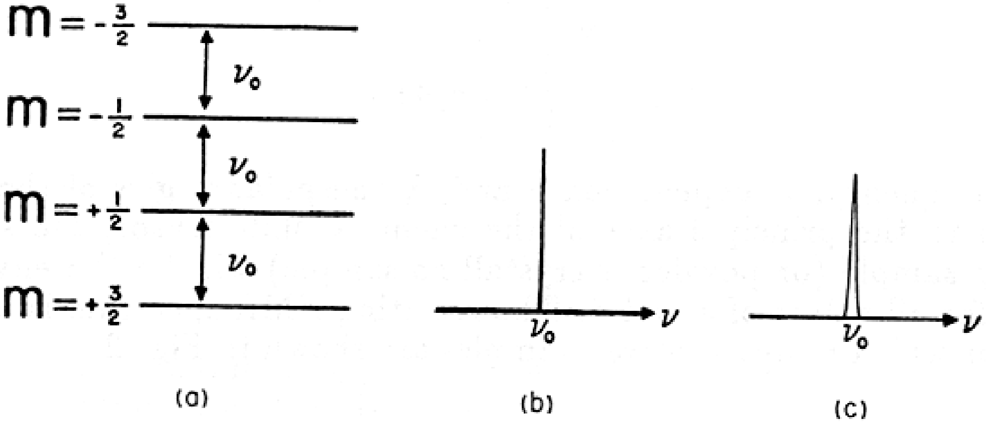
I = 1/2



I = 1



I = 3/2



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Various NMR Nucleii

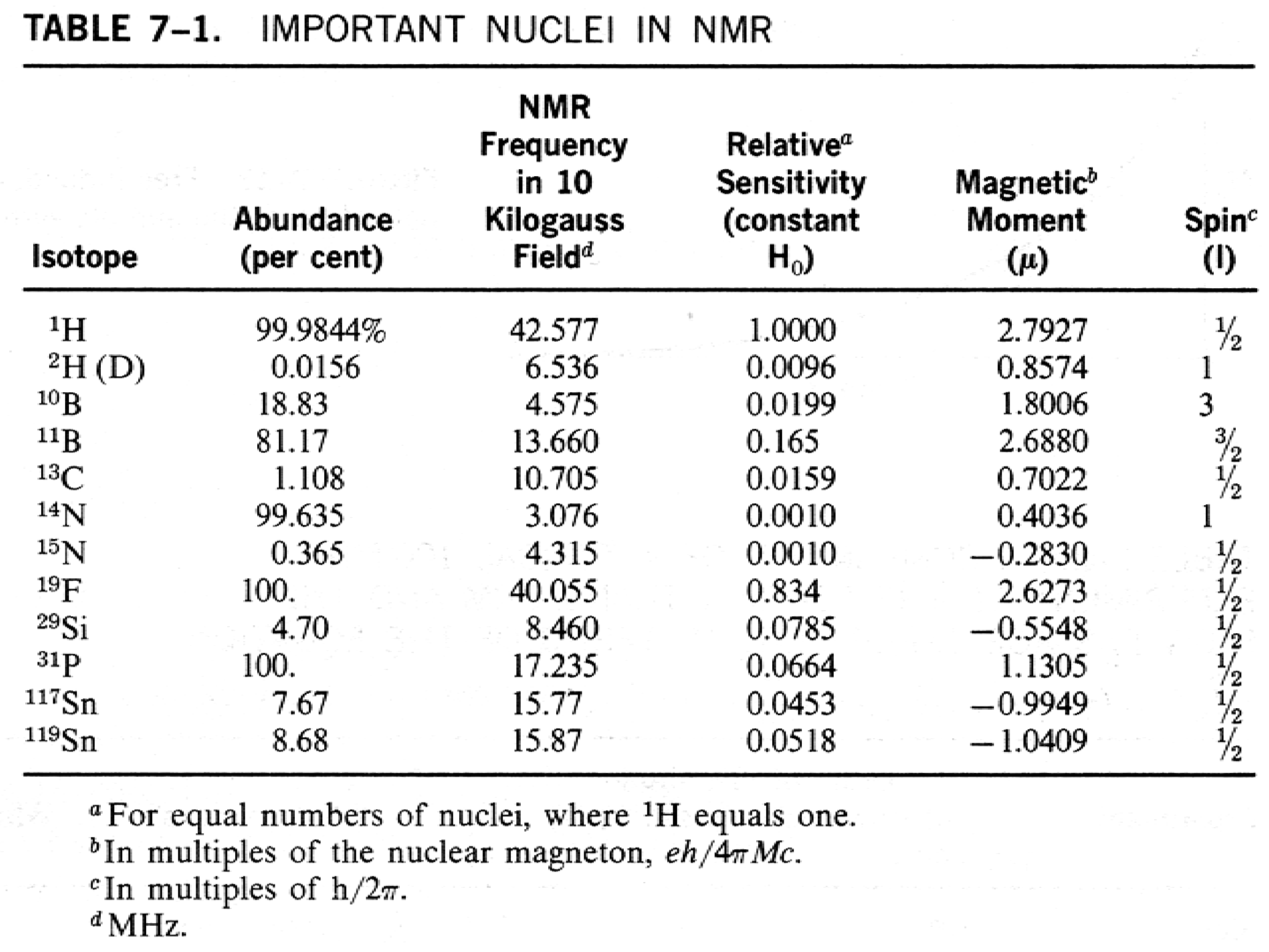

TABLE 7–1. IMPORTANT NUCLEI IN NMR

Isotope	Abundance (per cent)	NMR Frequency in 10 Kilogauss Field[d]	Relative[a] Sensitivity (constant H_0)	Magnetic[b] Moment (μ)	Spin[c] (I)
^{1}H	99.9844%	42.577	1.0000	2.7927	$\frac{1}{2}$
^{2}H (D)	0.0156	6.536	0.0096	0.8574	1
^{10}B	18.83	4.575	0.0199	1.8006	3
^{11}B	81.17	13.660	0.165	2.6880	$\frac{3}{2}$
^{13}C	1.108	10.705	0.0159	0.7022	$\frac{1}{2}$
^{14}N	99.635	3.076	0.0010	0.4036	1
^{15}N	0.365	4.315	0.0010	−0.2830	$\frac{1}{2}$
^{19}F	100.	40.055	0.834	2.6273	$\frac{1}{2}$
^{29}Si	4.70	8.460	0.0785	−0.5548	$\frac{1}{2}$
^{31}P	100.	17.235	0.0664	1.1305	$\frac{1}{2}$
^{117}Sn	7.67	15.77	0.0453	−0.9949	$\frac{1}{2}$
^{119}Sn	8.68	15.87	0.0518	−1.0409	$\frac{1}{2}$

[a] For equal numbers of nuclei, where ^{1}H equals one.

[b] In multiples of the nuclear magneton, $eh/4\pi Mc$.

[c] In multiples of $h/2\pi$.

[d] MHz.

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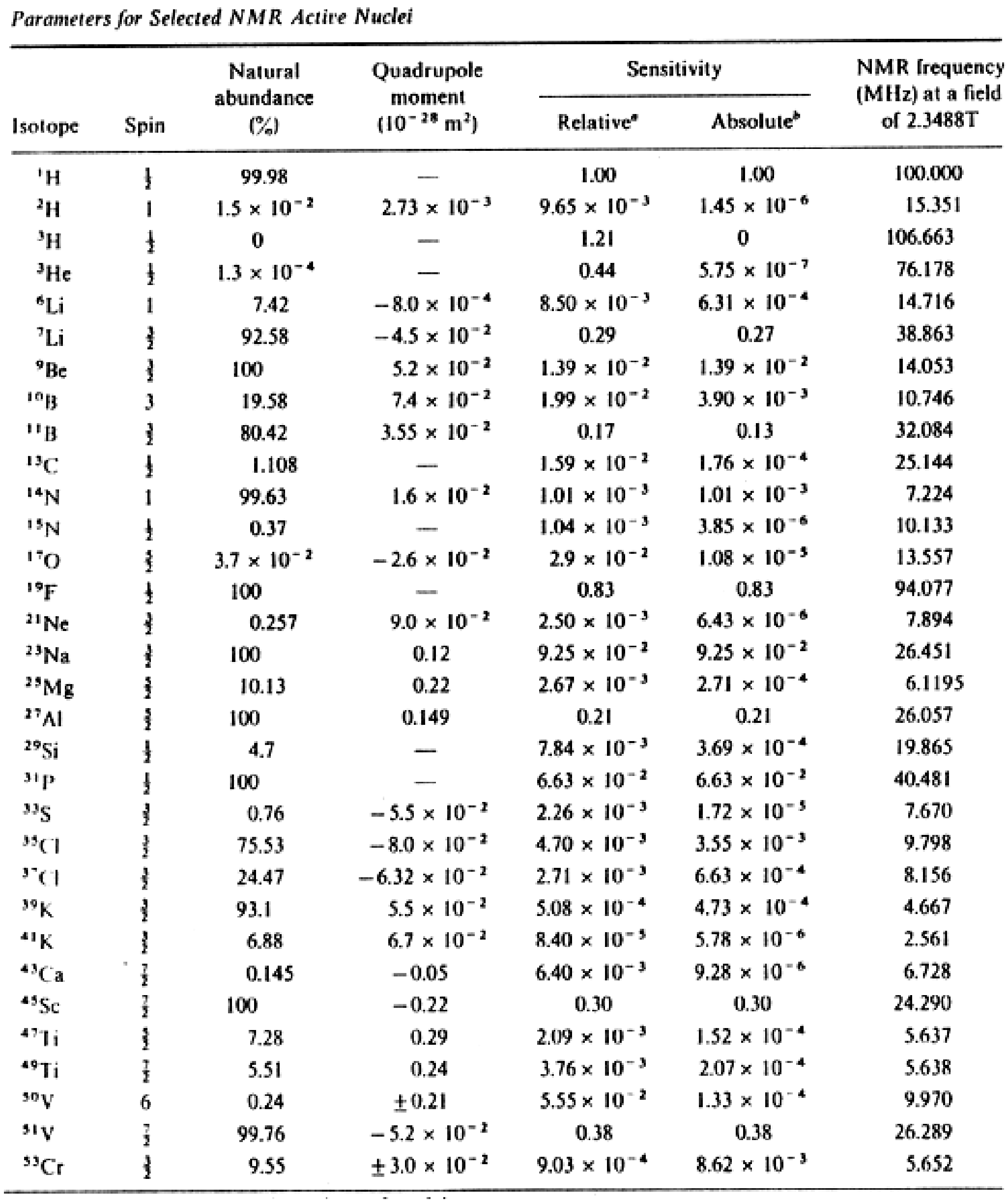
Various NMR Nucleii

- Spin determines complexity and number of the Zeeman energy levels
  - ½ is the simplest nuclei, only two energy levels
  - Higher spin, larger numbers of Zeeman levels and now quadrupolar interactions, line broadening occurs
- Natural abundance and sensitivity determine strength of signal
- Gyromagnetic ratio determines NMR frequency, higher the frequency the better the S/N, lower the weaker the S/N



Parameters for Selected NMR Active Nuclei

Isotope	Spin	Natural abundance (%)	Quadrupole moment (10^{-28} m²)	Sensitivity		NMR frequency (MHz) at a field of 2.3488T
				Relative[a]	Absolute[b]	
^{1}H	$\frac{1}{2}$	99.98	—	1.00	1.00	100.000
^{2}H	1	1.5×10^{-2}	2.73×10^{-3}	9.65×10^{-3}	1.45×10^{-6}	15.351
^{3}H	$\frac{1}{2}$	0	—	1.21	0	106.663
^{3}He	$\frac{1}{2}$	1.3×10^{-4}	—	0.44	5.75×10^{-7}	76.178
^{6}Li	1	7.42	-8.0×10^{-4}	8.50×10^{-3}	6.31×10^{-4}	14.716
^{7}Li	$\frac{3}{2}$	92.58	-4.5×10^{-2}	0.29	0.27	38.863
^{9}Be	$\frac{3}{2}$	100	5.2×10^{-2}	1.39×10^{-2}	1.39×10^{-2}	14.053
^{10}B	3	19.58	7.4×10^{-2}	1.99×10^{-2}	3.90×10^{-3}	10.746
^{11}B	$\frac{3}{2}$	80.42	3.55×10^{-2}	0.17	0.13	32.084
^{13}C	$\frac{1}{2}$	1.108	—	1.59×10^{-2}	1.76×10^{-4}	25.144
^{14}N	1	99.63	1.6×10^{-2}	1.01×10^{-3}	1.01×10^{-3}	7.224
^{15}N	$\frac{1}{2}$	0.37	—	1.04×10^{-3}	3.85×10^{-6}	10.133
^{17}O	$\frac{5}{2}$	3.7×10^{-2}	-2.6×10^{-2}	2.9×10^{-2}	1.08×10^{-5}	13.557
^{19}F	$\frac{1}{2}$	100	—	0.83	0.83	94.077
^{21}Ne	$\frac{3}{2}$	0.257	9.0×10^{-2}	2.50×10^{-3}	6.43×10^{-6}	7.894
^{23}Na	$\frac{3}{2}$	100	0.12	9.25×10^{-2}	9.25×10^{-2}	26.451
^{25}Mg	$\frac{5}{2}$	10.13	0.22	2.67×10^{-3}	2.71×10^{-4}	6.1195
^{27}Al	$\frac{5}{2}$	100	0.149	0.21	0.21	26.057
^{29}Si	$\frac{1}{2}$	4.7	—	7.84×10^{-3}	3.69×10^{-4}	19.865
^{31}P	$\frac{1}{2}$	100	—	6.63×10^{-2}	6.63×10^{-2}	40.481
^{33}S	$\frac{3}{2}$	0.76	-5.5×10^{-2}	2.26×10^{-3}	1.72×10^{-5}	7.670
^{35}Cl	$\frac{3}{2}$	75.53	-8.0×10^{-2}	4.70×10^{-3}	3.55×10^{-3}	9.798
^{37}Cl	$\frac{3}{2}$	24.47	-6.32×10^{-2}	2.71×10^{-3}	6.63×10^{-4}	8.156
^{39}K	$\frac{3}{2}$	93.1	5.5×10^{-2}	5.08×10^{-4}	4.73×10^{-4}	4.667
^{41}K	$\frac{3}{2}$	6.88	6.7×10^{-2}	8.40×10^{-5}	5.78×10^{-6}	2.561
^{43}Ca	$\frac{7}{2}$	0.145	-0.05	6.40×10^{-3}	9.28×10^{-6}	6.728
^{45}Sc	$\frac{7}{2}$	100	-0.22	0.30	0.30	24.290
^{47}Ti	$\frac{5}{2}$	7.28	0.29	2.09×10^{-3}	1.52×10^{-4}	5.637
^{49}Ti	$\frac{7}{2}$	5.51	0.24	3.76×10^{-3}	2.07×10^{-4}	5.638
^{50}V	6	0.24	± 0.21	5.55×10^{-2}	1.33×10^{-4}	9.970
^{51}V	$\frac{7}{2}$	99.76	-5.2×10^{-2}	0.38	0.38	26.289
^{53}Cr	$\frac{3}{2}$	9.55	$\pm 3.0 \times 10^{-2}$	9.03×10^{-4}	8.62×10^{-3}	5.652

Typical Calculation of typical Zeeman Energies

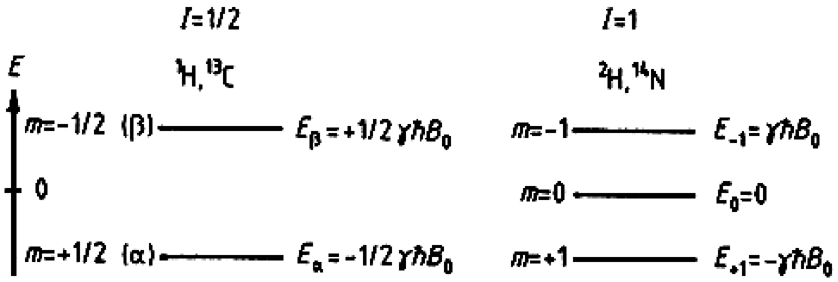
- Calculate the Zeeman energy separation in Joules for 1 and 10 T magnetic fields for:
  - ^{1}H, ^{11}B, ^{29}Si, and ^{31}P
- Calculate Larmor frequency in Hz at 1 and 10 T magnetic fields for:
  - H, B, Si, and P
- Calculate the Larmor frequency in cm^{-1} at 1 and 10 T magnetic fields for:
  - H, B, Si, and P

Typical Calculation of typical Zeeman Energies

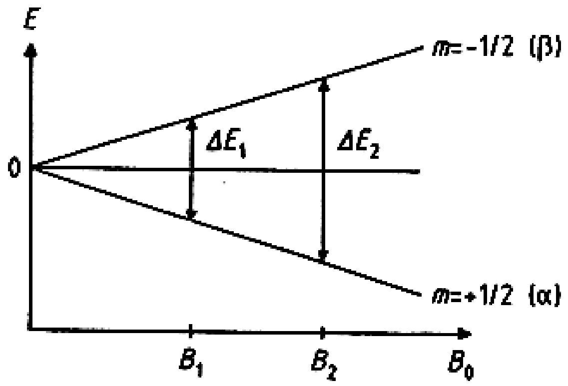
- ^{1}H
  - 100 MHz @ 2.3488 T = 42.5749 MHz @ 1 T, 425.7493 MHz @ 10 T
  - ΔE_Z(1 T) = $h\upsilon$ = 6.626 x 10^{-34}Js x 42.5749 x 10^{6}Hz x 2π rad/Hz = 1.7725 x 10^{-15}J
  - $c = \lambda\upsilon$, $1/\lambda = \upsilon/c$ = 42.5749 x 10^{6} Hz/2.9979 x 10^{10}cm/sec = 0.0014 cm^{-1}
  - Compare this wavenumber to a a C-H stretch, ~2,800 cm^{-1}
  - C-H stretch frequency is ~ 1 millions times more energtic than the Zeeman frequency (energy) of a C-H stretch!
- ^{11}B
- ^{29}Si
- ^{31}P

Calculation of the population statistics of the Zeeman energy levels

- Just as in vibrational spectroscopy, the population of the different nuclear Zeeman energy levels depends upon the energy difference between the ground and excited states
- The population statistics are governed by Boltzmann statistics



$$\frac{n_1}{n_0} = e^{-\Delta E_z / kT}$$



- For the 1H nuclide at 1 T,

  calculate the fraction of nuclei in the excited Zeeman state at 298K
- Compare this to the fraction for a 10 T field

The Zeeman Interaction

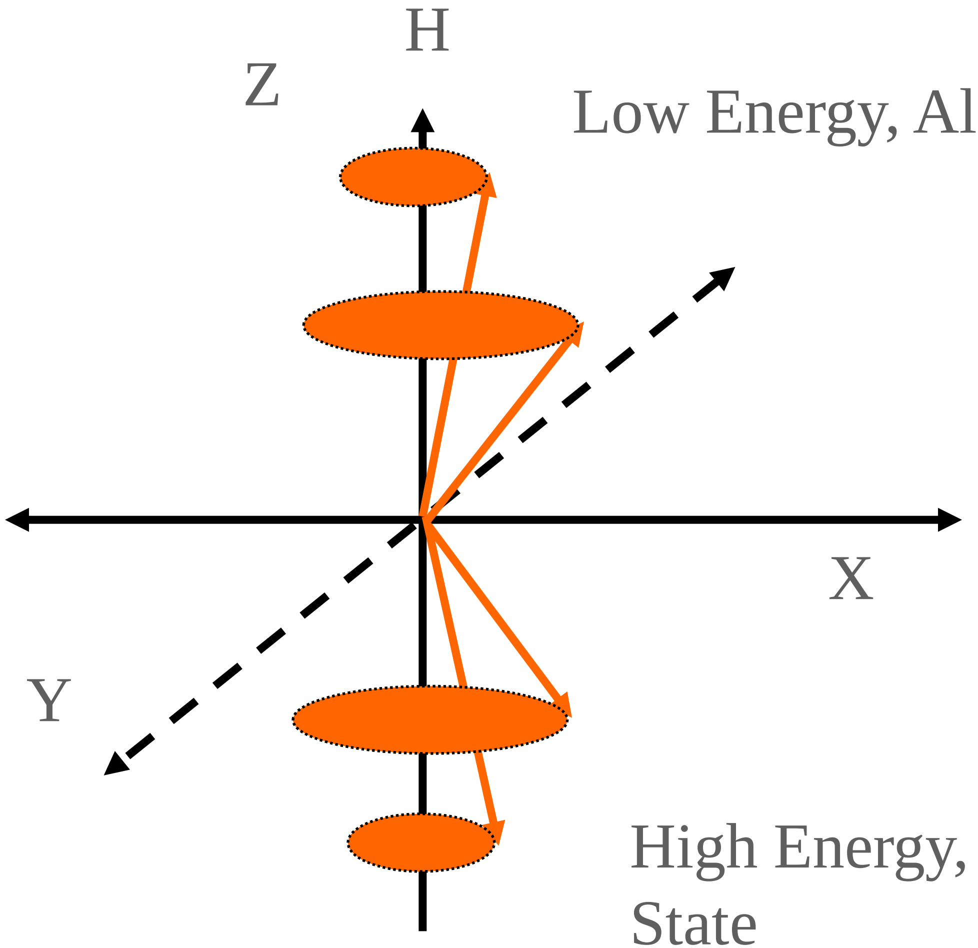
- $H_Z\Psi_n = E_Z\Psi_n$
- The Zeeman energy levels are set up by and are a function of the magnetic field, the magnetic spin quantum number of the nucleus, and the gyromagnetic ratio of the nucleii

$$\vec{I} \equiv \textit{spin} \quad \textit{angular} \quad \textit{momentum} \quad \textit{vector}$$

$$\left|\vec{I}\right| = \left[I(I+1)\right]^{1/2}\hbar$$

$$\vec{I}_Z = m_I\hbar \qquad -I \le m_I \le I \quad 2I+1 \quad m \quad \textit{values}$$

The Zeeman Interaction, I = 3/2 (B, Al…)



Low Energy, Aligned, State

High Energy, anti-aligned, State

The Zeeman Transition

- Transitions occur from low energy aligned states to high energy anti-aligned states
- The energy (frequency) of the transition is governed by the magnetic field, the spin angular momentum vector of the spin energy state, and proportionality factor for the nucleii

The Zeeman Interaction

$$\vec{\mu} = \gamma\hbar\vec{I} \qquad \gamma = \hat{g}\text{yromagneti c ratio}$$

$$\gamma = \frac{g}{\hbar}\left(\frac{e\hbar}{2m_p}\right) = \frac{g\mu_N}{\hbar} \qquad \mu_N = \text{Bohr nuclear magneton}$$

$$\vec{\mu} = \left(\frac{g\mu_N}{\hbar}\right)\vec{I}$$

$$\hat{H}_Z = -\vec{\mu}\cdot\vec{H}_o = -\gamma\hbar\vec{I}\cdot\vec{H}_o = \gamma\hbar m H_o$$

$$\Delta E_Z = -\gamma\hbar m H_o - \left[\gamma\hbar(m+1)H_o\right]$$

$$= \gamma\hbar H_o$$

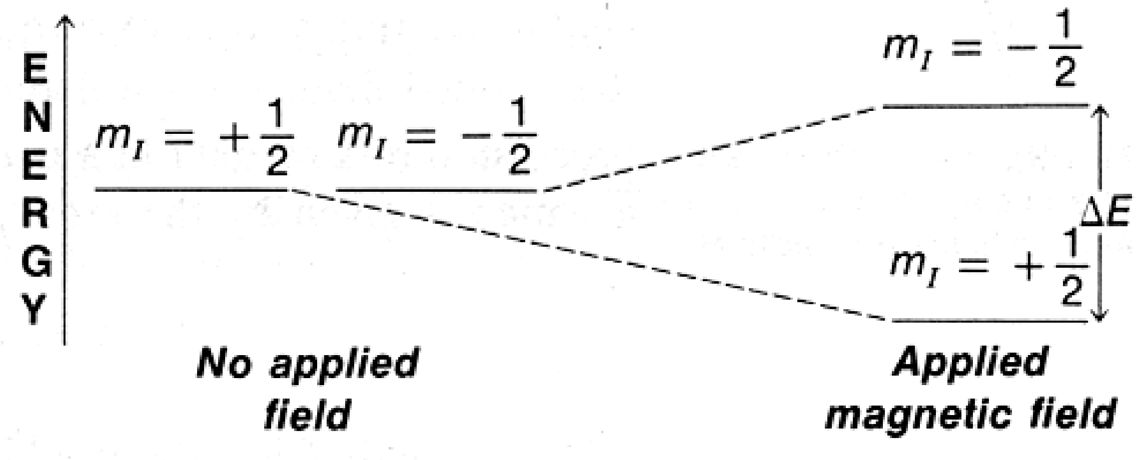
$$= h\nu_o \equiv h\nu_L = 2\pi h\omega_L$$

$$\omega_L \equiv \text{Larmor Frequency}$$

The Zeeman Interaction

- The Zeeman Splitting increases with magnetic field strength

$$\nu_o = \frac{\gamma \hbar B_o}{h} = \frac{\gamma B_o}{2\pi}$$



Calculation of the Zeeman Splitting

$$For \quad protons \quad ,$$

$$\nu_o = \frac{\gamma}{2\pi} H_o = \frac{g\mu_N}{h} B_o$$

$$g = 5.586$$

$$\mu_N = \frac{e\hbar}{2m_P}$$

Take a 1 Tesla field

μ_N = ?

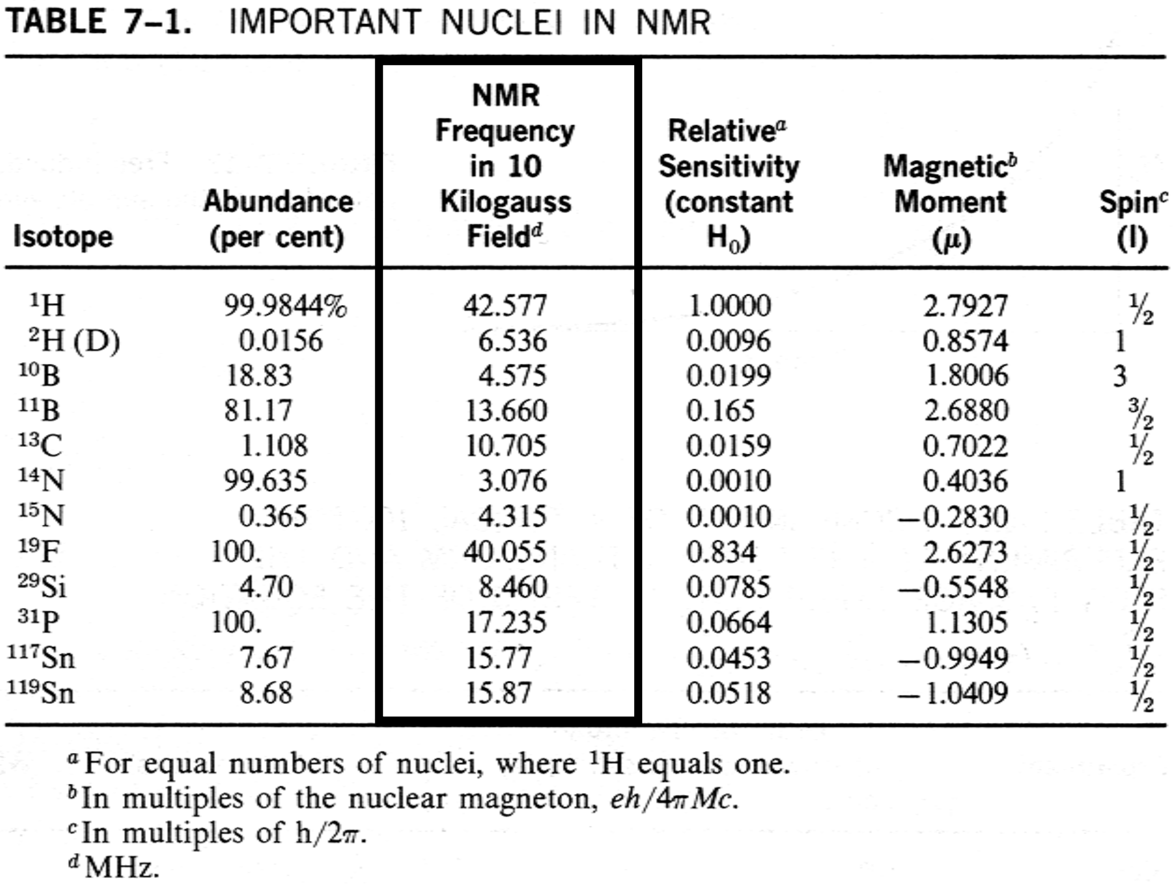
1 Tesla of magnetic force is created by 1 coulomb of charge moving at 1m/s

$$1T = 1N / C(m/s)$$

$$\nu_o = 5.586(5.05x10^{-27} J/T)(1T)/6.626x10^{-34} J-s$$

$$= 42.6 MHz$$

The Zeeman Interaction



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^{1}H	99.9844%	42.577	1.0000	2.7927	$\frac{1}{2}$
^{2}H (D)	0.0156	6.536	0.0096	0.8574	1
^{10}B	18.83	4.575	0.0199	1.8006	3
^{11}B	81.17	13.660	0.165	2.6880	$\frac{3}{2}$
^{13}C	1.108	10.705	0.0159	0.7022	$\frac{1}{2}$
^{14}N	99.635	3.076	0.0010	0.4036	1
^{15}N	0.365	4.315	0.0010	−0.2830	$\frac{1}{2}$
^{19}F	100.	40.055	0.834	2.6273	$\frac{1}{2}$
^{29}Si	4.70	8.460	0.0785	−0.5548	$\frac{1}{2}$
^{31}P	100.	17.235	0.0664	1.1305	$\frac{1}{2}$
^{117}Sn	7.67	15.77	0.0453	−0.9949	$\frac{1}{2}$
^{119}Sn	8.68	15.87	0.0518	−1.0409	$\frac{1}{2}$

[a] For equal numbers of nuclei, where ^{1}H equals one.

[b] In multiples of the nuclear magneton, $eh/4\pi Mc$.

[c] In multiples of $h/2\pi$.

[d] MHz.

- Because the Zeeman splitting is so large (relatively), NMR spectrometers are “tuned” to individual nuclei
- Each nuclei requires a separate tuning circuit
- This complicates the spectroscopy, but makes the NMR spectra nuclei specific

The Chemical Shift Interaction – Chemical information

- Electrons circulating about the nucleii given rise to magnetic fields and as such affect (reduce) the net magnetic field experienced by the nuclei, more electrons shield the nuclei more and less electrons shield the nuclei less…

$$\vec{H}_{Nucleus} = -\vec{\sigma} \cdot \vec{B}_o$$

$$\vec{\sigma} \equiv chemical \quad shift \quad tesnsor$$

$$\hat{H}_{cs} = \vec{\mu} \cdot \vec{B}_{Nucleus} = \vec{\mu} \cdot \vec{\sigma} \cdot \vec{B}_o$$

In first order treatment

$\nu = \nu_L(1- \sigma_{ZZ})$

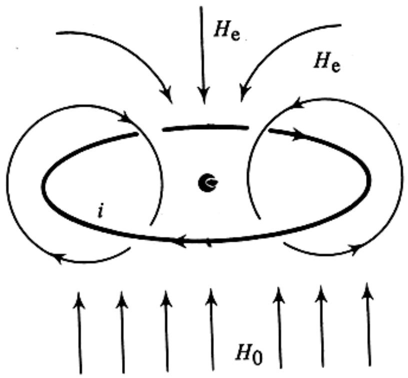
$B_{Net} = B_0(1 - \sigma_{zz})$, net field is less than B_0

σ_{ZZ} is the Z projection of the Chemical Shift Tensor

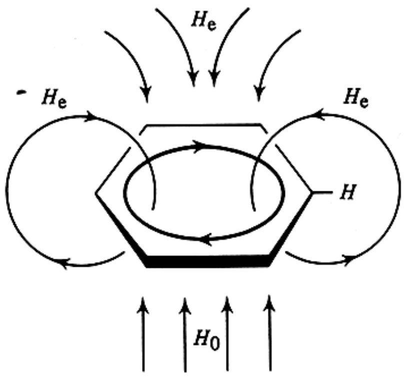
Frequencies are “Chemically Shifted” away from ν_L

Chemical Shielding by core and valence electrons

- A bare proton will have an NMR resonance at H_0
- A Hydrogen atom will resonate at a slightly higher applied magnetic field due to the shielding caused by the rotating electron around the nuclei
- The NMR resonance can be affected by chemical bonding as well
  - The H resonance will be affected by the motion of electrons around the benzene ring as well as by electrons around the proton
  - Note that the benzene ring effect is anisotropic, depends upon orientation to the applied magnetic field
  - Magnetically isotropic groups will not exert any net shielding because thermal motion (liquid) will average the shielding to zero.



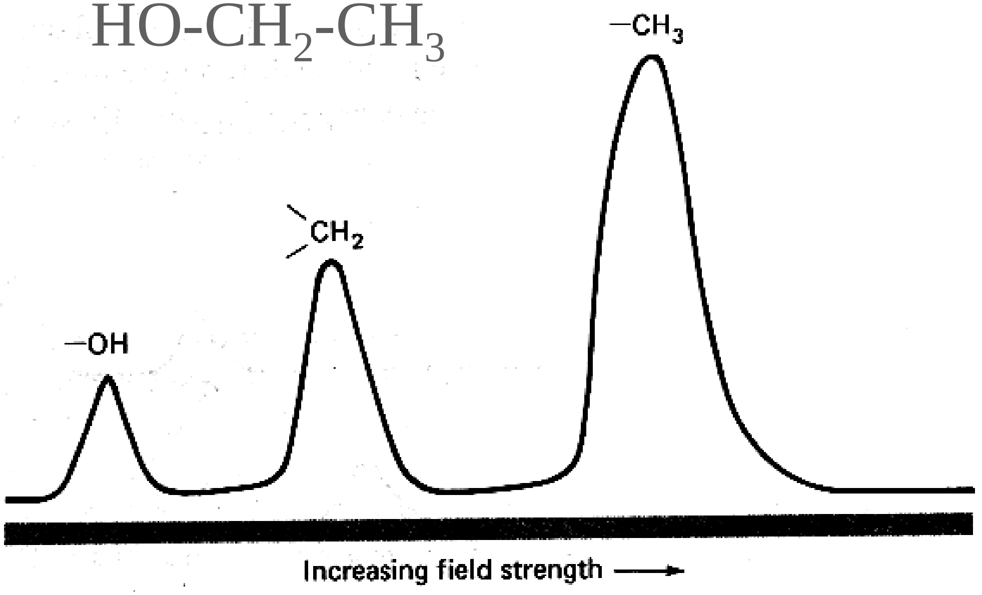
Core electron effect



Valence bonding electron effect

Chemical Shift Effect

$HO\text{-}CH_2\text{-}CH_3$



← Less shielding
Less electron density

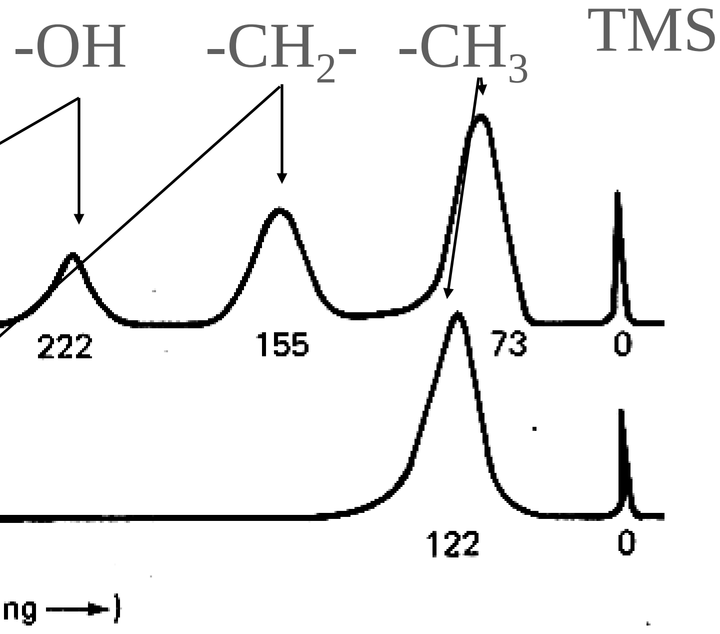
More shielding →
More electron density

Resonances closer to H_0
Bare proton

Resonances farther from H_0
Highly shielded proton

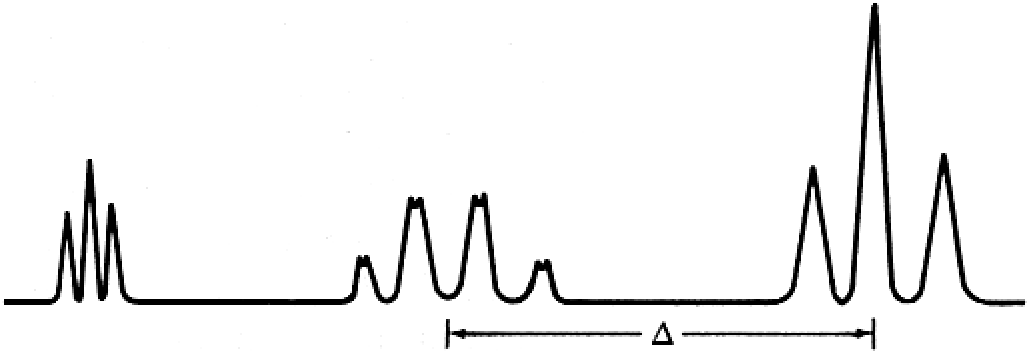
Chemical Shift Effect – Referencing to a Standard

- Use a highly shielded standard all reference frequencies to this standard
  - TMS for ^{1}H and ^{29}Si Si$(CH_3)_4$
  - Note higher field strengths will create higher frequencies for the resonances and greater resolution between identical resonances
  - Reference remains at “shifted” 0, its resonance also changes with field strength but it is referenced to 0



Ethanol at higher resolution – Higher fields

$OH\text{-}CH_2\text{-}CH_3$



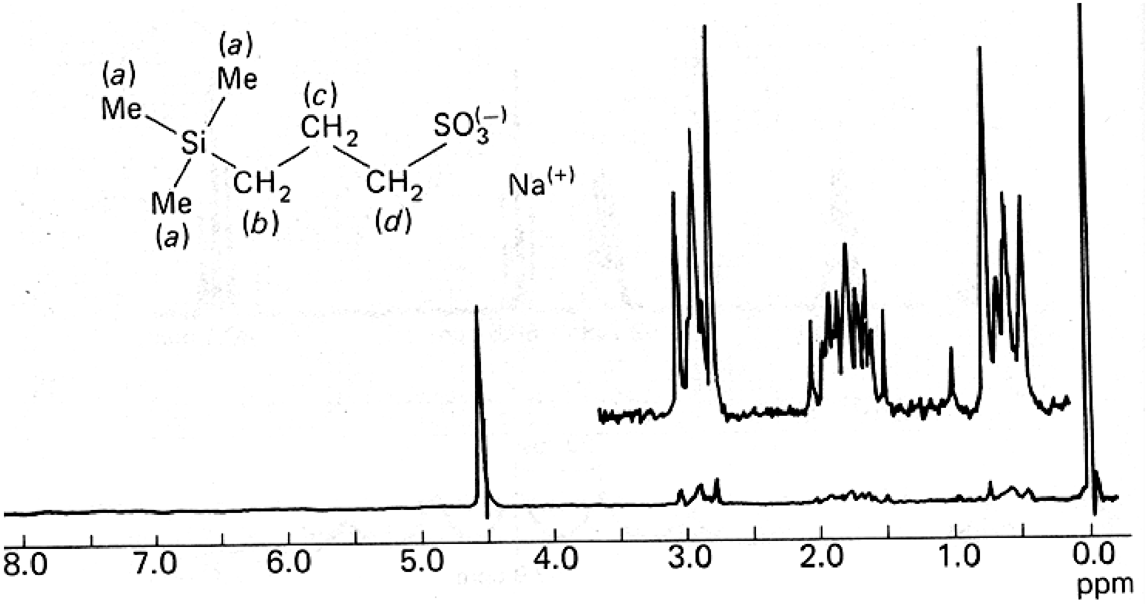
$-OH$ $-CH_2-$ $-CH_3$

H, ν increasing →

Chemical Shift Effect – The ppm scale

- Typical resonances are in the MHz range, so 10^6 factor creates scale in parts per million
- ppm
- Note that resonances in ppm scale are insensitive to the magnitude of B_0 used
- ppm resonance will be the same for all spectrometers
- Enables accurate comparison between different experiments

$$\delta = \frac{\Delta}{\nu_{reference}} \times 10^{6}$$



The Chemical Shift Interaction

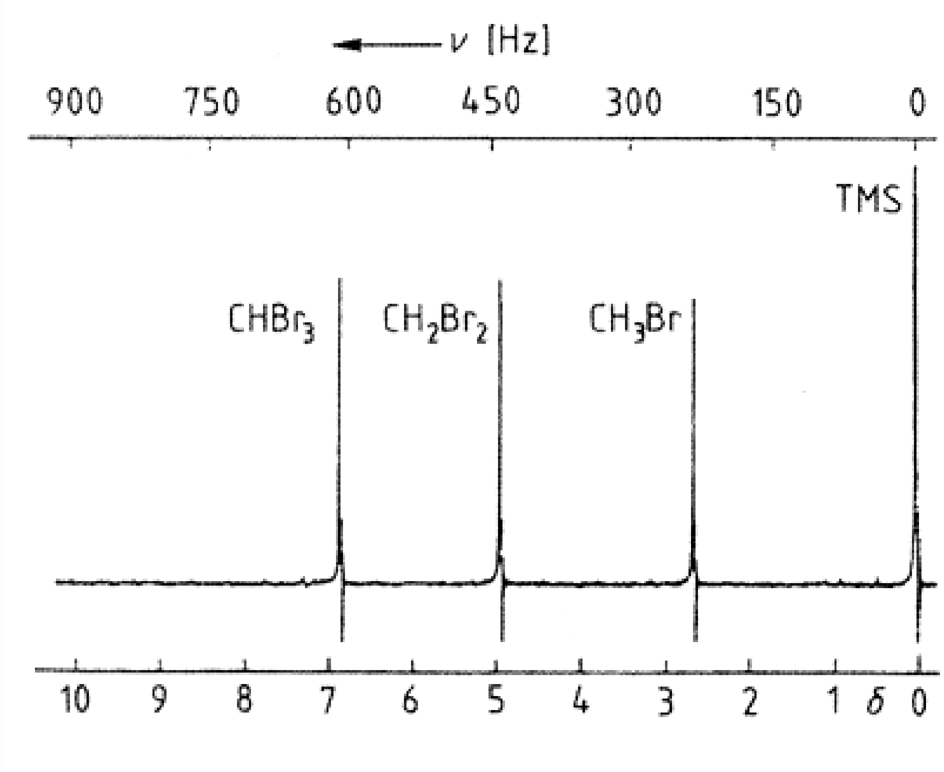
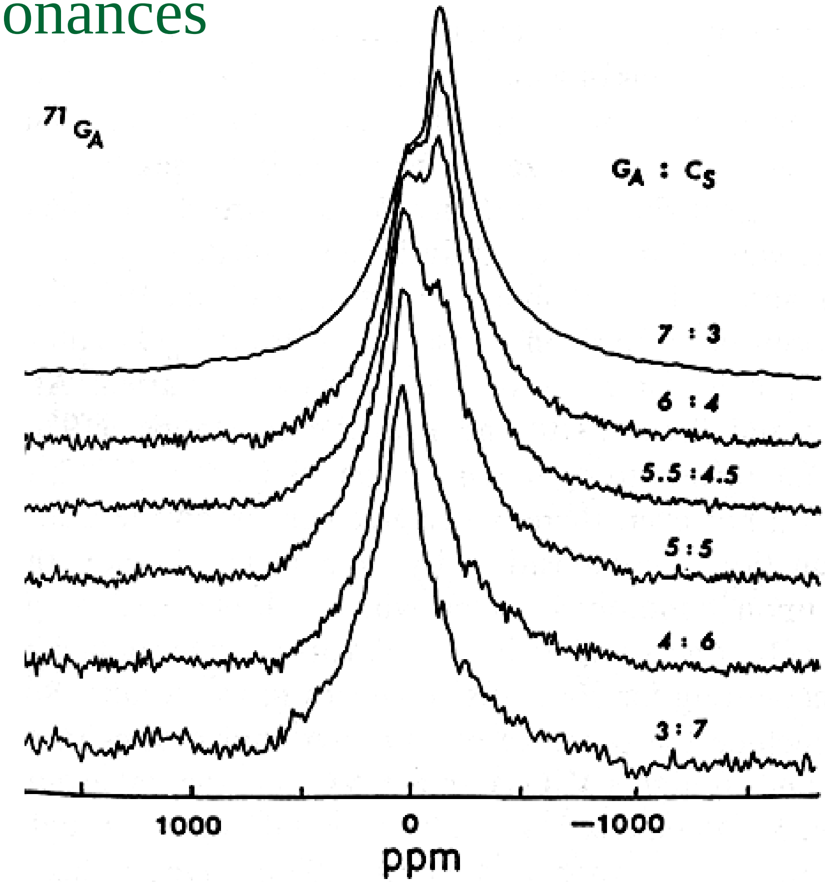


Figure 1-19.
90 MHz ^1H NMR spectrum of a mixture of $CHBr_3$ (**3**), CH_2Br_2, (**4**), CH_3Br (**5**) and TMS (**6**).

The Dipolar Interaction

NMR of the Solid State – Static resonances

- $Cs_2O + Ga_2O_3$ glasses
- Static ^{71}Ga NMR
- Note extremely broad resonance scale
- 2000 ppm!
- What is the cause of the broad lines in the solid state?
- How do we get chemical bonding information from such broad lines?



The Dipolar Interaction

- Nuclear spins interact with other spins over atomic distances
- Spins act as small nuclear magnets that change the "effective" magnetic field that each other nucleii experiences
- This effect tends to severely broaden NMR "lines" in the solid state
- Liquids don't suffer "dipolar" broadening as significantly because the average position of the molecules change so rapidly so as to average out the dipolar effect
- Liquid "lines" are much narrower, solids lines are much broader
- Sample spinning techniques can be used to artificially narrow dipolar broadened lines
- Magic Angle Sample Spinning NMR – MASS NMR

The Dipolar Interaction

- The Dipolar Hamiltonian

$$\hat{H}_D = 1/4 \sum_{J=1}^{N} \sum_{k=1}^{N} \left[\frac{1 - 3\cos^2(\theta_{JK})(3 I_{ZJ} \cdot I_{ZK} - I_J \cdot I_K}{r_{JK}^3} \right]$$

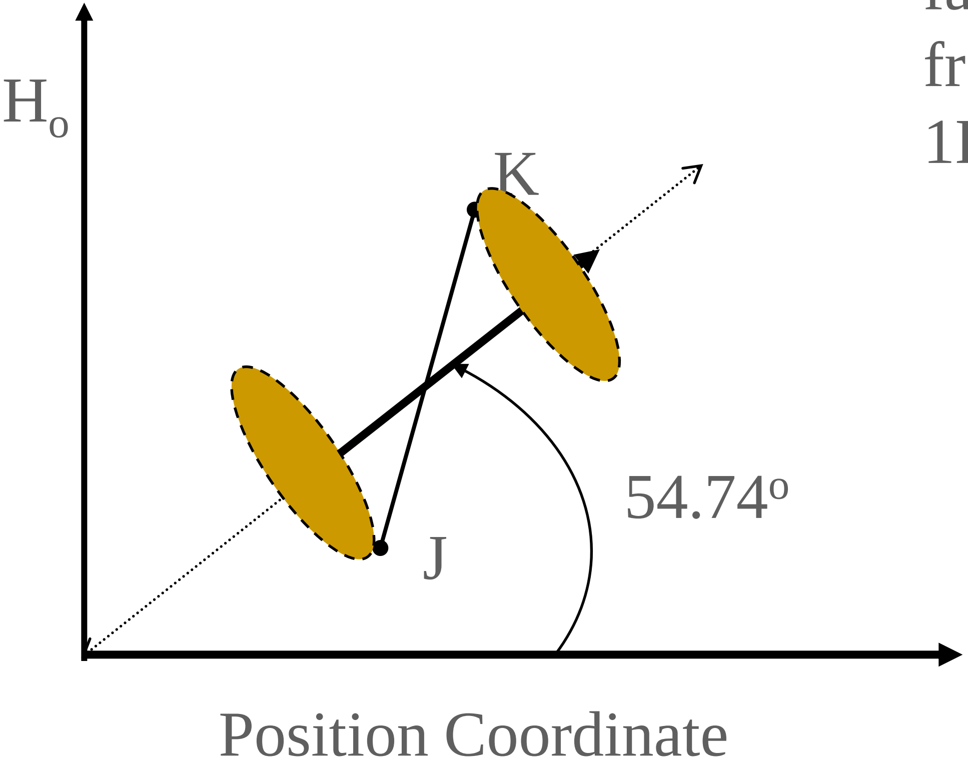
◆ Note that the Dipolar Hamiltonian has an average angle dependence of $(1\text{-}3\cos^2(\theta_{JK}))$

◆ By averaging about an angle θ_{JK} that zeroes this term, the dipolar interaction can be dramatically reduced

◆ What is the “magic angle”?

Magic Angle Sample Spinning NMR

- $\theta_m \sim 54.74^o$



Rotation speed must be faster than dipolar interaction frequency
1Hz to as high as 50,000 Hz!

Examples of the Effect of MASS

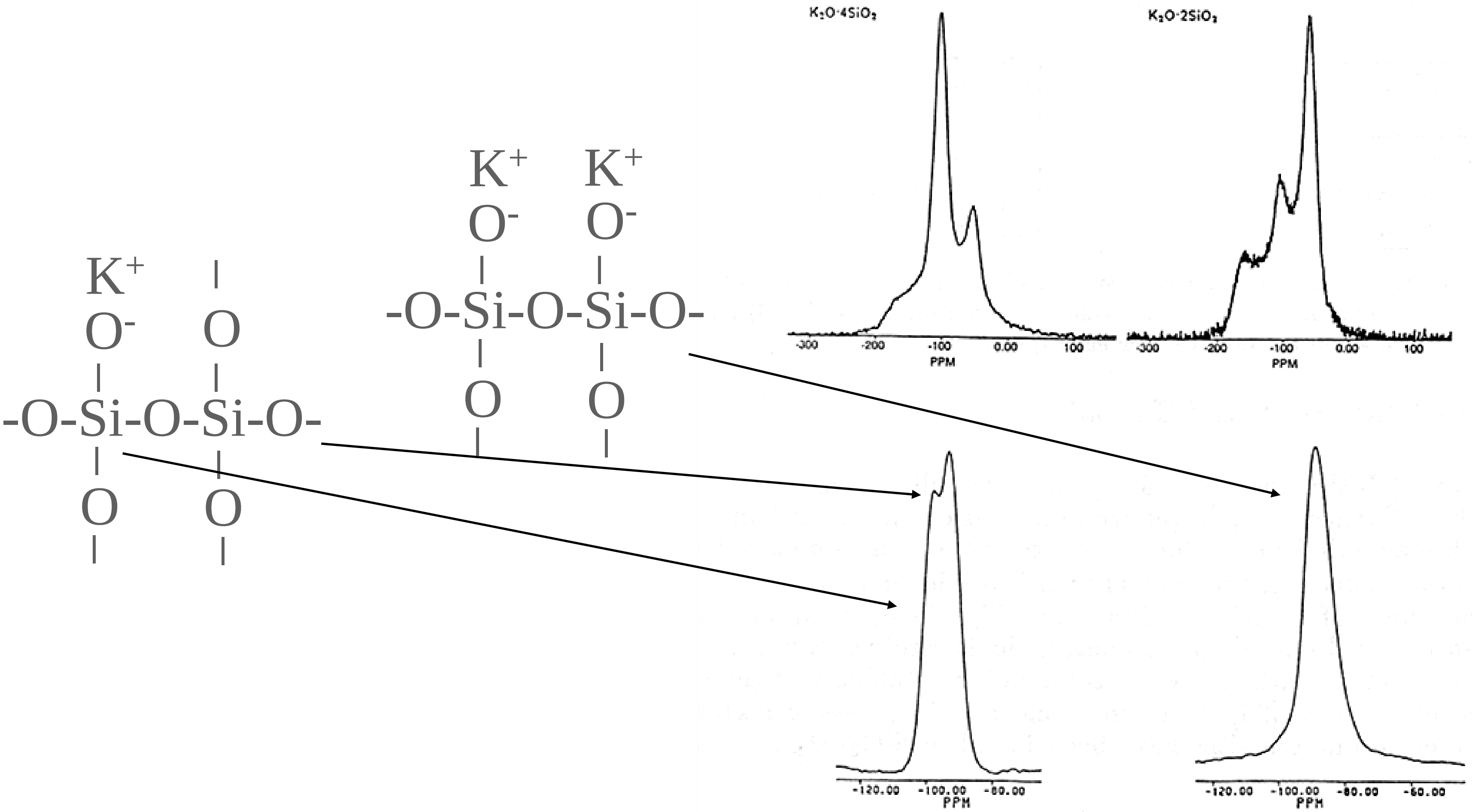
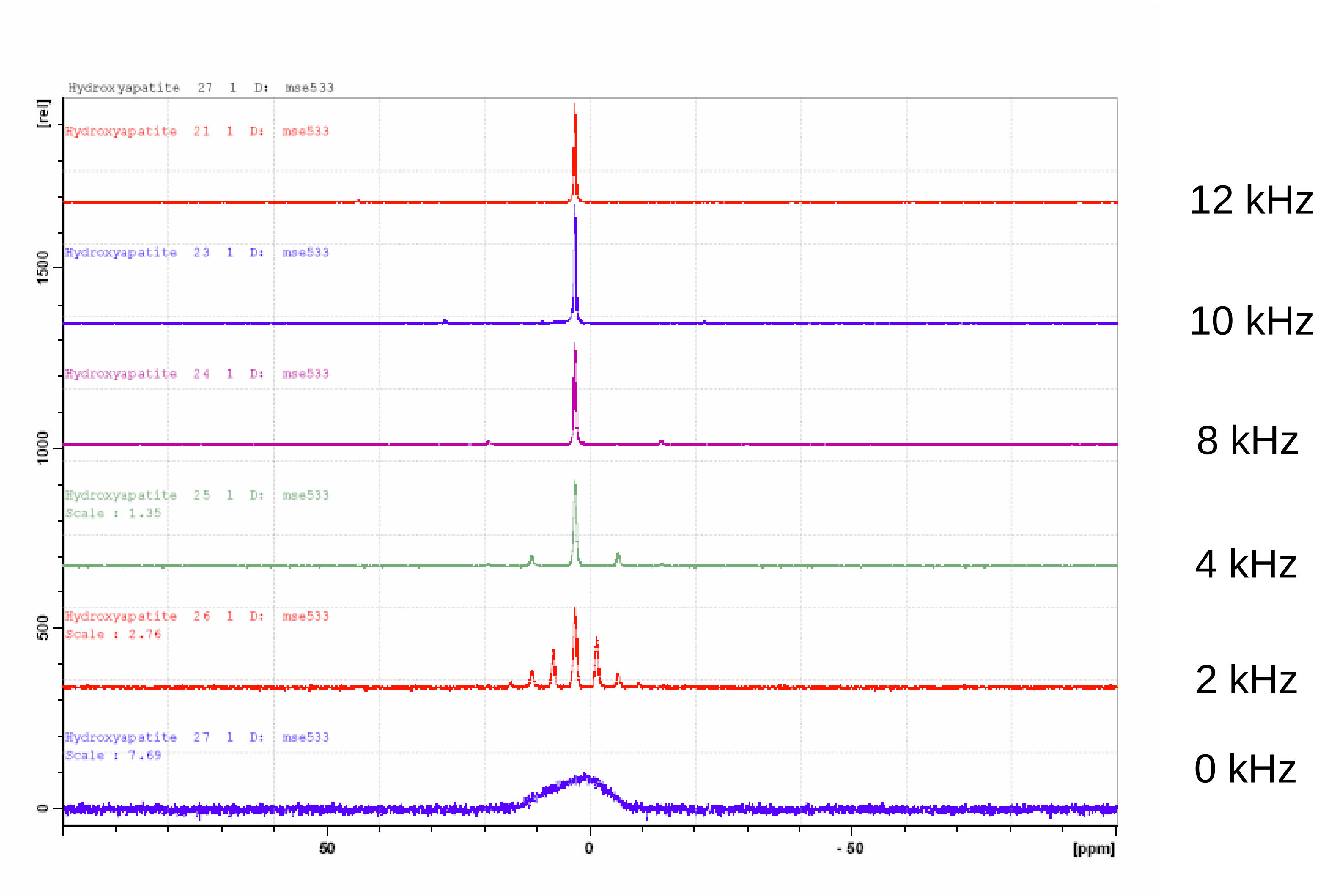


Fig. 10. Static (upper) and MASS (lower) ^{29}Si NMR spectra of potas
icate (left) and potassium disilicate (right) glasses. The scale is in p
to the ^{29}Si response in tetramethylsilane (TMS).

Hydroxyapatite – $Ca_5(PO_4)_3$ 2 H_2O – Effect of Spinning Rate

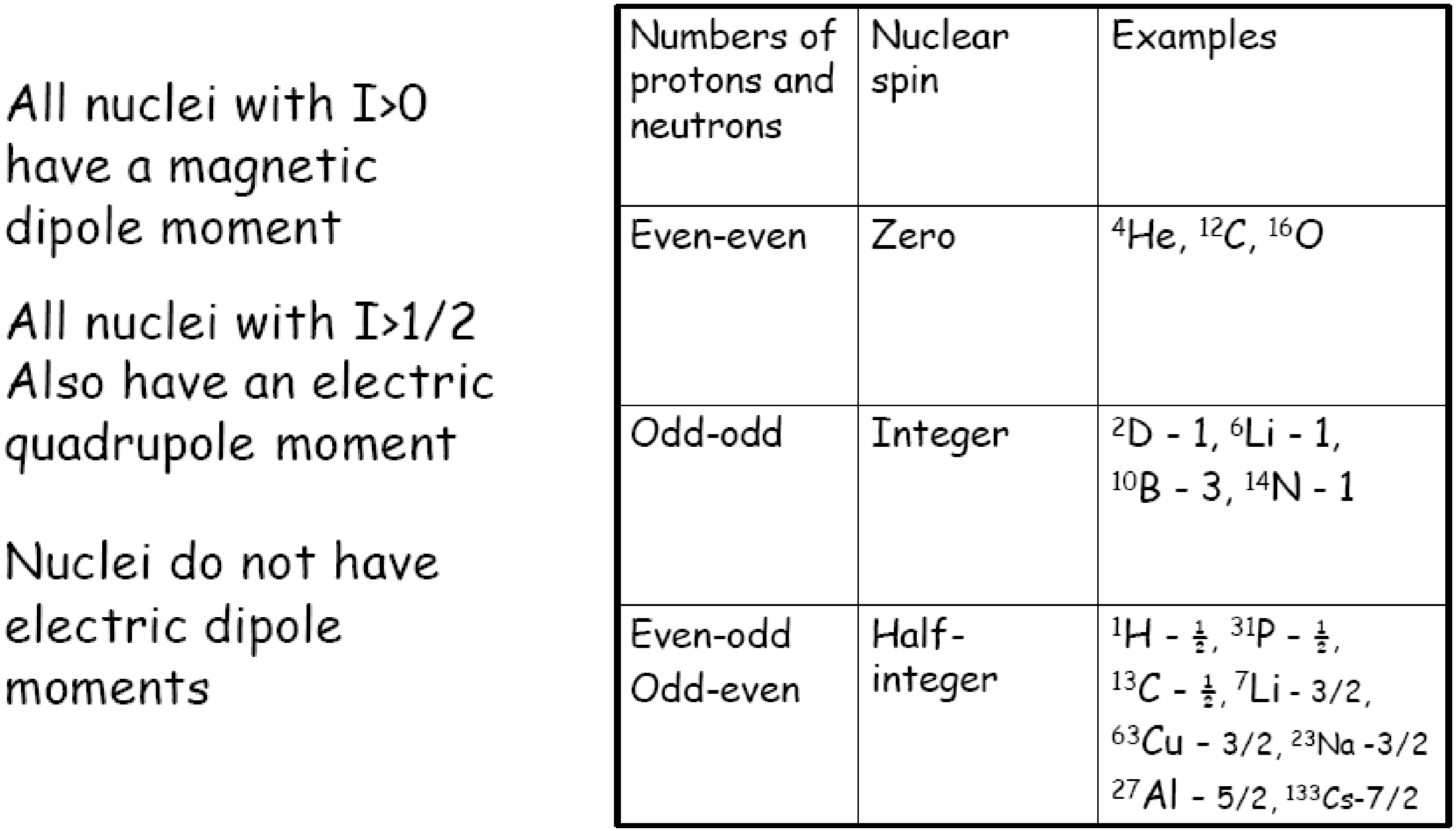


The Nuclear Quadrupole Interaction

- References:
- C.P. Slichter, Principles of Magnetic Resonance 3rd. Ed. Springer-Verlag (1992) Chapter 10
- A. Abragam, Principles of Nuclear magnetism, Oxford University Press, (1960) Chapter VI and VII
- A.D. Bain and M. Khasawneh, Concepts in Magnetic Resonance 22A, 69 (2004) (see references)
- D.J. Philp and P.W. Kuchel Concepts in Magnetic Resonance 25A 40 (2005)

The Nuclear Quadrupole Interaction

- Quadrupolar Nuclei



All nuclei with I>0 have a magnetic dipole moment

All nuclei with I>1/2 Also have an electric quadrupole moment

Nuclei do not have electric dipole moments

Numbers of protons and neutrons	Nuclear spin	Examples
Even-even	Zero	^{4}He, ^{12}C, ^{16}O
Odd-odd	Integer	^{2}D - 1, ^{6}Li - 1, ^{10}B - 3, ^{14}N - 1
Even-odd Odd-even	Half-integer	^{1}H - $\frac{1}{2}$, ^{31}P - $\frac{1}{2}$, ^{13}C - $\frac{1}{2}$, ^{7}Li - 3/2, ^{63}Cu - 3/2, ^{23}Na -3/2 ^{27}Al - 5/2, ^{133}Cs-7/2

Jeffries, Physics, University of Waterloo, Waterloo, CA

The electric interaction of a Nucleus with its surroundings

- Consider a nucleus with a nuclear charge distribution ρ(r) interacting with a electric potential V(r) setup by the action of the electrons around the nucleus

$$V\left(\vec{r}\right) = V(0) = \sum_{\alpha} x \frac{\partial V}{\partial \alpha}\Big|_{\vec{r}=0} + \frac{1}{2!}\sum_{\alpha,\beta} \alpha\beta \frac{\partial^2 V}{\partial \alpha \partial \beta}\Big|_{\vec{r}=0} + H.O.T$$

$$\alpha = x, y, z$$

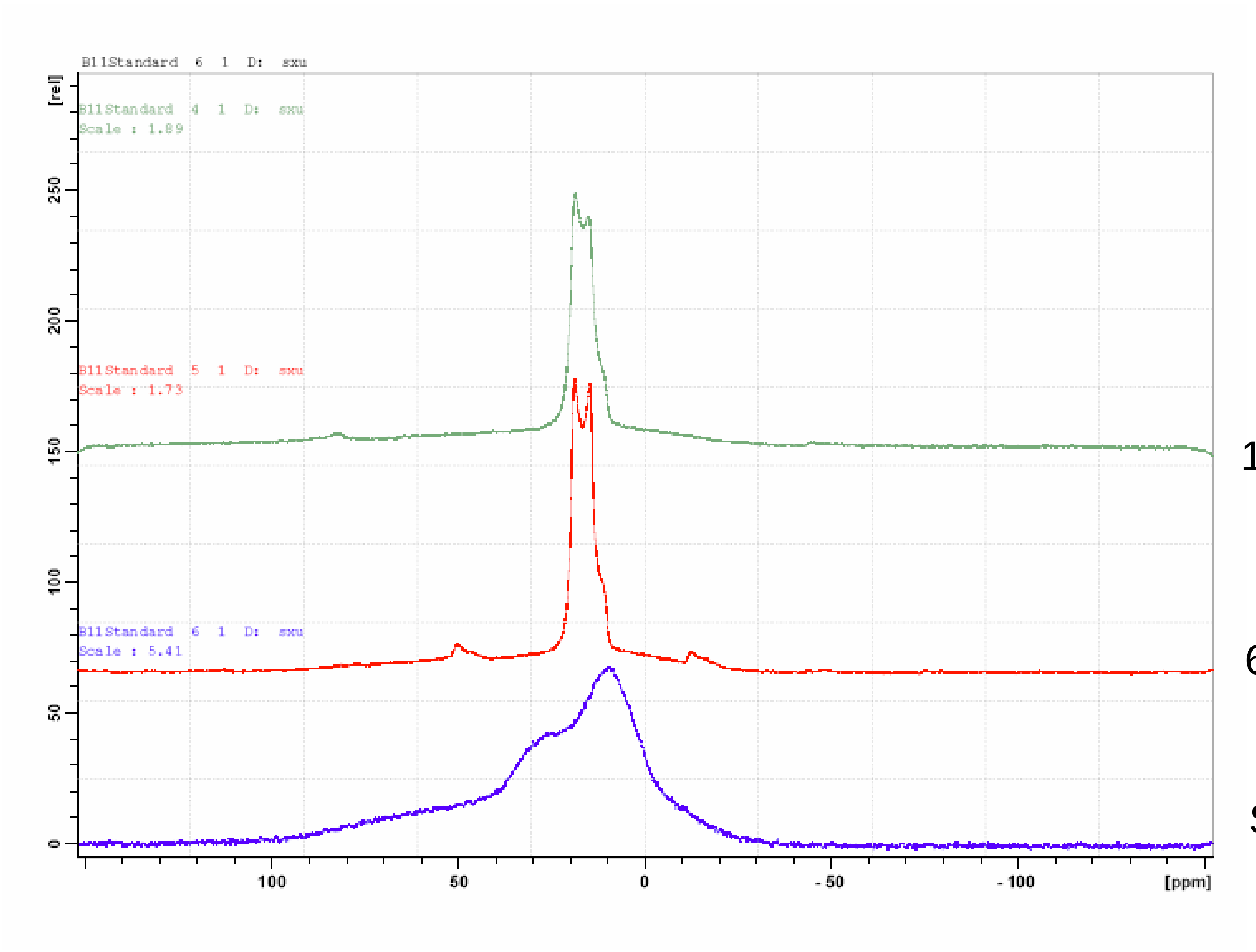
$$E = V(0)\int \rho(r)dr + \sum_{\alpha} V_{\alpha} \int \alpha\rho \, dr + \sum_{\alpha,\beta} V_{\alpha\beta} \int \alpha\beta\rho \, dr + H.O.T$$

- $V_{\alpha\,\beta}$ is the Electric Field Gradient

The Electric Field Gradient (EFG)

- In a crystalline material
  - $V_{xx} = V_{yy} = V_{zz} = 0$ in cubic site symmetery
  - $V_{xx} = V_{yy} \neq V_{zz}$ for axial symmetry
- In liquids, fast random motion can average $V_{\alpha\beta}$ to zero
- In glasses, site symmetry is often determined by chemical bonding (hybridization) of the atom
- ^{11}B $I = 3/2$ quadrupole nuclei, quadrupole interaction can be non-zero
  - Trigonal coordination axial symmetry, EFG is non-zero
  - Tetrahedral borons, tetrahedral symmetry, and EFG is near zero

^{11}B Quadrupole Nuclei – Boric Acid $B(OH)_3$ trigonal planar

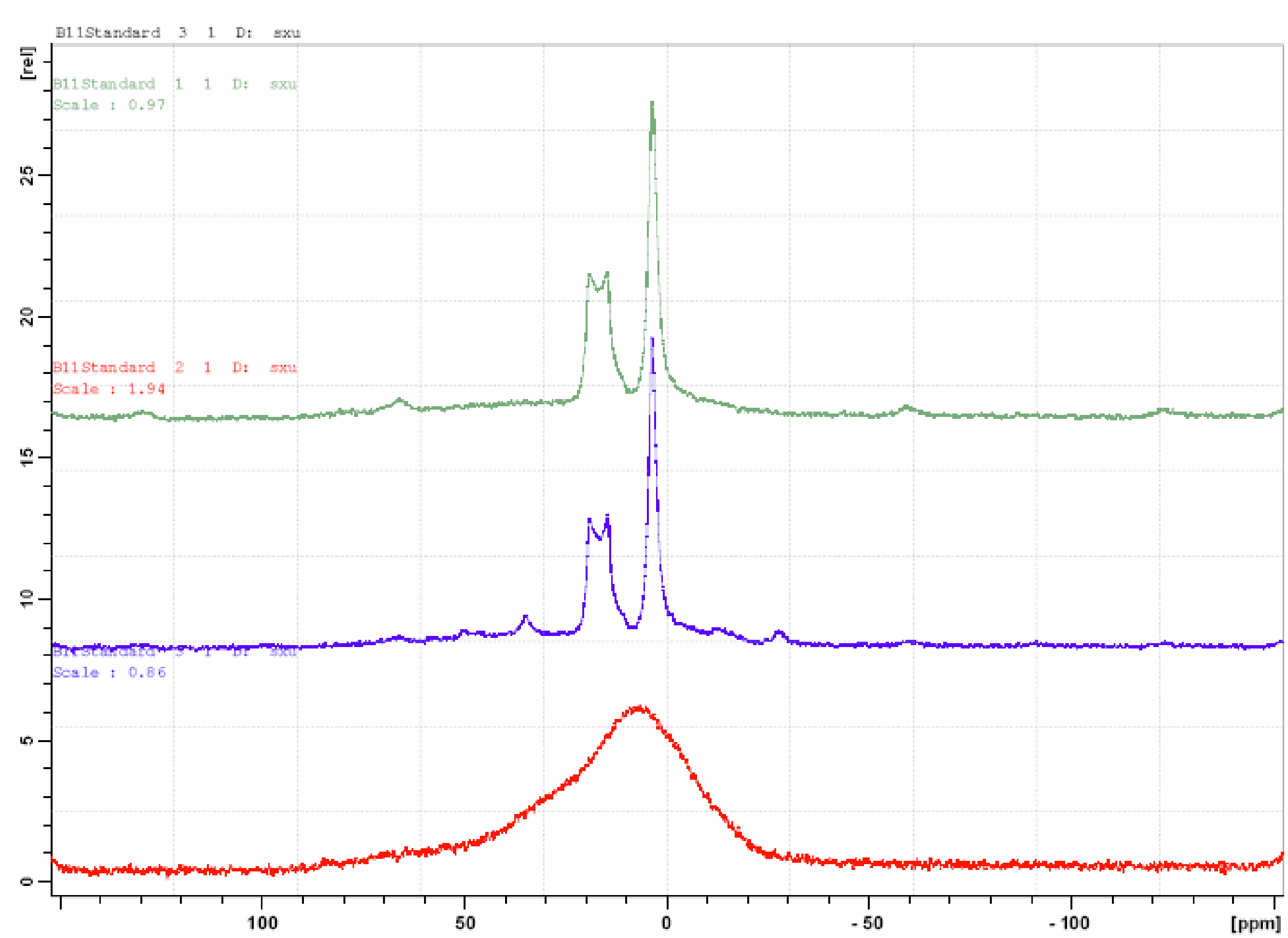


12 kHz

6 kHz

Static

^{11}B Quadrupole nuclei – Borax $Na_2B_4O_7$ 10 H_2O



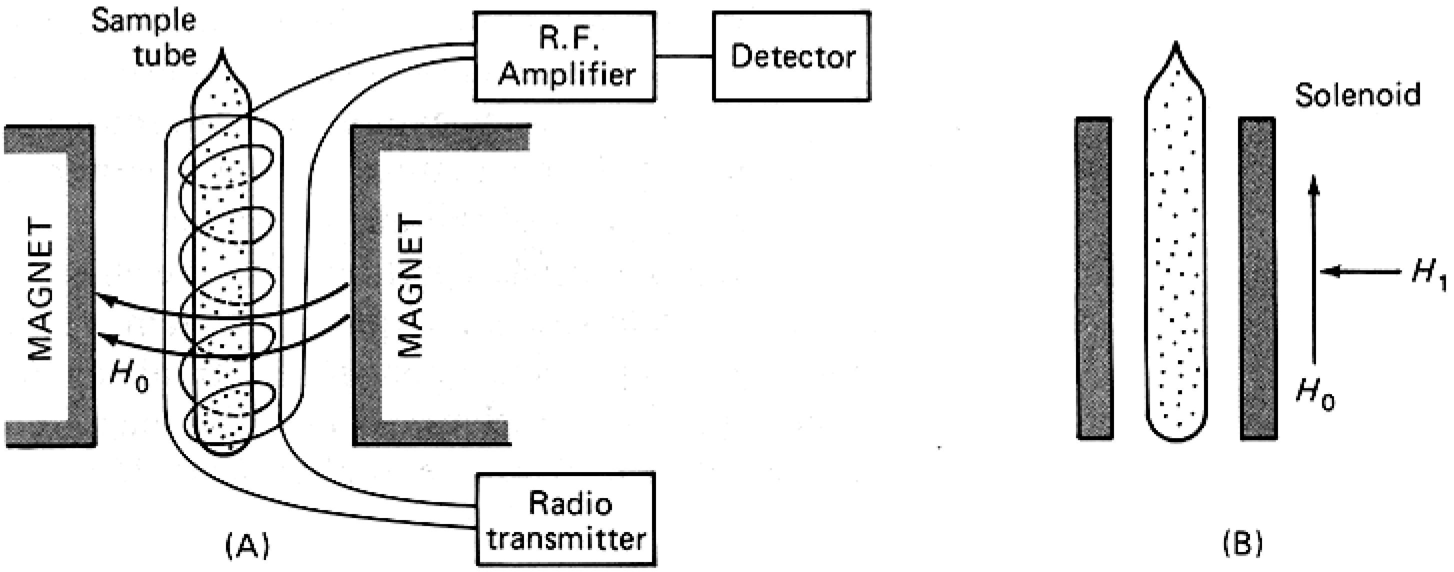
12 kHz

6 kHz

static

The cw-NMR Experiment

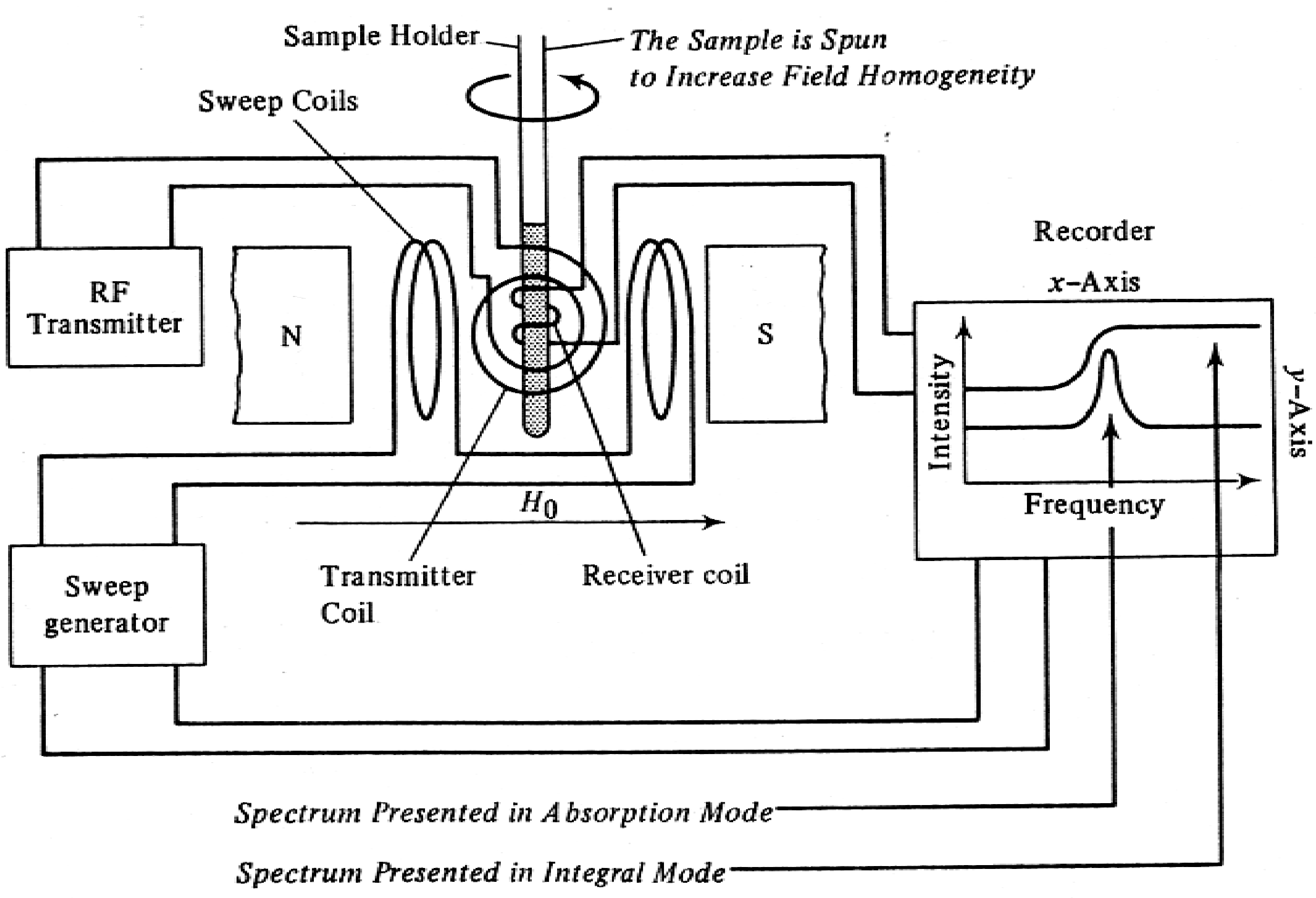
- The magnetic field sets up the Zeeman energy levels
- The radio frequency transmitter transmits radio waves that match the Larmor frequency
- The radio frequency amplifier and detector detect the absorption of energy from the radio transmitter at the Larmor frequency



The cw-NMR Experiment

- The NMR spectra can be observed in one of two ways:
  - The strength of the applied magnetic field can be held constant and the radio frequency spectrum can be swept until resonance occurs
  - The radio frequency can be fixed and the strength of the magnetic field can be swept until resonance occurs
- Fixed field (permanent and superconducting) magnets are used for the constant applied magnetic field
- Variable field (typically lower field strength) magnets are used for the variable applied magnetic field
- However, the technique is slow and requires many “sweeps” to accumulate spectra with good S:N ratios.

The Typical *CW* - NMR Spectrometer



The Typical *Pulsed* NMR Spectrometer

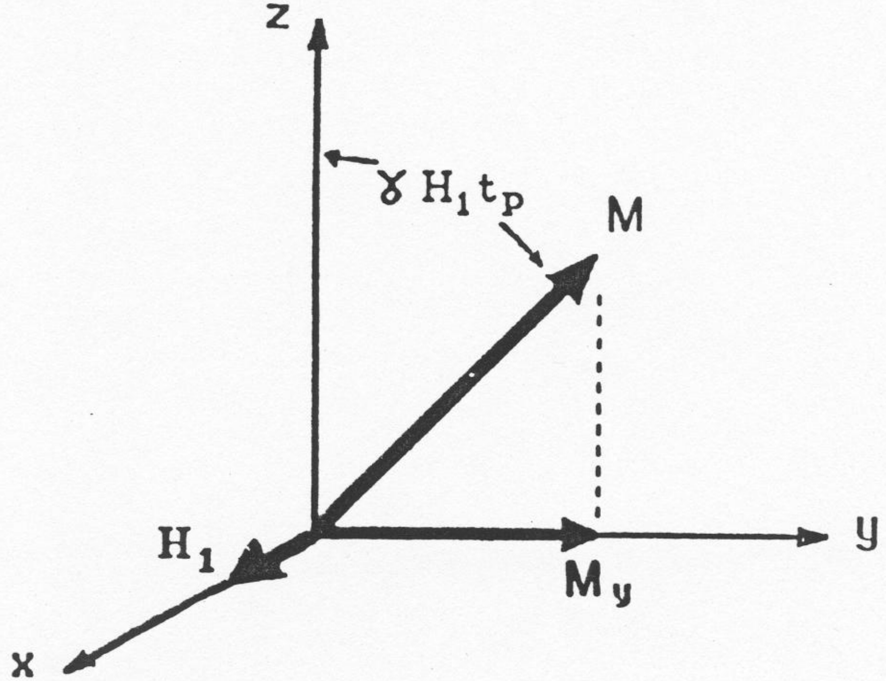
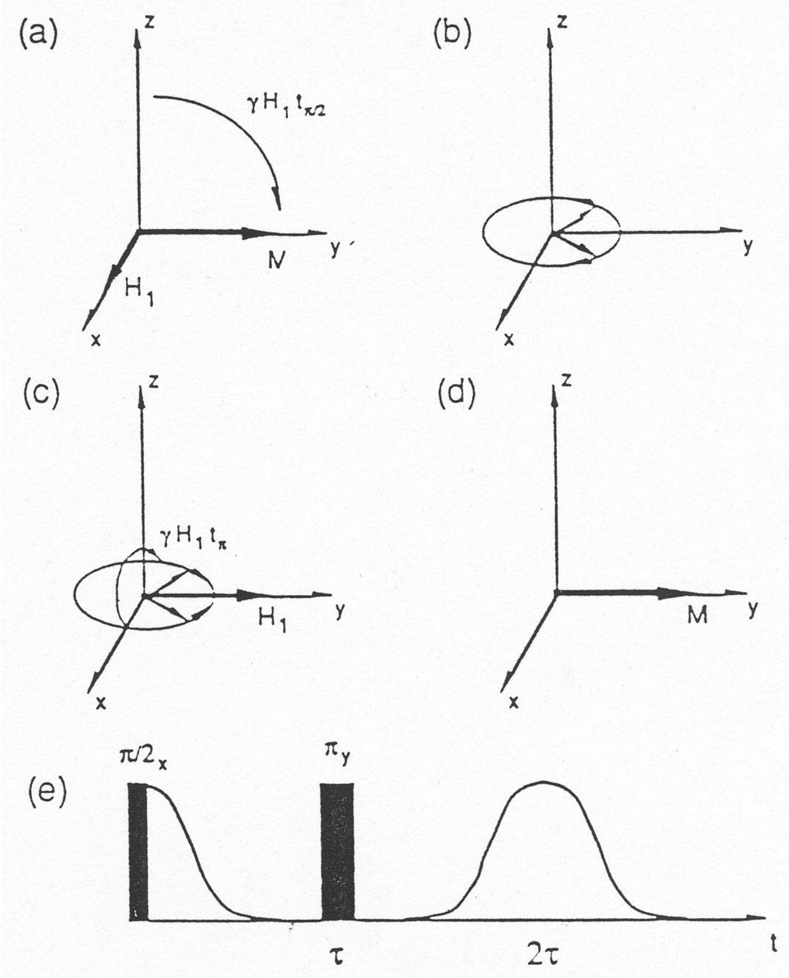


Fig. 5. A pulse of length t_p rotates the magnetization vector from its equilibrium position by an angle $\theta_p = \gamma H_1 t_p$.

Pulse Sequences to Improve Spectra

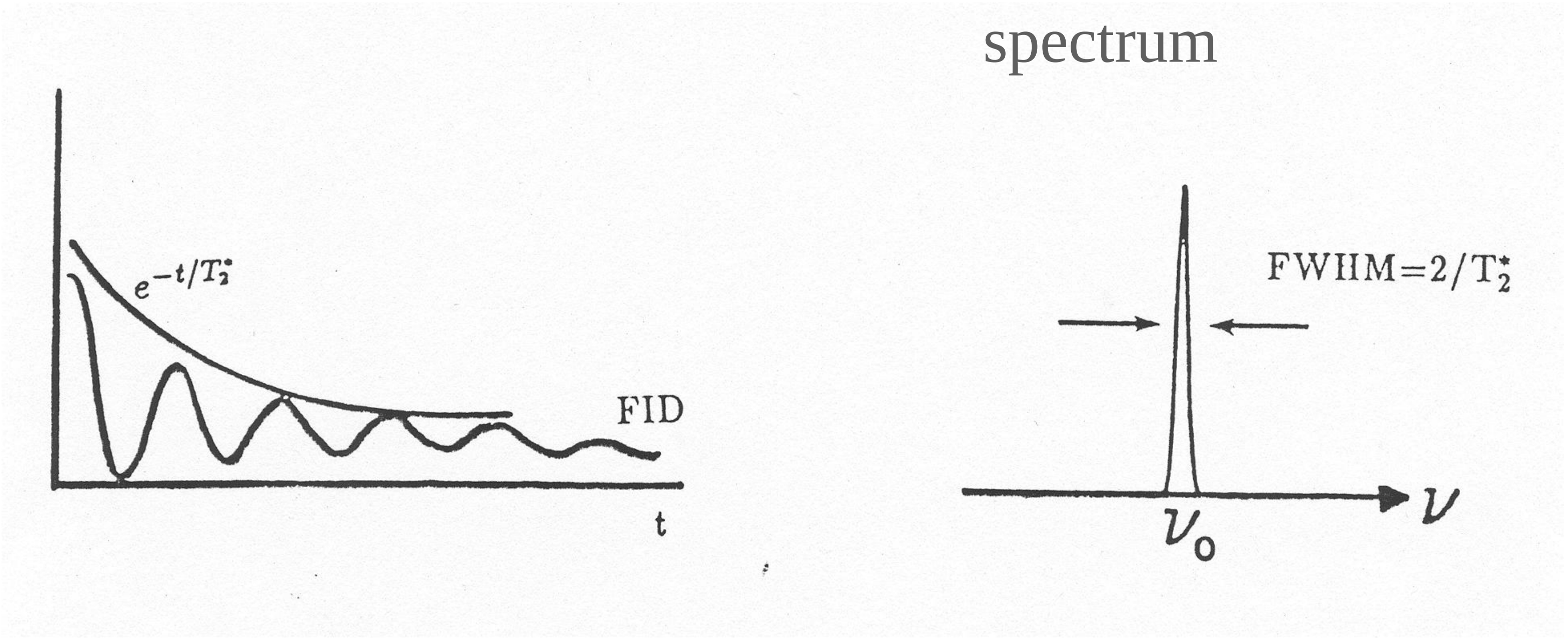
- First pulse “flips”spin down to $\pi/2$ (90^o)
- Relaxation causes the spins to “precess” about z axis
- Second (stronger) pulse flips spins a full π (180^o)
- Relaxation now causes the spins to rephase and cause an absorption
- Spectra can be obtained for the whole FID, since both sides
- Increase and decrease in magnetization are observed



Free Induction Decay in a Pulsed NMR Experiment

Free induction decay response

Fourier Transform of FID leads to absorption spectrum

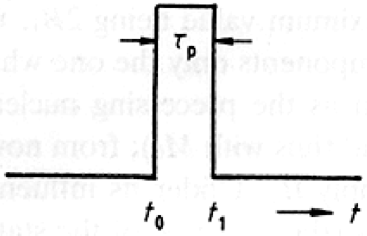


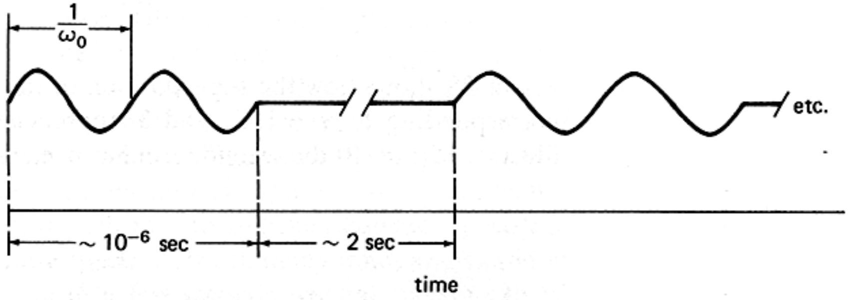
Pulsed FT-NMR Spectroscopy

- The problem is the typical NMR frequencies are in the MHz range
- We must be able to scan these low frequencies with high resolution MHz signals with Hz ($1/10^6$) resolution
- Frequency range changes with every nuclei
  - Requiring a new transmitter and detector for every different nuclei
  - ^{1}H at 42.6 MHz and ^{11}B at 13.6 MHz
- Pulsed FT-NMR uses short RF pulses at one frequency ν_0 to excite all nuclei, across the range of chemical shifts for that nuclei, at the same

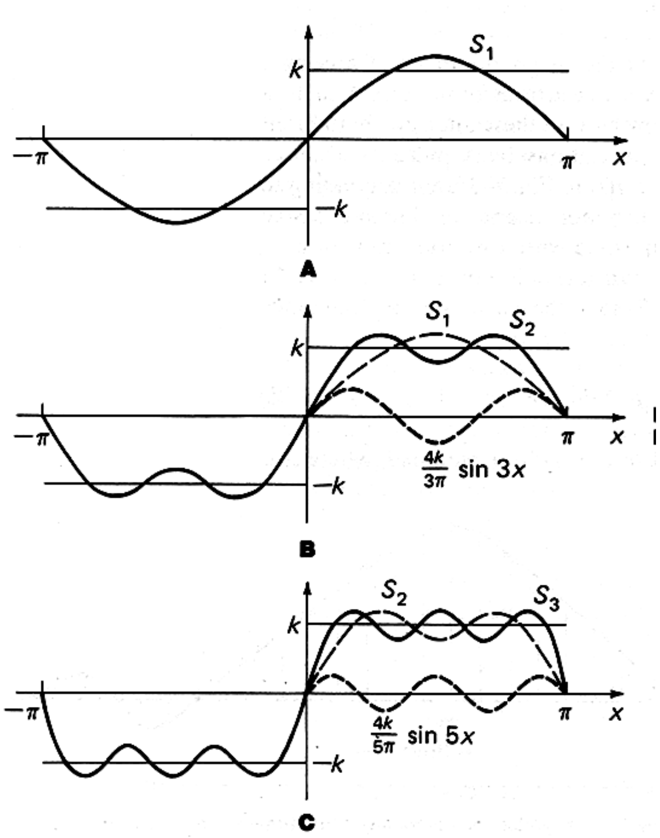
Pulse FT-NMR Spectroscopy

- A RF (MHz) pulse at ν_0 (Hz), ω_0 (rad/sec) can be shown to be equivalent to a summation of a range of frequencies
- A RF (MHz) pulse at ν_0 (Hz), ω_0 (rad/sec) has three characteristics
  - The pulse frequency - ν_0 (Hz), ω_0 (rad/sec)
  - The pulse length - t_p
  - The time between pulses, delay time - Δt
- ν_0 and t_p determine the range of frequencies that will are accessible for the NMR experiment
  - Shorter pulses for shorter periods of time increases the average frequency
  - Longer pulses for longer periods of time, decreases the average frequency
- By adjusting and optimizing ν_0 and t_p one can optimize the particular average frequency, ^{1}H at 42.6 MHz, for example, and the range of frequencies (resolution) around this central frequency
- The delay time, Δt, determines the repetition rate and can be used to determine the rate of relaxation of the excited spin states to the ground state





Pulsed FT-NMR Spectroscopy



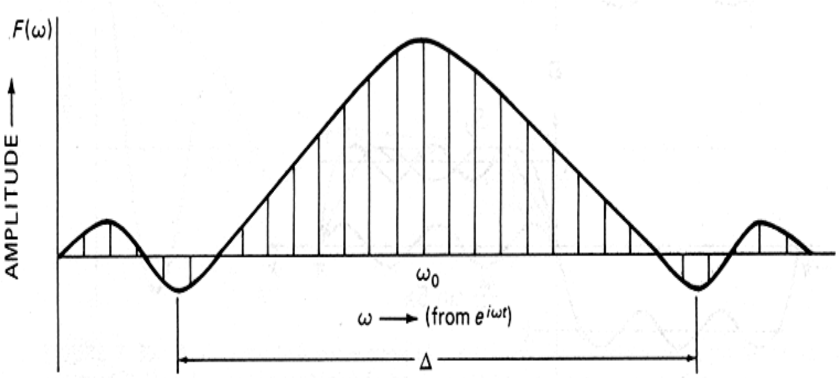
- A square wave pulse can be created from a Fourier Series

$$f(t) = a_0 + \sum_{i=1}^{n} \left(a_n \cos(2\pi nt) + b_n \sin(2\pi nt) \right)$$

- The greater the number of components, the greater accuracy of the square wave pulse

Pulsed FT-NMR Spectroscopy

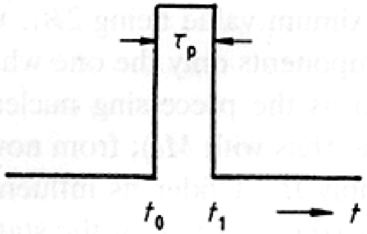
$$F(\omega) = 2\pi \int_{-\infty}^{+\infty} e^{i\omega t} f(t)\,dt$$

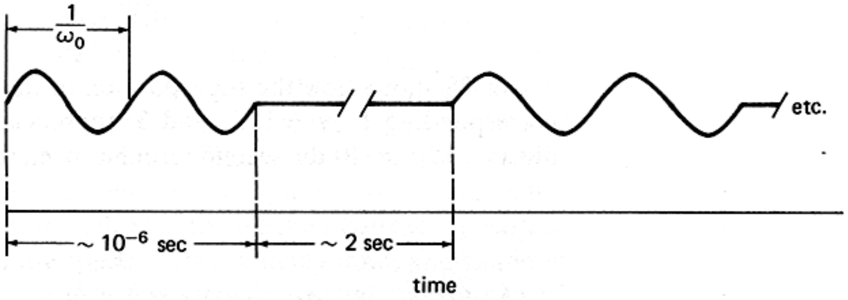


- The “power” spectrum F(ω) then is unique for every pulse sequence
- Hence, we tailor our pulse sequence to excite the specific nuclei we are studying
- And to obtain the required level of spectral width
- In order that we excite all of the nuclei in the sample
- Across the range of chemical shifts
- Expected for the sample

Pulsed FT-NMR Spectroscopy

- Pulses are generally 10^{-5} to 10^{-6} seconds long
  - In the microsecond range
- Pulses are generally in the MHz frequency range
  - Typical nuclei in typical magnetic fields
  - Resonate in the MHz range

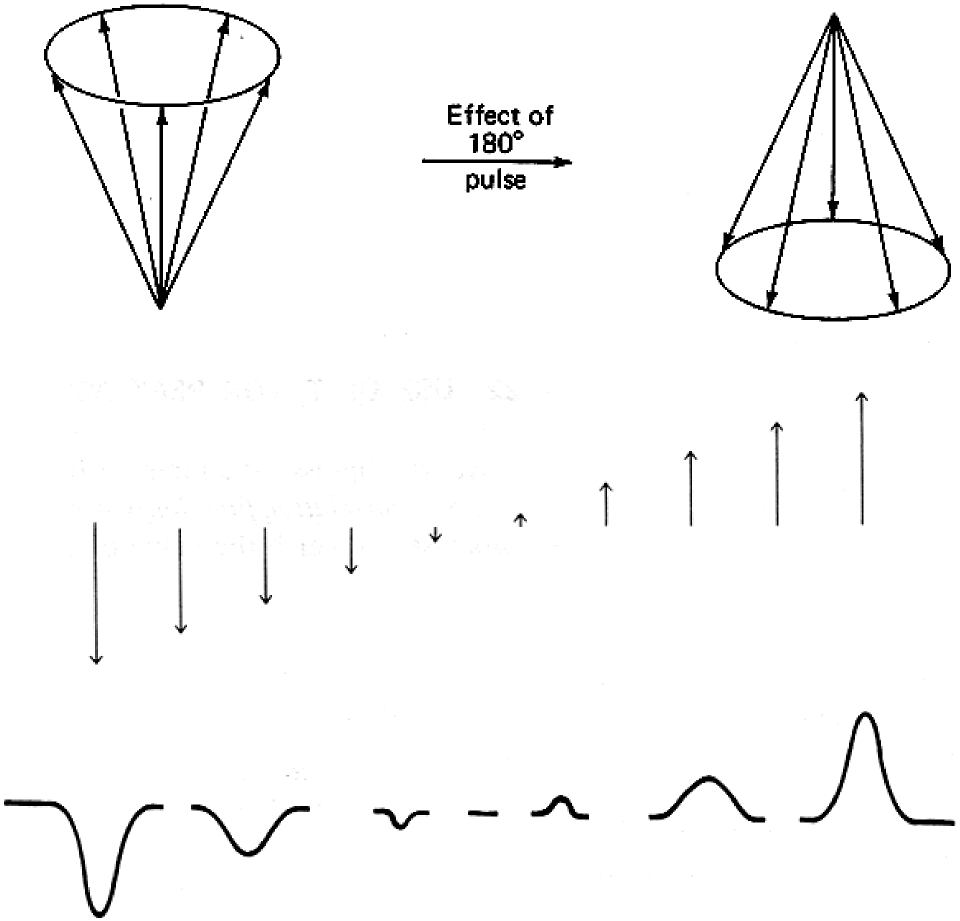




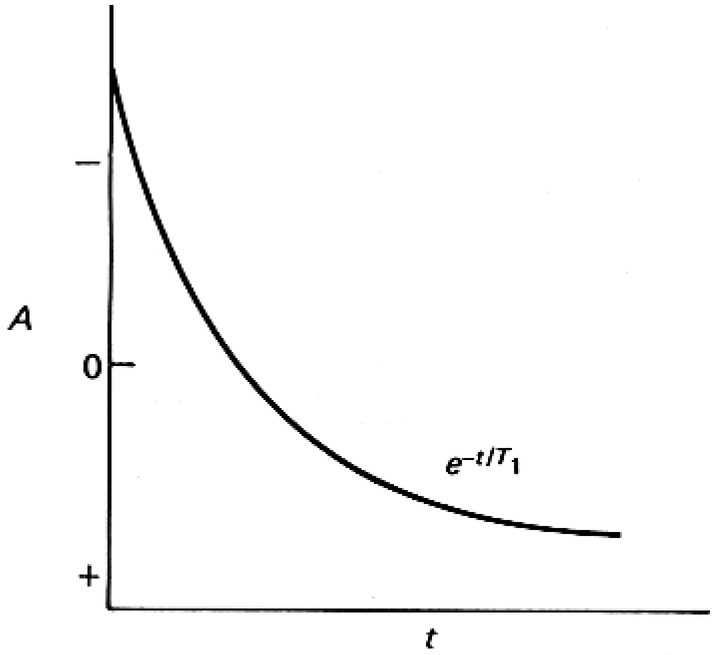
Pulsed FT-NMR Spectroscopy

- Pulse delay times are typically in the range of seconds
  - Delay time is dependent upon the “Relaxation rate” of the nuclei
  - Depends upon how fast the excited spin state relax back to the nuclear spin ground state
  - Process is generally slow, seconds or more
  - Faster for liquids where there is strong interaction among spin states
    - Seconds to milliseconds to microseconds
    - Liquids NMR can use very short delay times, “faster spectroscopy”
  - Slower for solids where there is less interaction among spin states
    - Seconds to minutes to hours
    - Solids NMR can be very slow, one pulse every hour and taking days to collect enough spectra for good S:N

Pulsed FT-NMR Spectroscopy

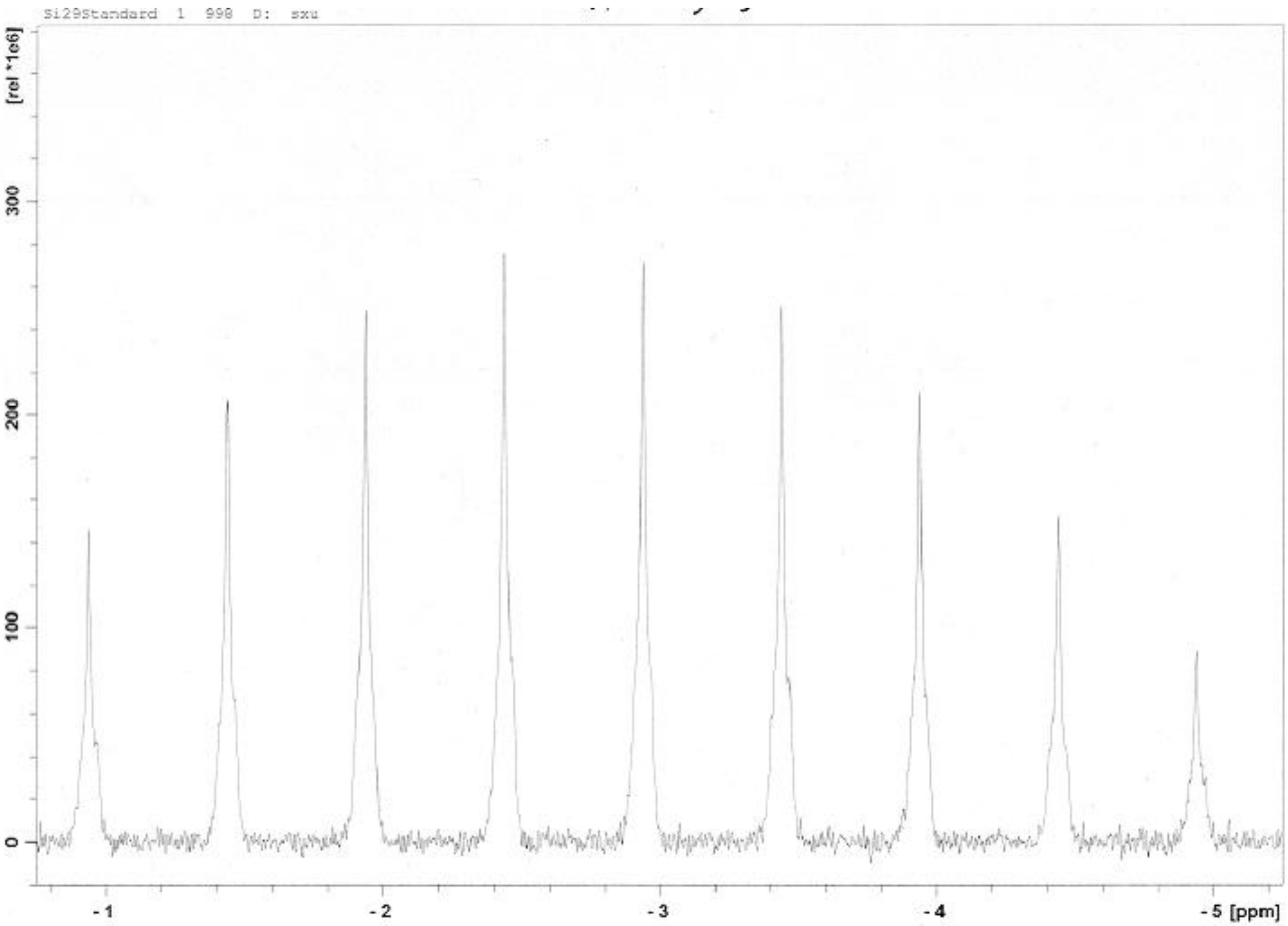


Pulse FT-NMR Spectroscopy

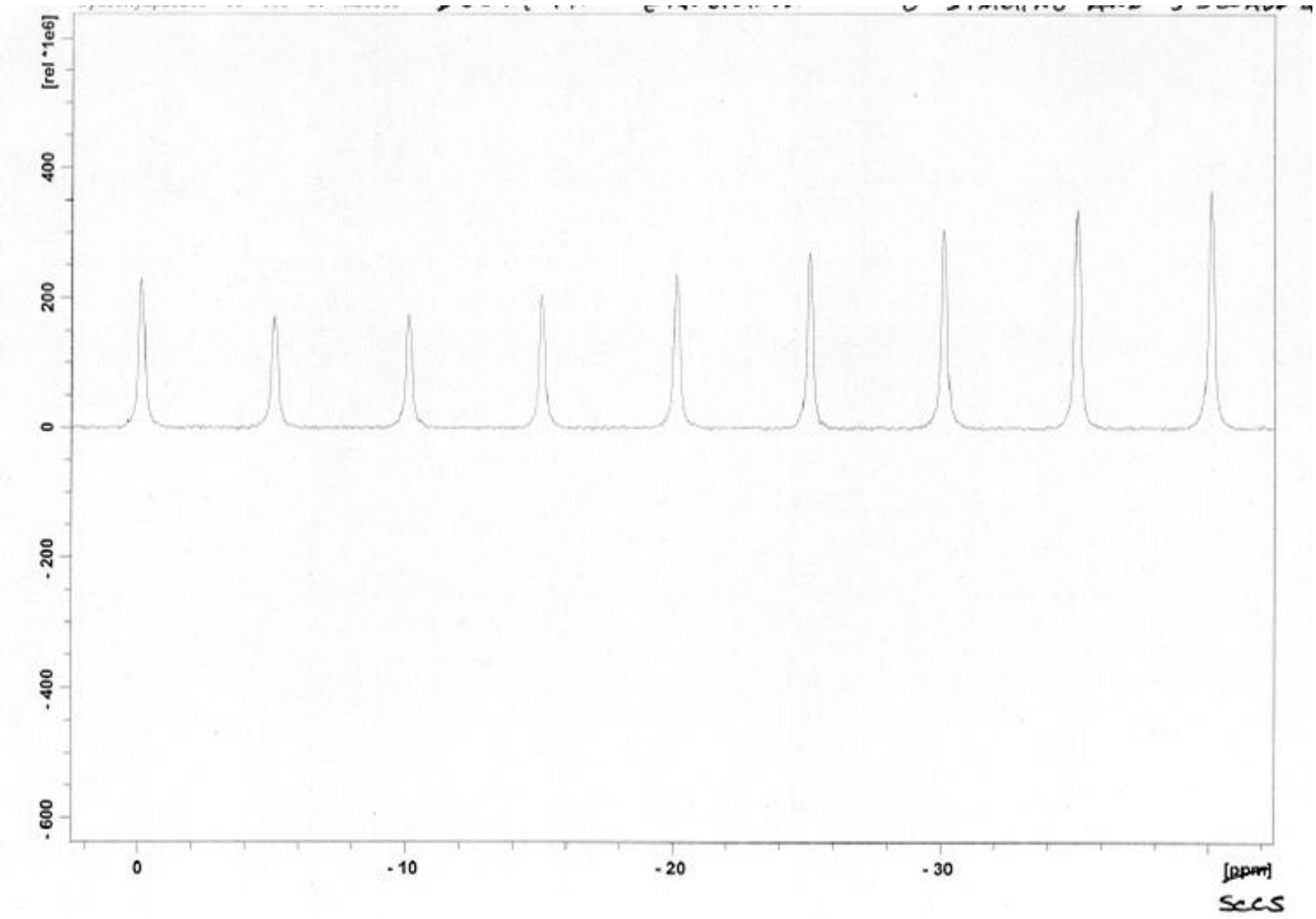


- Amplitude decay rate
- Is exponential
- And decay constant is the relaxation time T_1
- T_1 is the spin-lattice relaxation rate
- Fast (short) for liquids
- Slow (long) for solids

Effect of the Pulse Length of Signal Intensity – ^{31}P HAP



Effect of Pulse Delay between Pulses ^{31}P HAP



Effect of the number of Pulses (scans) – ^{31}P HAP