

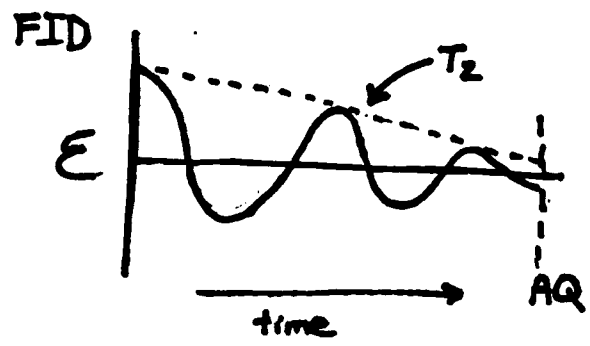
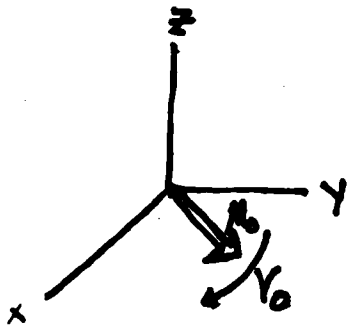
CHEM / BCMB 4190/6190/8189

Introductory NMR

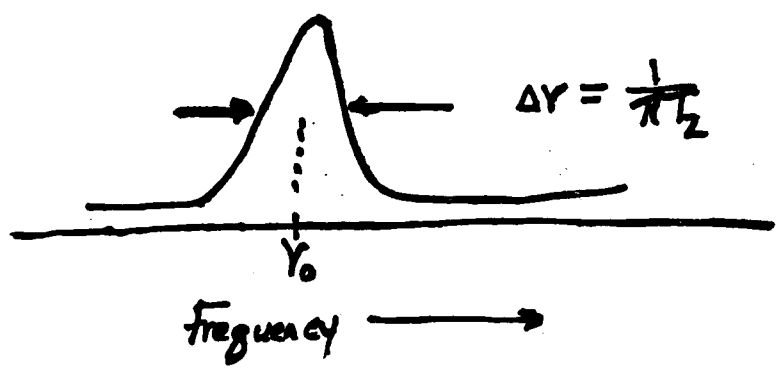
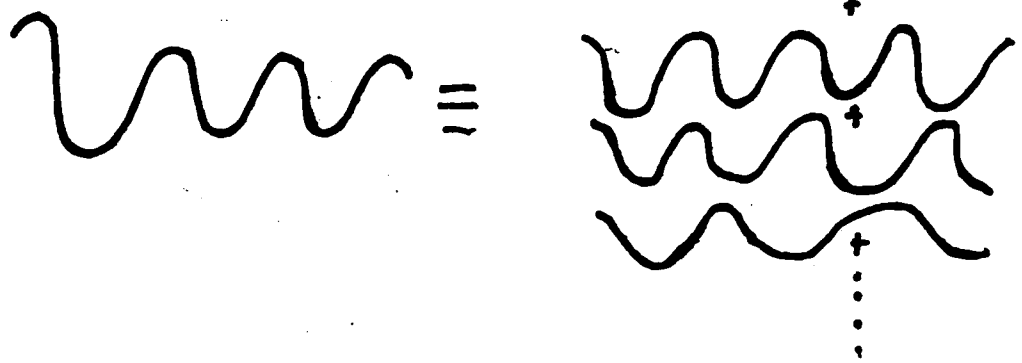
Lecture 3

Sauk

FID & FT



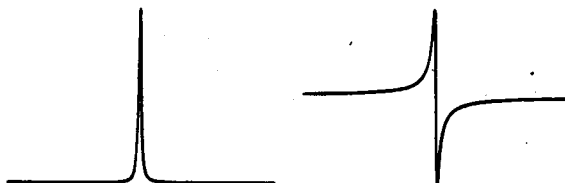
FT



Fourier Transformation (FT):

$$g(\omega) = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt$$

$$e^{-i\omega t} = \underbrace{\cos \omega t}_{\text{real part (Absorption)}} + i \underbrace{\sin \omega t}_{\text{imaginary part (Dispersion)}}$$



- dispersion component is removed by phase cycling.

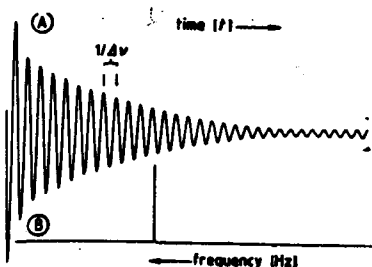


Figure 1-15.
90 MHz ^1H NMR spectrum of methyl iodide CH_3I (1); one pulse, spectral width 1200 Hz, 8 K data points, acquisition time 0.8 s. A: time domain spectrum (FID); the generator frequency is almost exactly equal to the resonance frequency of the sample; B: frequency domain spectrum obtained by Fourier transformation of A.

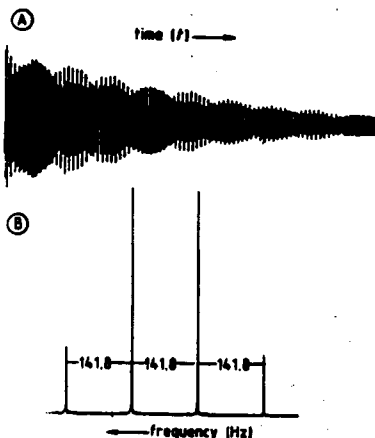
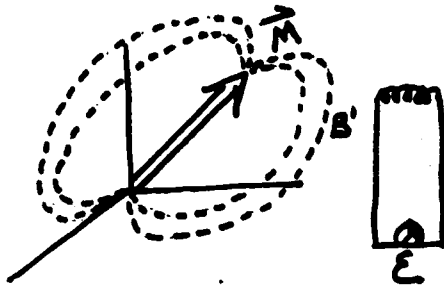


Figure 1-16.
22.63 MHz ^{13}C NMR spectrum of methanol $^{13}\text{CH}_3\text{OH}$ (2); solvent: D_2O , 17 pulses, spectral width 1000 Hz, 8 K data points. A: Time domain spectrum (FID); B: frequency domain spectrum obtained by Fourier transformation of A. This consists of a quartet, as the ^{13}C nucleus is coupled to the three protons of the methyl group.

Sensitivity of the NMR Signal

ϵ = electromagnetic induction force in a detection coil (Faradays Law of Induction).

Precession of a bulk magnetic moment about a static field yields a time varying magnetic field. This produces an induced electromotive force.



$$\epsilon \propto dM(t)/dt = \gamma M_0 B$$

$$M_0 = N\gamma^2 \hbar^2 B_0 I(I+1)/(3k_b T)$$

$$\gamma M_0 B = N\gamma^3 \hbar^2 B_0^2 I(I+1)/(3k_b T)$$

Higher field = higher signal (lose some to noise)

For two nuclei with same value of I their sensitivity is related by:

$$(\gamma_a/\gamma_b)^3 \text{ for } ^1\text{H vs } ^{13}\text{C} \propto (1/4)^3 = .0159$$

$$a = ^{13}\text{C}$$

$$b = ^1\text{H}$$

Table 1-1.

Properties of some nuclides of importance in NMR spectroscopy.

Nuclide	Spin I	Electric quadrupole moment ^{a)} [eQ] [10^{-28} m^2]	Natural abundance ^{a)} [%]	Relative sensitivity ^{b)}	Gyromagnetic ratio γ ^{a)} [$10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]	NMR frequency [MHz] ^{b)} ($B_0 = 2.3488 \text{ T}$)
¹ H	1/2	—	99.985	1.00	26.7519	100.00
² H	1	2.87×10^{-3}	0.015	9.65×10^{-3}	4.1066	15.351
³ H ^{c)}	1/2	—	—	1.21	28.5350	106.664
⁶ Li	1	-6.4×10^{-4}	7.42	8.5×10^{-3}	3.9371	14.716
¹⁰ B	3	8.5×10^{-2}	19.58	1.99×10^{-2}	2.8747	10.746
¹¹ B	3/2	4.1×10^{-2}	80.42	0.17	8.5847	32.084
¹² C	0	—	98.9	—	—	—
¹³ C	1/2	—	1.108	1.59×10^{-2}	6.7283	25.144
¹⁴ N	1	1.67×10^{-2}	99.63	1.01×10^{-3}	1.9338	7.224
¹⁵ N	1/2	—	0.37	1.04×10^{-3}	-2.7126	10.133
¹⁶ O	0	—	99.96	—	—	—
¹⁷ O	5/2	-2.6×10^{-2}	0.037	2.91×10^{-2}	-3.6280	13.557
¹⁹ F	1/2	—	100	0.83	25.1815	94.077
²³ Na	3/2	0.1	100	9.25×10^{-2}	7.0704	26.451
²⁵ Mg	5/2	0.22	10.13	2.67×10^{-3}	-1.6389	6.1195
²⁹ Si	1/2	—	4.70	7.84×10^{-3}	-5.3190	19.865
³¹ P	1/2	—	100	6.63×10^{-2}	10.8394	40.481
³⁹ K	3/2	5.5×10^{-2}	93.1	5.08×10^{-4}	1.2499	4.667
⁴³ Ca	7/2	-5.0×10^{-2}	0.145	6.40×10^{-3}	-1.8028	6.728
⁵⁷ Fe	1/2	—	2.19	3.37×10^{-5}	0.8687	3.231
⁵⁹ Co	7/2	0.42	100	0.28	6.3015	23.614
¹¹⁹ Sn	1/2	—	8.58	5.18×10^{-2}	-10.0318	37.272
¹³³ Cs	7/2	-3.0×10^{-3}	100	4.74×10^{-2}	3.5339	13.117
¹⁹⁵ Pt	1/2	—	33.8	9.94×10^{-3}	5.8383	21.499

Relaxation:

T_1 : spin-lattice relaxation time (longitudinal)

T_2 : spin-spin relaxation time (transverse)

After we remove the pulse, the magnetization vector returns to equilibrium.

Bloch assumed that the processes were first-order and defined them by T_1 and T_2 .

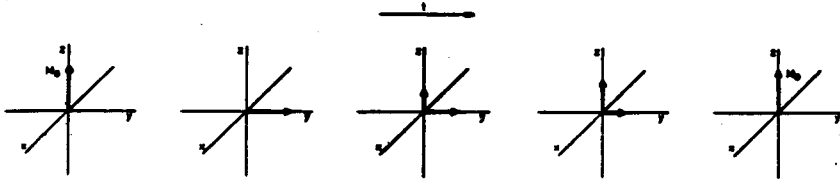
$$dM_z/dt = -M_z - M_0/T_1$$

so

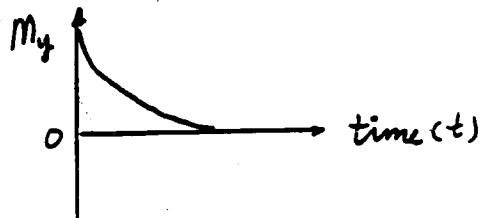
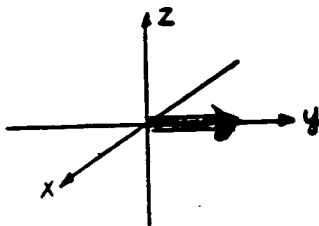
$$M_z = M_0(1 - e^{-t/T_1})$$

$$dM_x/dt = -M_x/T_2$$

$$dM_y/dt = -M_y/T_2$$



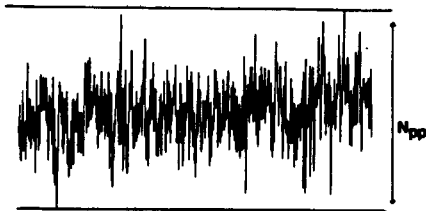
On-resonance



Signal-to-noise (S/N):

S/N = intensity of peak/ rms noise level

$$S/N = 2.5 A / N_{pp}$$



99% of noise points fall within +/- units of zero by Gaussian distribution.

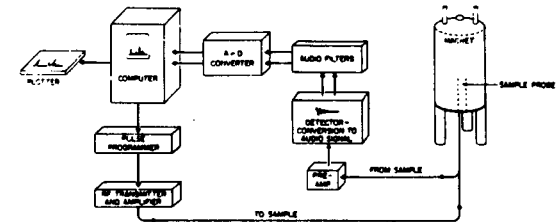
What does this mean to you?

1. Signal increases with the number of scans (N).
2. Noise increase by $N^{1/2}$.

$$S/N \propto N/N^{1/2} = N^{1/2}$$

$$16 \text{ X scans} = 4 \text{ X } S/N$$

Detection of Signal:



- Signal is weak so it is amplified by the preamp.
- The preamp can be tuned for selective signals.
- Signal is in MHz (radio frequency) which we will convert to an audio signal. This is done by stripping off the radio frequency of the carrier leaving only a frequency modulated signal.
- Audio signal carries information about offset from the carrier frequency.
- Audio filters remove bands outside the spectral bandwidth

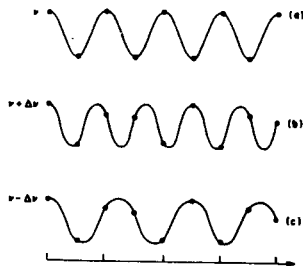
Time Domain Spectral Parameters:

Spectral Width (SW):

- This is nothing more than setting the audio filter.

Digitization: Rate, Resolution and Range.

Rate: A sine wave must be defined by two points in a single period to be properly presented.



(a) To be properly represented, a signal of frequency ν must be sampled twice per cycle. (b) When sampled at this rate, a signal of higher frequency, $\nu + \Delta\nu$, cannot be distinguished from (c) a signal at the lower frequency, $\nu - \Delta\nu$.

Dwell time (DW):

- Time difference between two adjacent points.

$$SW = 1/2DW = \text{Nyquist Frequency } (\nu_{NQ})$$

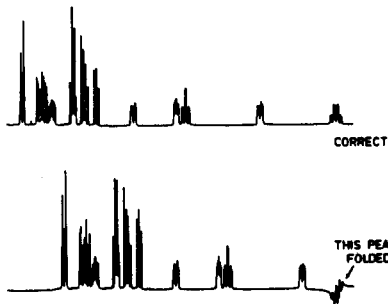
FT NMR assumes all peaks fall within $\pm \nu_{NQ}$

Time Domain Size (TD):

- Number of points of FID.

Acquisition Time (AQ):

$$AQ = DW \cdot TD$$



Chemical Shift:

So far we have assumed one nuclear resonance signal for each nuclear species given by the Larmor frequency:

$$\nu_1 = \gamma B_0 / 2\pi$$

This would be of very little use.

The resonances are influenced by the environment in which the nuclei are present. Usually, the nuclei are surrounded by electrons and other atoms. In a diamagnetic molecule, the effective magnetic field (B_{eff}) is always less than the applied magnetic field (B_0).

$$B_{eff} = B_0 (1 - \sigma)$$

σ - the shielding constant.

- independent of magnetic field

New Resonance Condition:

$$\nu_1 = \gamma (1 - \sigma) B_0 / 2\pi$$

Reference Compounds and the δ scale:

- $\Delta\nu$ = frequency difference between two signals.
- this difference will change as B_0 changes.

Internal Standard (example TMS):

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_{\text{reference}}} \times 10^6$$

- values expressed in parts per million (ppm)

If we replace $\nu_{\text{reference}}$ with the observing frequency of the spectrometer:

$$\delta = \Delta\nu / \text{observing frequency} \times 10^6$$

$$\delta (\text{TMS}) = 0$$

- δ scale is referred to as chemical shift reference.
- It is independent of the magnetic field strength.

For signals left of TMS δ is positive

For signals right of TMS δ is negative.

Signals with lower values of δ :

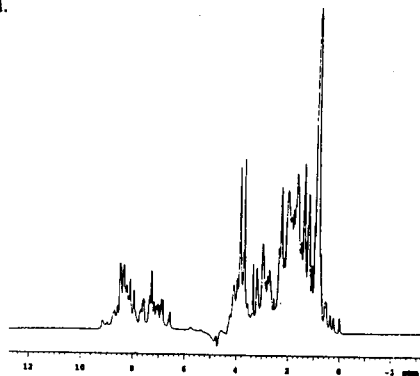
- low frequency, high field, more shielded, upfield shifted.

Signals with larger values of δ :

- high frequency, low field, less shielded, downfield shifted.

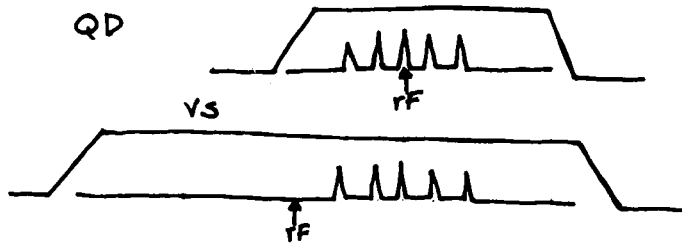
Chemical Shift Ranges:

$^1\text{H}, ^2\text{H}$	10 ppm
^{13}C	300 ppm
$^{15}\text{N}, ^{31}\text{P}$	500 ppm
$^{59}\text{Co}, ^{195}\text{Pt}$	10,000 ppm



Quadrature Detection:

- allows us to put carrier in the middle of region of interest.



Advantage: Get half the noise so increase sensitivity by $\sqrt{2}$

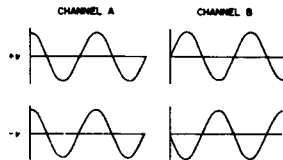
Problem: How do we distinguish $\pm v$ relative to carrier?

Solution: Two detectors out of phase by 90° .

(a)



(b)



Optimizing Parameters:

What is optimal acquisition time?

What is optimal pulse length?

A. Pulse Length:

1. Recovery of Magnetization

$$M(t) \approx M_0 (1 - e^{-\lambda Q/T_1})$$

99% at $5T_1$, 95% at $3T_1$ and 72% at $1.27 T_1$

2. More scans per unit time:

$$S/N \propto N^{1/2}$$

Balance: Ernst Angle $\alpha < 90^\circ$

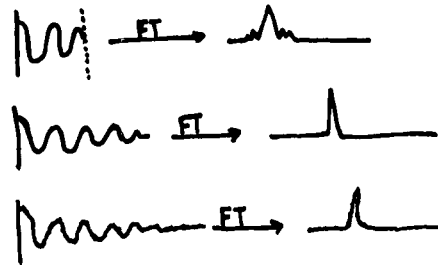
$$\cos \alpha_{\text{Ernst}} = e^{-\lambda Q/T_1}$$

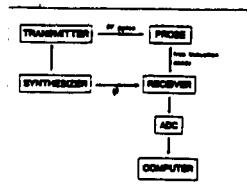
B. Acquisition Time:

1. Long Acquisition = high resolution

2. Long Acquisition = Low S/N

Balance: $T \approx (1-2) T_2$





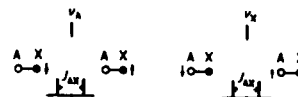
- Transmitter** - high power amplifiers create short radio frequency (RF) pulses that contain appropriate frequencies.
- Synthesizer** - generate Larmor frequencies
- Probe** - coil surrounding sample creates and responds to the oscillating electromagnetic field.
- Receiver** - the incoming signals at around Larmor frequency are mixed with the carrier frequency, which is subtracted to give a signal (0 to ± 1500 Hz). This latter signal (the free induction decay) is then amplified and analyzed by the computer.
- ADC** - digitizer. The incoming analog RF signal is digitized. There is a limit to the amount of signal a digitizer can handle.
- Computer** - controls data acquisition, data processing, display and other functions.

Spin-Spin Coupling through Chemical Bonds: (Indirect, scalar, J-coupling)

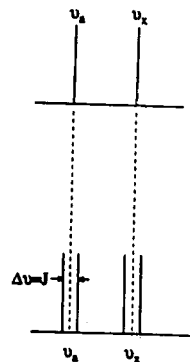
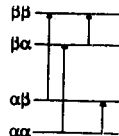
- neighboring magnetic dipoles in a molecule interact with each other
- this effects the magnetic field at the position of the nuclei being observed and the effective field can be stronger or weaker than in the absence of coupling.
- In indirect spin-spin coupling it occurs through bonds while direct spin-spin coupling is through space.

1. AX spin system:

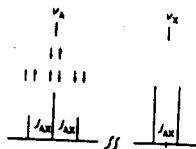
- two frequencies ν_A and ν_X if they are coupled we will see two signals for both frequencies.



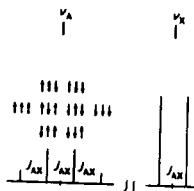
Coupling values depend on nuclear magnetic moments (μ) thus the values are independent of field strength (B_0) so they are always given in Hz.



2. AX_2



3. AX_3



4. AX_n

$$M = n + 1$$

M: multiplicity of the NMR signals, number of lines in a multiplet.

$n = 0$	1
$n = 1$	1 1
$n = 2$	1 2 1
$n = 3$	1 3 3 1
$n = 4$	1 4 6 4 1
\vdots	\vdots

AMX System- three non-equivalent nuclei.

