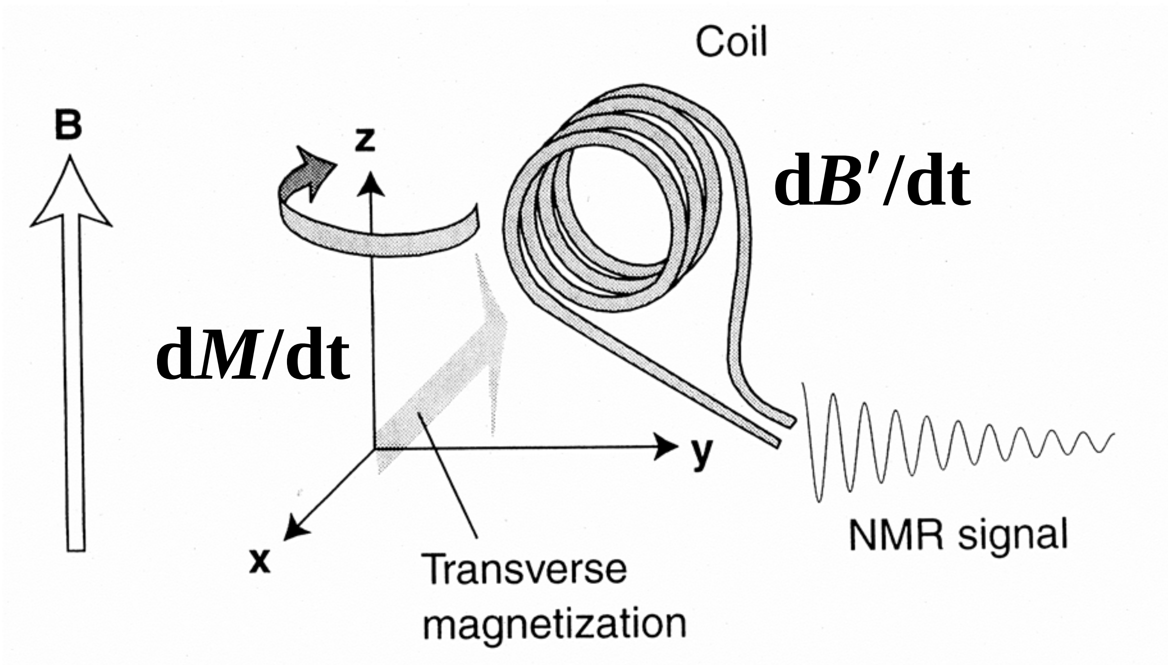
NMR Spectroscopy:
2

Signal Detection and Sensitivity

- A bulk magnetic moment (M) precessing about a static magnetic field (B_0) results in a local magnetic field (B') varying in time ($dM/dt \propto dB'/dt$)

- The voltage (emf, ε) induced in the detector coil is proportional to the rate of change of the magnetic flux in the coil, which in turn is proportional to the rate of change of the oscillating transverse magnetization (Faraday's Law of Induction)



oscillating magnetic field generates and emf in the receiver coil

Signal Detection and Sensitivity

- A bulk magnetic moment (M) precessing about a static magnetic field (B_0) results in a local magnetic field (B') varying in time ($\mathrm{d}M/\mathrm{dt} \propto \mathrm{d}B'/\mathrm{dt}$)

- The voltage (emf) induced in the detector coil is proportional to the rate of change of the magnetic flux in the coil, which in turn is proportional to the rate of change of the oscillating transverse magnetization

$$\varepsilon \propto \mathrm{d}B'/\mathrm{d}t \propto \mathrm{d}M/\mathrm{d}t \propto \gamma B_0 M_0 = \mathrm{N}\gamma^3 B_0^2 \hbar^2 I(I+1)/(3k_\mathrm{B}T)$$

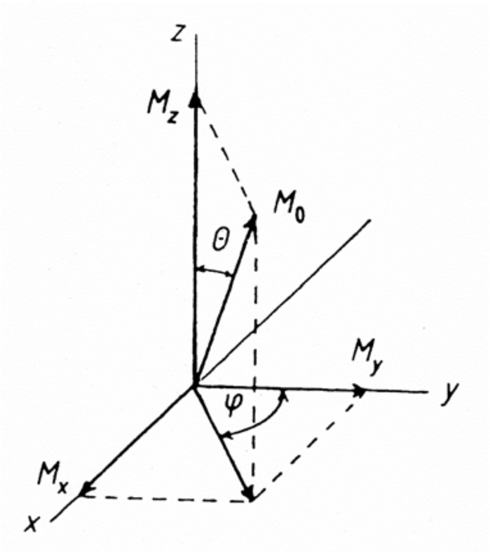
- **Thus, sensitivity is dependent on γ^3 and B_0^2 !**

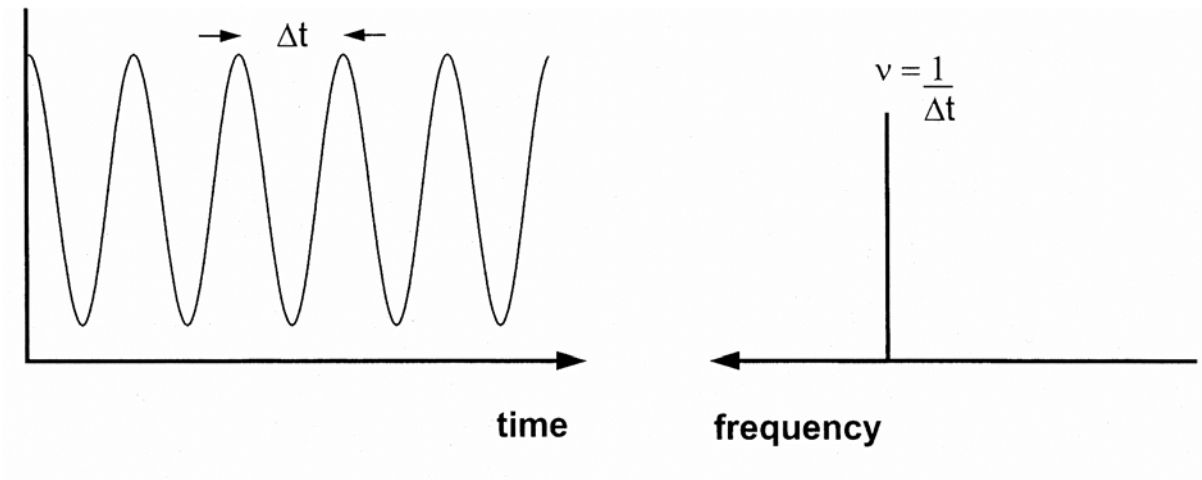
Consider equal numbers of two nuclei with the same value of I (i.e. ^{1}H and ^{13}C):

$$\mathbf{S/N \propto (\gamma_C / \gamma_H)^3 = 64^{-1}}$$

Free Induction Decay

- A radiofrequency pulse (applied with frequency ν_1) will rotate $\boldsymbol{M}_0$ into the transverse (x-y) plane
- In the transverse plane, $\boldsymbol{M}$ precesses about z with Larmor frequency ν_L
- In NMR, we detect the difference ($\Delta\nu$) between ν_1 (the reference or "carrier" frequency) and ν_L
- The signal oscillates with time, defining the frequency of oscillation

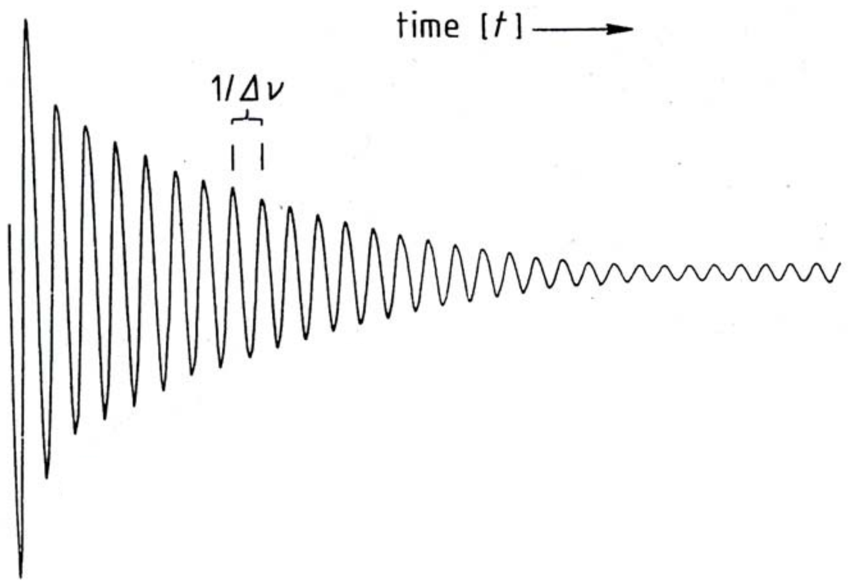




Free Induction Decay

- Our oscillating signal decays as a function of time as the phase coherence between the precessing magnetic dipoles (vectors) is lost
- The process is called ***free induction decay***
- The oscillating signal is called the **FID** or free induction decay and represents our signal in the time domain (signal amplitude as a function of time)

Free Induction Decay (FID)

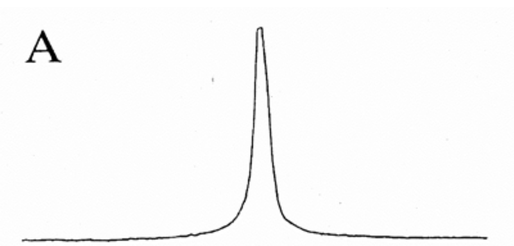


Frequency Domain: Fourier Transform

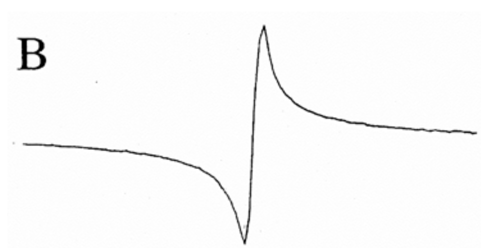
- Time domain signals are converted into frequency domain signals (amplitude versus frequency) using the **Fourier Transform**

$$g(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} \mathrm{d}t \qquad e^{-i\omega t} = \cos \omega t + i \sin \omega t$$

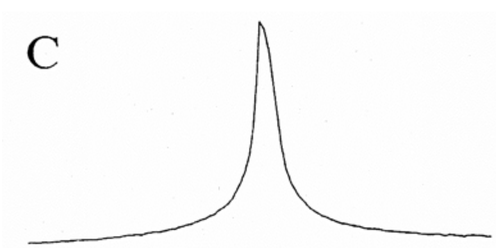
- $f(t)$corresponds to the time domain, and $g(\omega)$ corresponds to the frequency domain
  - $g(\omega)$ is a complex function, consisting of both a real (*Re*) and an imaginary (*Im*) part
  - the signals from these are absorptive and dispersive
  - the dispersive contribution can be removed by "phase correction" to give purely absorptive signals
  - spectra can also be viewed in the "absolute value" mode, which gives purely absorptive signals
  - line shape is **Lorentzian** (Fourier transform of a decaying exponential function)



absorption signal



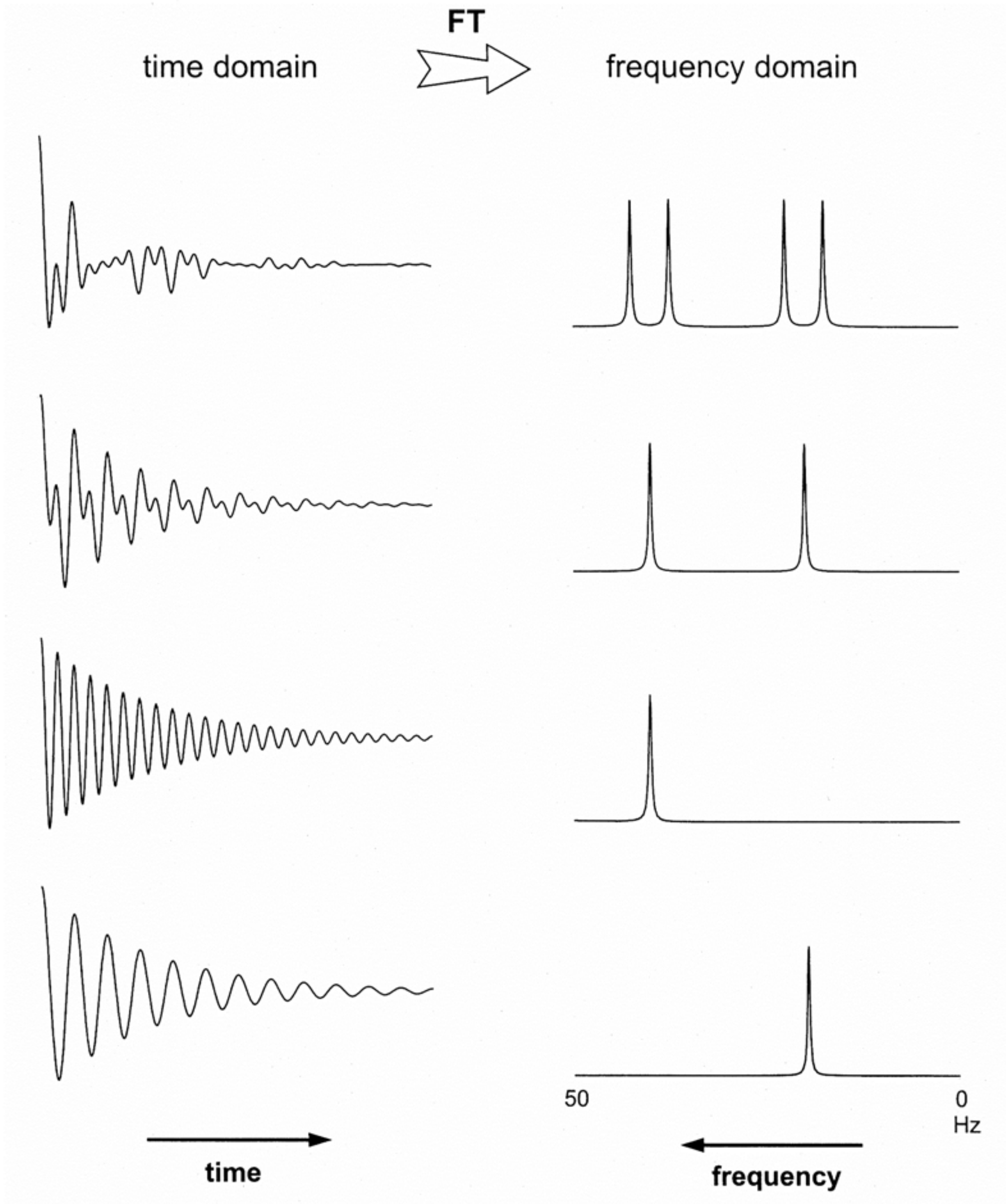
dispersion signal



absolute value signal

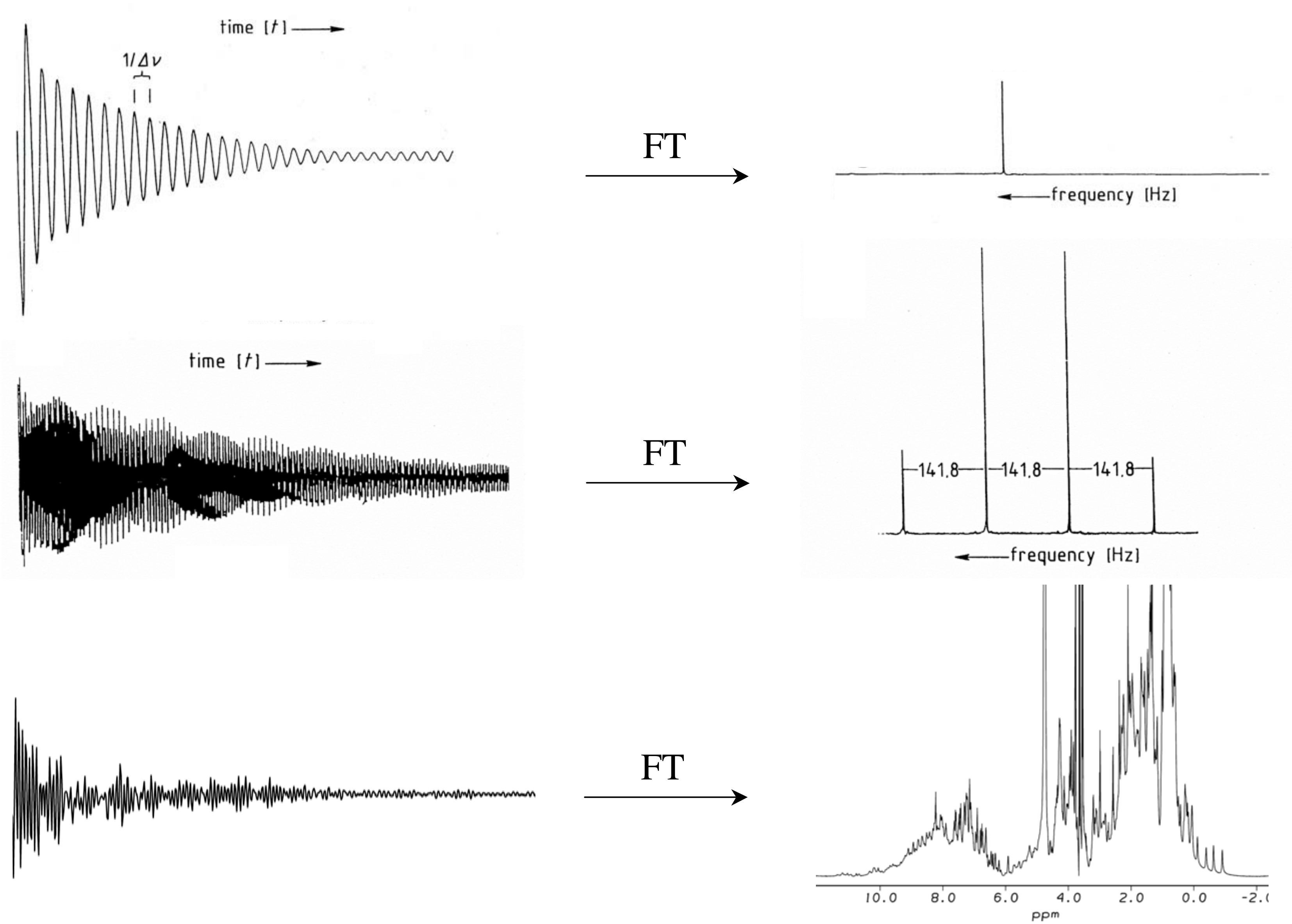
$$\sqrt{(Re)^2 + (Im)^2}$$

Frequency and Time Domain Signals



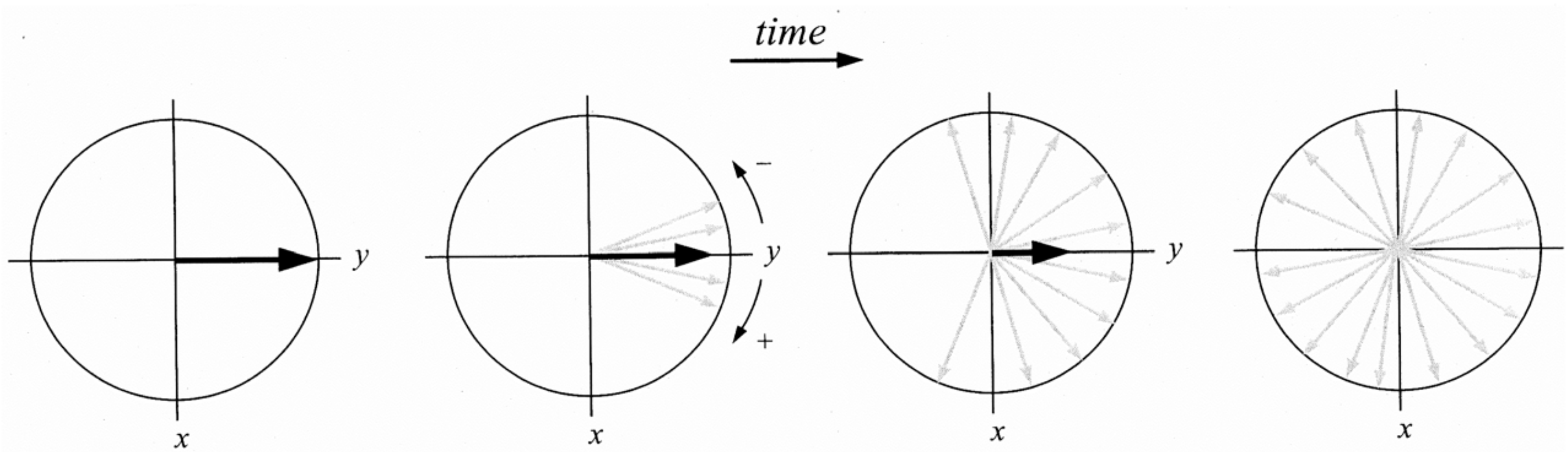
Frequency Domain Spectra

- The frequency domain spectra readily report the frequencies for individual spins



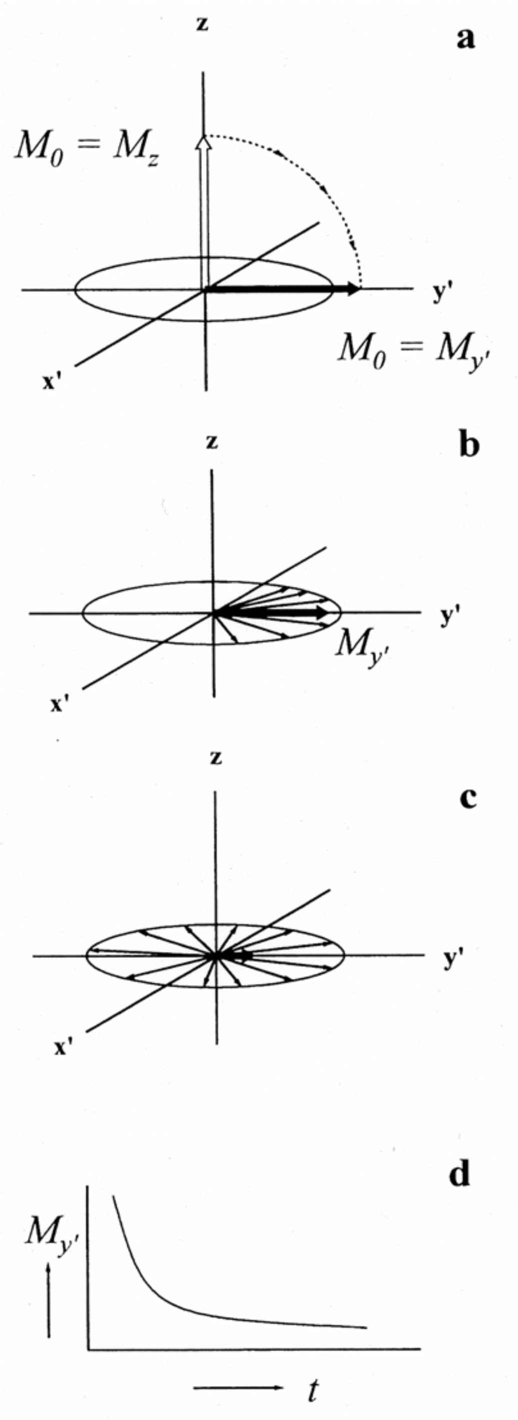
Transverse (Spin-Spin, T_2) Relaxation

- Our oscillating signal decays as a function of time as the phase coherence between the precessing magnetic dipoles (vectors) is lost
- Transverse (spin-spin) or T_2 relaxation refers to loss of phase coherence in the transverse (*x*-*y*) plane
- This loss of coherence is due to local magnetic field differences experienced by the nuclei



- T_2 relaxation is characterized both by a component due to magnetic field inhomogeneity (the uninteresting component) and a by component arising from local fluctuating magnetic fields produced by the nuclei themselves

$$\frac{1}{T_2*} = \frac{1}{T_2} + \frac{1}{T_{2(\Delta B_0)}}$$

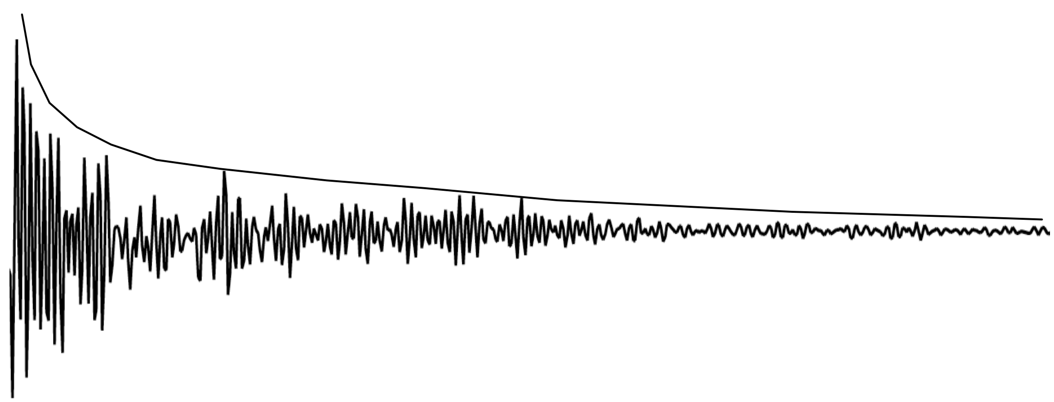


Transverse (T_2) Relaxation

- The decay of signal due to T_2 relaxation is first order

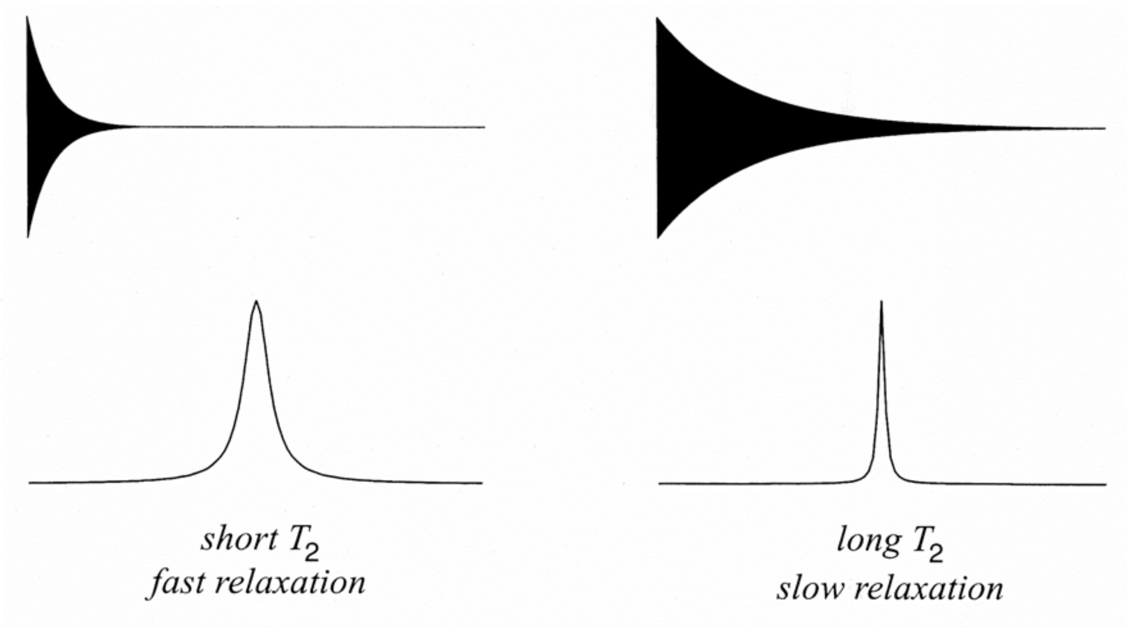
$$\frac{dM_y}{dt} = -\frac{M_y}{T_2^*}$$

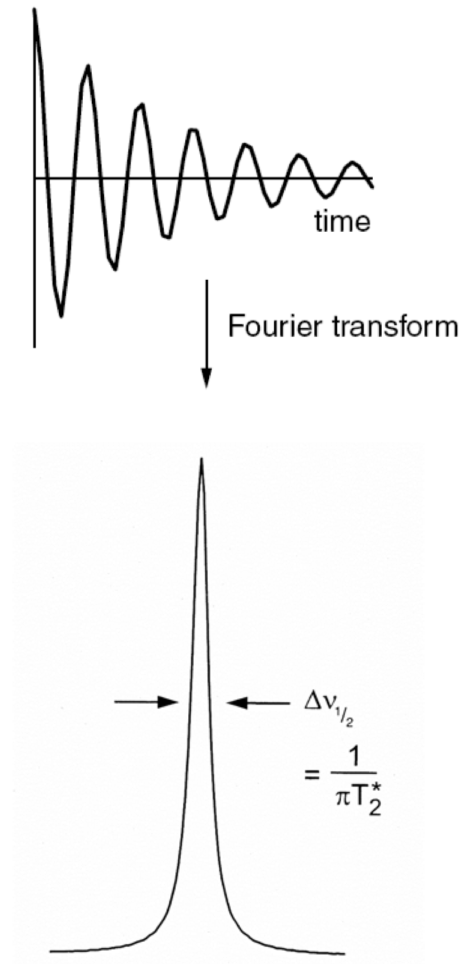
$$M_y = M_{y_0} e^{(-t/T_2^*)}$$



Transverse (T_2) Relaxation

- Short T_2 times lead to broad lines (undesirable, lower signal-to-noise)
- A poorly shimmed magnet leads to short T_2 times and broad peaks



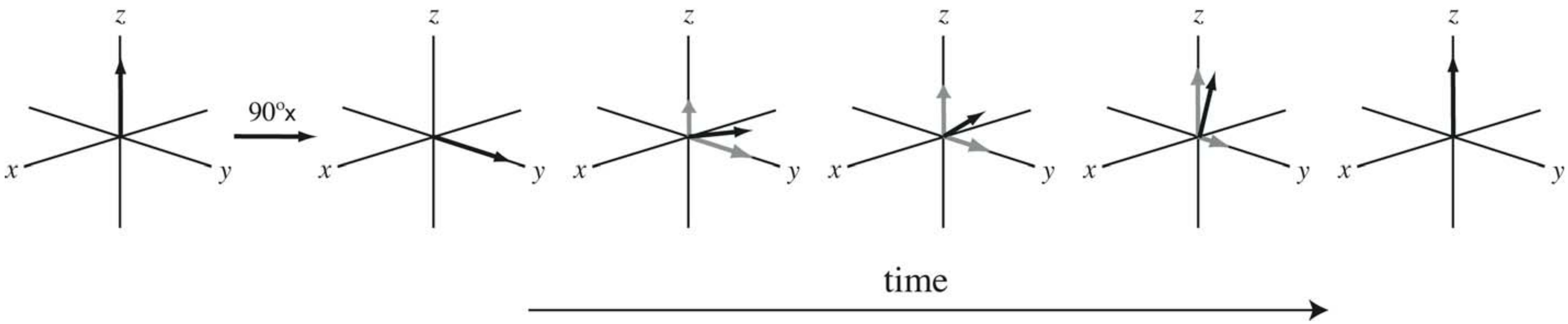


- The Fourier transform of a decaying exponential function ($\cos\omega t \bullet e^{(-t/T_2)}$) gives a **Lorentzian** line shape
- The width of a Lorenztian peak at 1/2 of the maximum height is $1/(\pi\, T_2{}^*)$

$$\Delta\upsilon_{1/2} = \frac{1}{\pi T_2 *} = \frac{1}{\pi T_2} + \gamma\Delta B_0$$

Longitudinal (Spin-Lattice, T_1) Relaxation

- Longitudinal (spin-lattice) or T_1 relaxation refers to return to thermal equilibrium (along the z axis) of the spin populations (return to equilibrium N_α and N_β values) following perturbation
- T_1 relaxation represents a loss of energy (heat) from the spins to the surroundings



- The return to equilibrium is first order

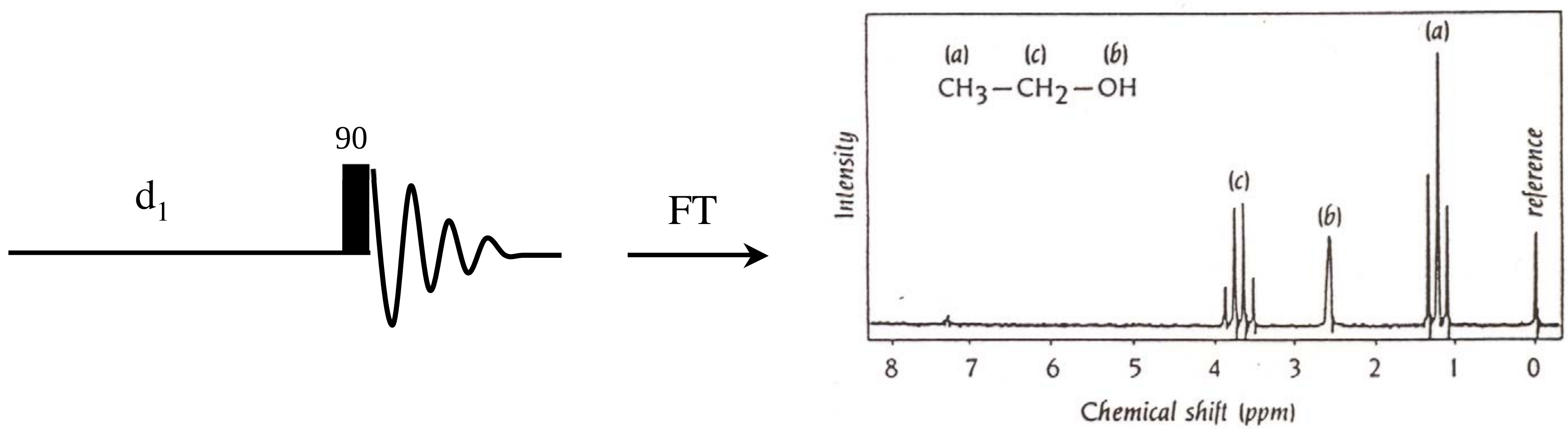
-after a 90° pulse, the return to equilibrium is described as shown below:

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1} \qquad M_z = M_0(1 - e^{(-t/T_1)})$$

-after a 180° pulse…..

$$M_z = M_0(1 - 2e^{(-t/T_1)})$$

One Dimensional NMR



- Need to wait for a time ("d_1") after acquisition of the FID in order for the spin populations to return to thermal equilibrium
  - -after a 90° pulse, should wait for ~5T_1
  - -thus, are limited in the number of "scans" that can be acquired in a given amount of time
- Important point: signal-to-noise (S/N) increases in proportion to the square root of the number of scans

$$S/N \propto \sqrt{NS}$$

- For instance, if 1 scan gives a particular S/N, in order to double the S/N, 4 scans are required (unfortunately)