(Nuclear) Magnetic Resonance (NMR)

- Based on precession of spin of the nucleus in magnetic field.
- $\Rightarrow$ Can be used only for nuclei having magentic moment (i.e. spin).
- $\Rightarrow$ The isotope must have odd number of protons and/or of neutrons. I.e. zero spin have only nuclides with even numbers of protons and neutrons.
    - magnetic moment of neutron: $-1.9130427(5)\mu_N$
    - magnetic moment of proton: $2.792847351(28)\mu_N$
    - magnetic moment of electron: $-1.00115965218111\mu_B$

  where
    - Bohr magneton: $\mu_B = \frac{e\hbar}{2m_e}$, m_e rest mass of electron.
    - Nuclear magneton: $\mu_N = \frac{e\hbar}{2m_p}$, m_p rest mass of proton.
- Isotopes of particular interest and use to organic chemists are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all of which have $I = 1/2$.

Larmor frequency

- Precession of magnetic moment inside magnetic filed.

- Larmor frequency of nucleus

$$\omega = \frac{2\mu_N}{\hbar}B$$

- Corresponding frequencies are:
  - $f_{\mathrm{proton}} = 42.578\,\mathrm{MHz/T}$
  - $f_{\mathrm{electron}} = 28.025\,\mathrm{GHz/T}$

- The spin of nucleus can be driven by an external electro-magnetic (EM) wave. When its frequency is in resonance (i.e. is equal) with Larmor frequency of the spin, the spin precesses more and the EM wave gets damped.
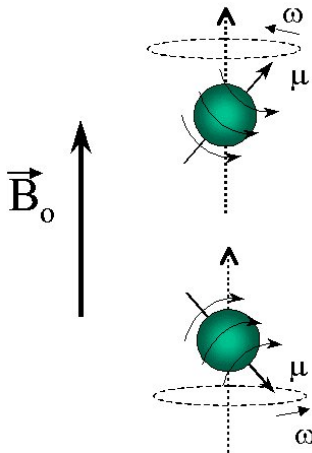
Larmor frequency - quantum picture

Alternatively, driving precession can be understand as absorption of photon

- Energy levels of nucleus spin direction are split by an external magnetic field (spin-up and spin-down)

$$\Delta E = \gamma \hbar B \equiv 2\mu_N B$$

- As electric-dipolar transition is not allowed, the transition is magnetic-dipolar transition.

- Note, magnetic dipole transitions are typically about 10^5 times more unlikely than similar electric dipole transitions.
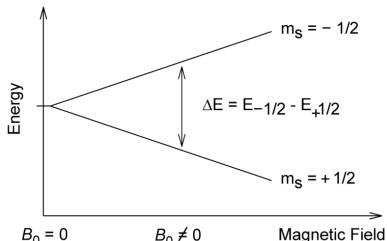
Example of NMR typical frequencies

isotope	magnetic moment
^1H	$\mu = 2.7927\mu_N$
^{19}F	$\mu = 2.6273\mu_N$
^{31}P	$\mu = 1.1305\mu_N$
^{13}C	$\mu = 0.7022\mu_N$

Nuclear magneton: $\mu_N = \frac{e\hbar}{2m_p}$, m_p rest mass of proton.

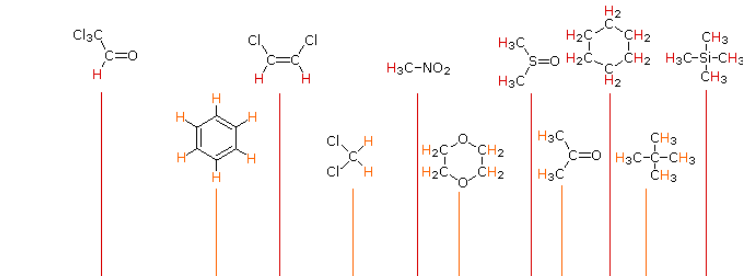$B_0 = 2.35\,T$

$$\nu = \frac{\mu B_0}{hI} = \frac{4.68\mu}{h}$$

^{13}C ^{31}P ^{19}F ^1H

0   25.2   40.5   **ν** (MHz)   94   100
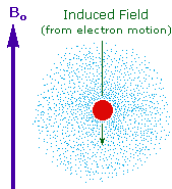
NMR spectroscopy

- Nucleus serves as a sensitive probe of local magnetic field.

- Local magnetic field in nucleus position slightly varies due to screening of surrounding electrons (chemical shift). Typical change in ppm - part per million.

- Sensitive only to one isotope (typically ^{1}H, i.e. proton).

^{1}H NMR Resonance Signals for some Different Compounds

NMR: Why different nuclei have different resonance frequency?

- Electrons are charged particles ⇒ they move in response to the external magnetic field ⇒ secondary field opposed to the applied field is created.

- The external magnetic field acting on nuclei are screened by surrounding electrons ⇒ the field acting on nuclei is smaller (i.e. resonance frequency get smaller)

- typical change due to electron screening is 0.005% (5 ppm).

B_o

Induced Field
(from electron motion)

Increasing Magnetic Field at Fixed Frequency →

← Increasing Frequency at Fixed Magnetic Field

Increased Shielding by Extranuclear electrons →

proton

H atom

H_2O liq 0°

CH_4

Most Organic Hydrogen is found in this region

H_2SO_4 $CHCl_3$ H_2

HCl   HBr   HI
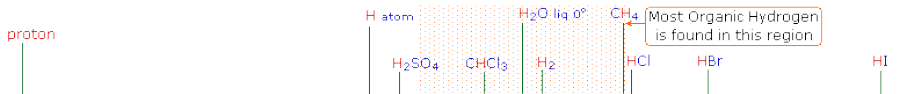
NMR spectroscopy

- Signal strength → concentration of a given nucleus in a given enviroment.

- Exchange (spin-spin) interaction provides splitting of energy levels (so called J-coupling).
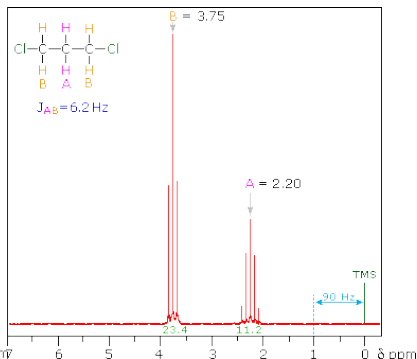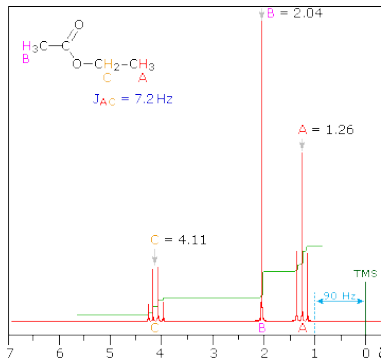
NMR relaxation

Measuring relaxation time of magnetization upon its excitation to its thermodynamically stable state.

- Spin excitation be external rf pulse $\rightarrow$ relaxation of spins back to thermodynamic state (i.e. aligned along applied field). At this stage, relaxation time is measured.
- two different relaxation times are measured, longitudinal T_1 and transversal T_2.
- those time constants says about surrounding electronic structure and inhomogeneity of magnetic field.

NMR relaxation: longitudinal

- longitudinal (or spin-lattice) relaxation time T_1: the decay constant for the recovery of the $\hat{z}$ component of the nuclear spin magnetization M_z, towards its thermal equilibrium value $M_{z,eq}$.

- $\vec{B} \parallel \hat{z}$. If M has been tilted into the xy plane, then and the recovery is simply $M_z(t) = M_{z,eq}(1 - \exp(-t/T_1))$
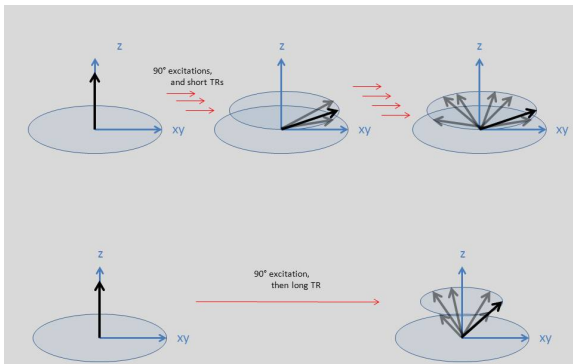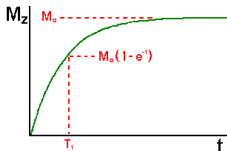
NMR relaxation: transversal

- transversal (or spin-spin) relaxation time T_2: the net magnetization starts to dephase as the spins feel a slightly different magnetic field and hence rotates at its own Larmor frequency.
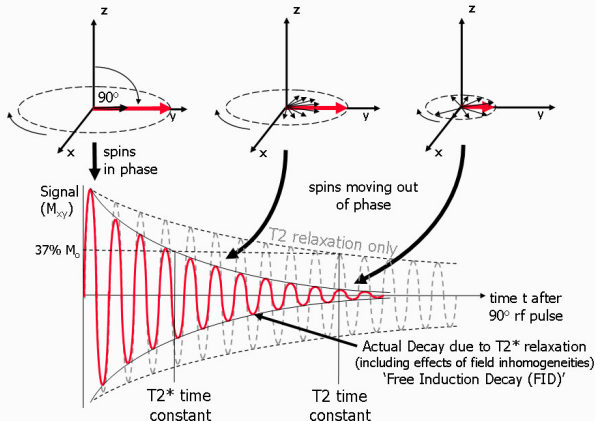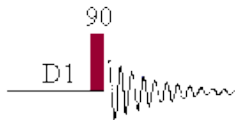
NMR — $\pi/2$-pulse and π-pulse

- $\vec{B} \parallel \hat{z} \Rightarrow$ Larmor frequency of magnetization at frequency ω.
- pulse of oscillating magnetic field in xy-plane
  $\vec{B} = B_1(\hat{x}\cos\omega t + \hat{y}\sin\omega t)$ applied in y direction.
$\Rightarrow$ than the magnetization precess with increasing amplitude.
$\Rightarrow$ when duration of pulse has correct length, the magnetization
  precession angle reaches $90°$, i.e. it rotates in xy-plane (so
  called $\pi/2$-pulse).
$\rightarrow$ similarly, one can create π-pulse, which reverses magnetization
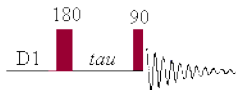 direction.
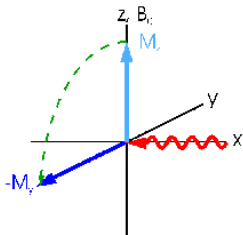
Determination of relaxation by pulse trains: T_1 determination
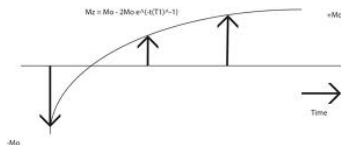
Progressive Saturation	Inversion Recovery

$$M(\tau)/M_0 = 1 - \exp(-\tau/T_1)$$

$$M(\tau)/M_0 = 1 - 2\exp(-\tau/T_1)$$

http://www.chem.queensu.ca/facilities/nmr/nmr/webcourse/
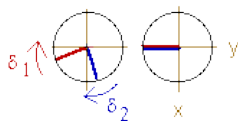
Determination of relaxation by pulse trains: T_2 determination

- first $\pi/2$ pulse move spins to xy plane.

- then, spins starts to become out-of-phase, due to slightly different precession frequencies.

- after time τ, π-pulse is applied. Spins are still in xy-plane, but their position is mirrored by yz-plane.

- spins goes the same way, and go to coherence back (so called spin echo).
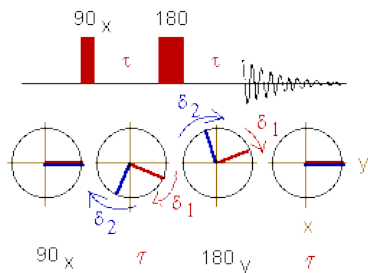
or:

NMR imaging: encoding I

T_1 and T_2 relaxation times measured for selected points in the body.

Field gradient selects spin under resonance frequency.

Frequency encoding

- field B_0 with added gradient of field G_z: $B(z) = B_0 + G_z z$
- then, resonance frequency is $f(z) = \gamma B_0 + \gamma G_z z$
- $\Rightarrow$ different resonance frequencies at different positions
- base of all NMR imaging.

NMR imaging: encoding II

Slice selection

- switch on gradient of the field
- apply $90°$ excitation pulse at a given frequency $\Rightarrow$ spins starts to precess only in one plane, where resonance condition is fulfilled
- gradient of field turns off $\Rightarrow$ *spin precesses only in a slice selected by applied field gradient*
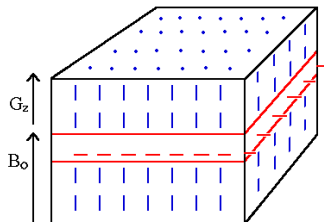
Phase Encoding Gradient

1. spins are excited (precessing)
2. gradient of field along x is applied
3. then, spins starts to precess at different frequencies
4. gradient is off, spin precess again at equal frequency, but with different phases $\Rightarrow$ *spin precession modulated in phase*
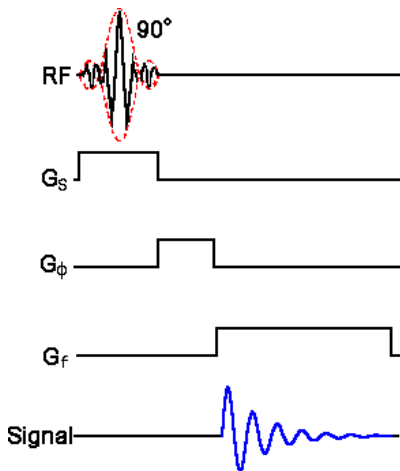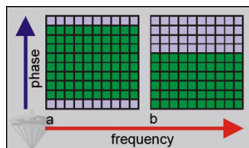
NMR imaging: example of imaging sequence I

RF : $90°$ rf pulse

G_s : slice selection pulse (e.g. along z)

G_φ : phase encoding gradient pulse (e.g. along y)

G_f : frequency encoding gradient pulse (e.g. along x)

$\Rightarrow$: spins at different locations precess by a unique phase angle φ and precessional frequency f!
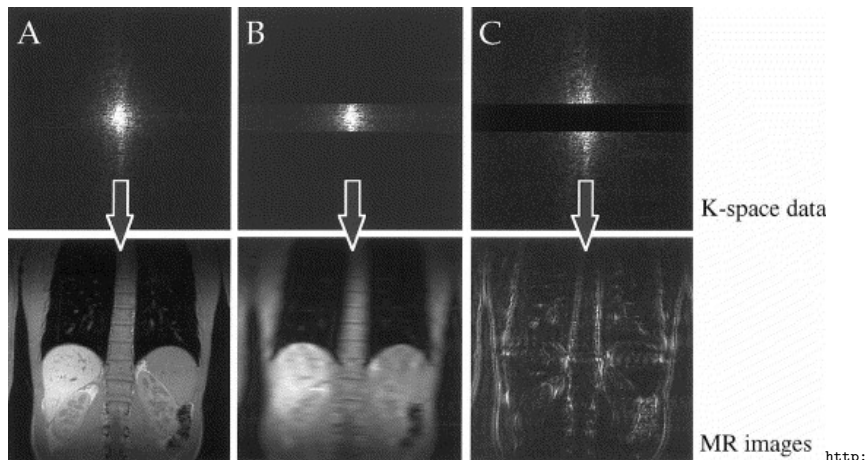
NMR imaging: example of imaging sequence II

System is excited at different strengths of phase encoding gradient pulse $\Rightarrow$ various precession signal are detected.

Fourier transform can recovers both phase and frequency of a signal $\Rightarrow$ by determining frequency and phase, one can determine strength of oscillation in each position of the slice.

nice overview of NMR: http://www.cis.rit.edu/htbooks/mri/inside.htm
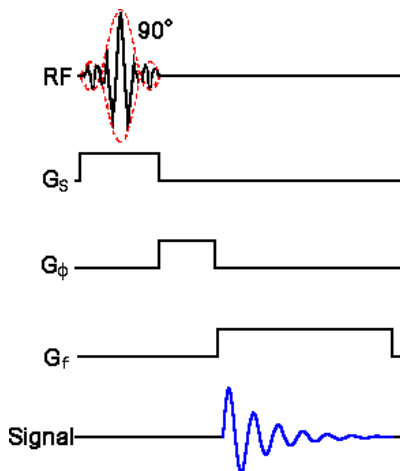
Example of *k*-space to *r*-space conversion by Fourier trans.