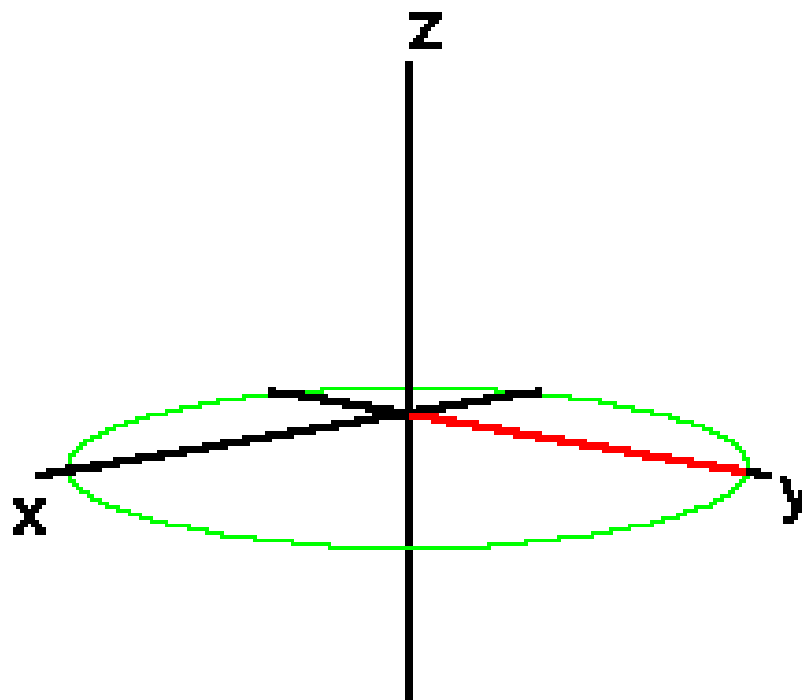
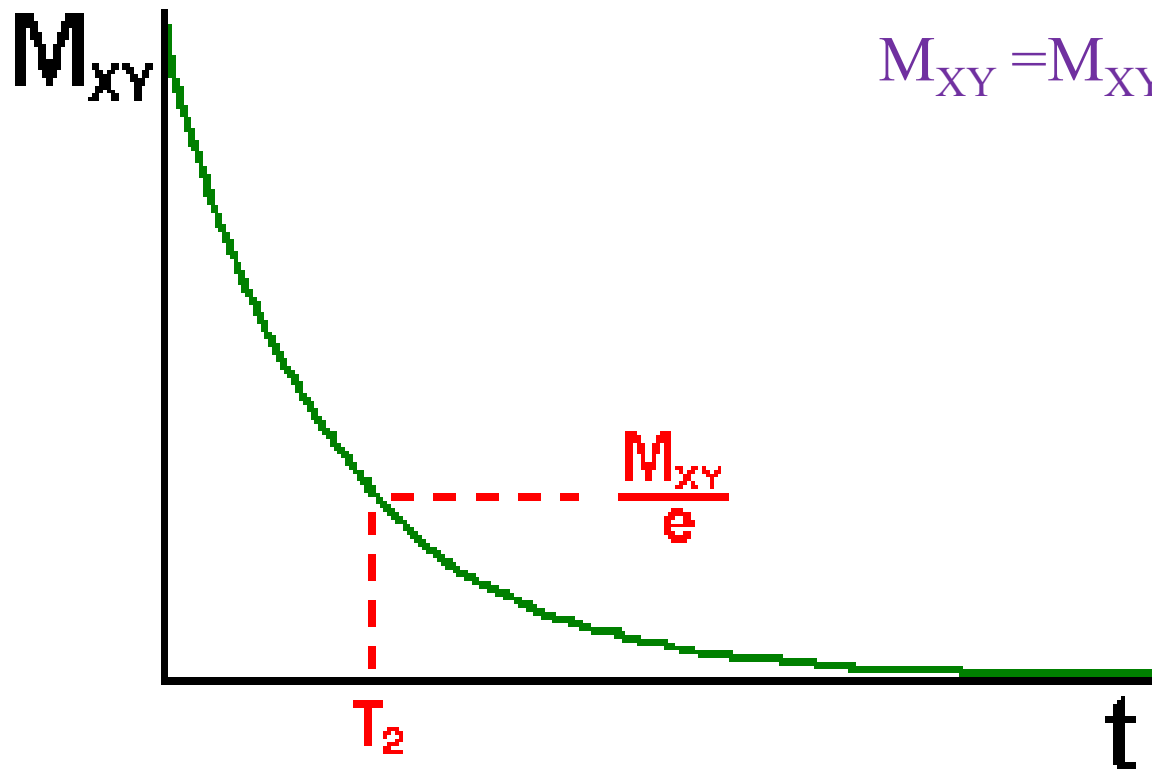


T₂ Processes

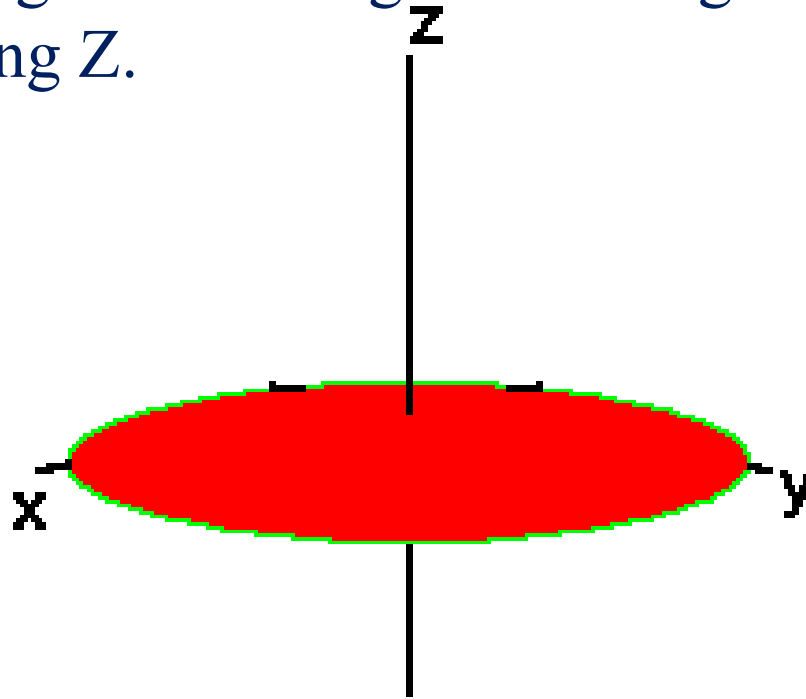
- spin-spin relaxation time, T₂



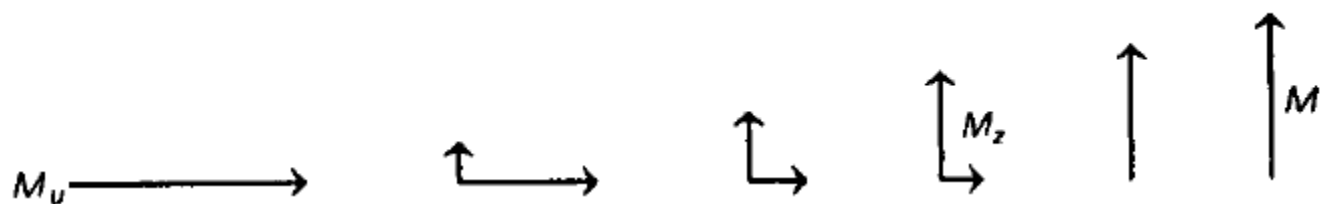


$$M_{xy} = M_{xy0} e^{-t/T_2}$$

- T_2 is always less than or equal to T_1
- The net magnetization in the XY plane goes to zero and then the longitudinal magnetization grows in until we have M_0 along Z .



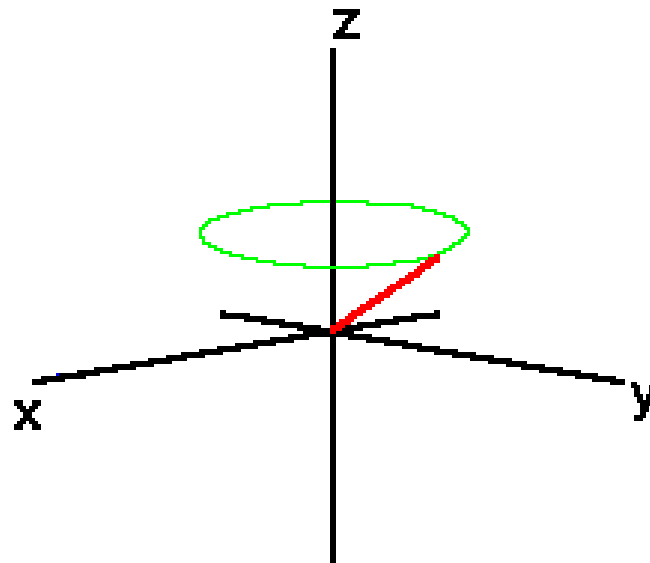
T₂ Mechanism



- In this type of relaxation the energy released when a nucleus makes the transition from high to low energy state is absorbed by another nucleus. This allows the other nucleus to move from low energy to high.
- In this case the total number of nuclei in the excited state doesn't change. What happens is that the newly excited nuclei are no longer in synch so that the signals are out-of-phase and are subtractive instead of additive

- Short relaxation times result in broad signals. This is a result of the Heisenberg uncertainty principle. The shorter the time frame for observation the more uncertainty exists in the frequency. Longer relaxation times then produce narrower signals.
- Instrument parameters such as a lack of homogeneity of the magnetic field can also produce broadening of the NMR signal.

- Any transverse magnetization behaves the same way. The transverse component rotates about the direction of applied magnetization and dephases. T_1 governs the rate of recovery of the longitudinal magnetization.



- In summary, the spin-spin relaxation time, T_2 , is the time to reduce the transverse magnetization by a factor of e .

- both processes occur simultaneously with the only restriction being that T_2 is less than or equal to T_1 .

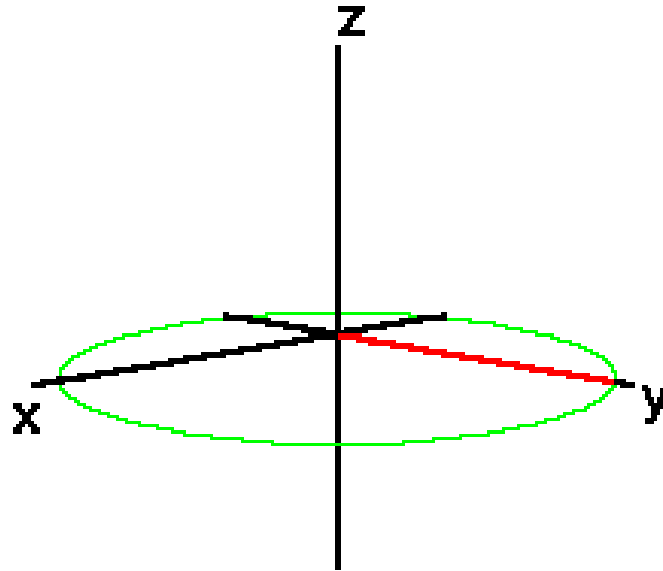
combined time constant (T_2^*)

- Two factors contribute to the decay of transverse magnetization.
 - 1) molecular interactions (said to lead to a pure *pure* T_2 molecular effect)
 - 2) variations in B_0 (said to lead to an *inhomogeneous* T_2 effect)

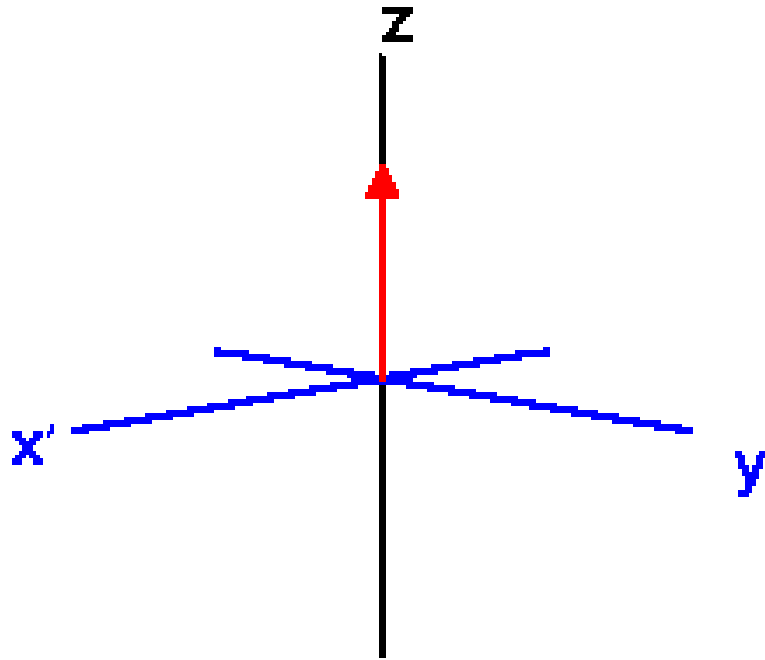
$$1/T_2^* = 1/T_2 + 1/T_{2\text{inhomo}}$$

Rotating Frame of Reference

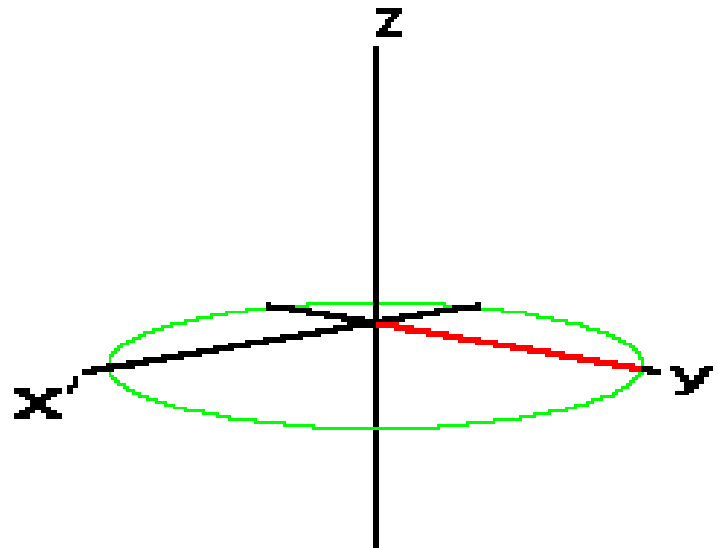
- magnetization vector rotating at the Larmor frequency



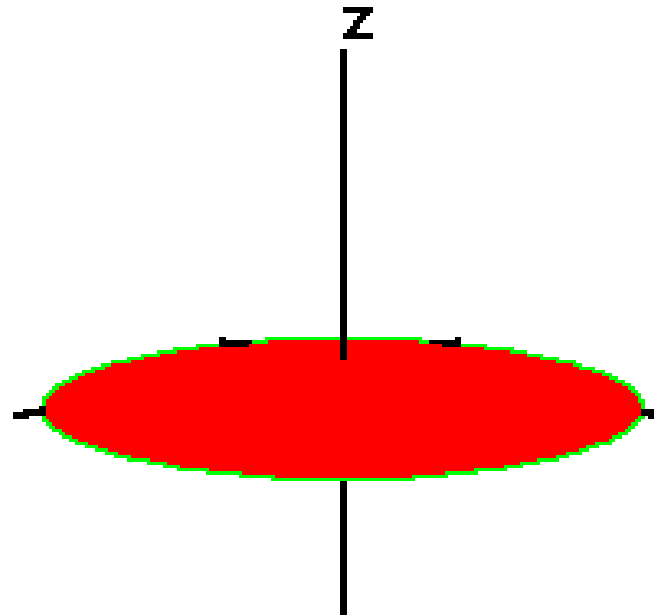
- relaxation of M_Z magnetization to its equilibrium value looks the same as it did in the laboratory frame.

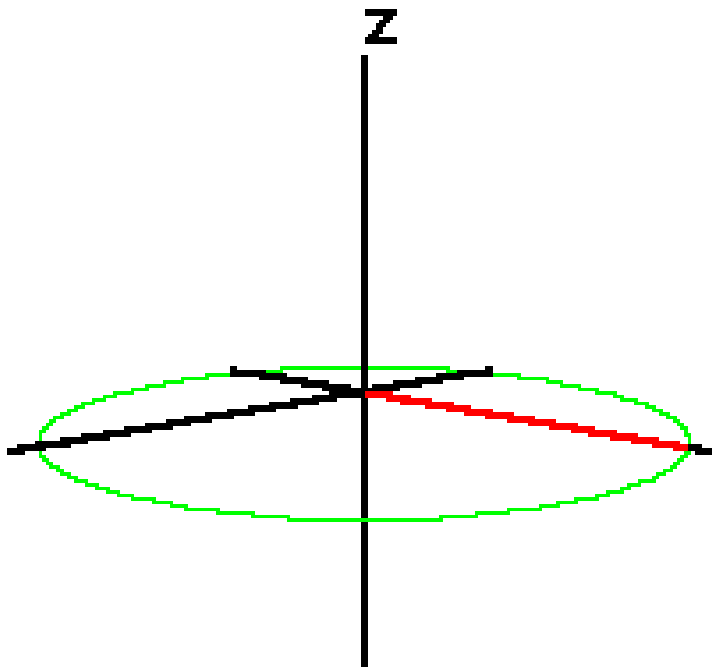


- A transverse magnetization vector rotating about the Z axis at the same velocity as the rotating frame will appear stationary in the rotating frame. A magnetization vector traveling faster than the rotating frame rotates clockwise about the Z axis. A magnetization vector traveling slower than the rotating frame rotates counter-clockwise about the Z axis .

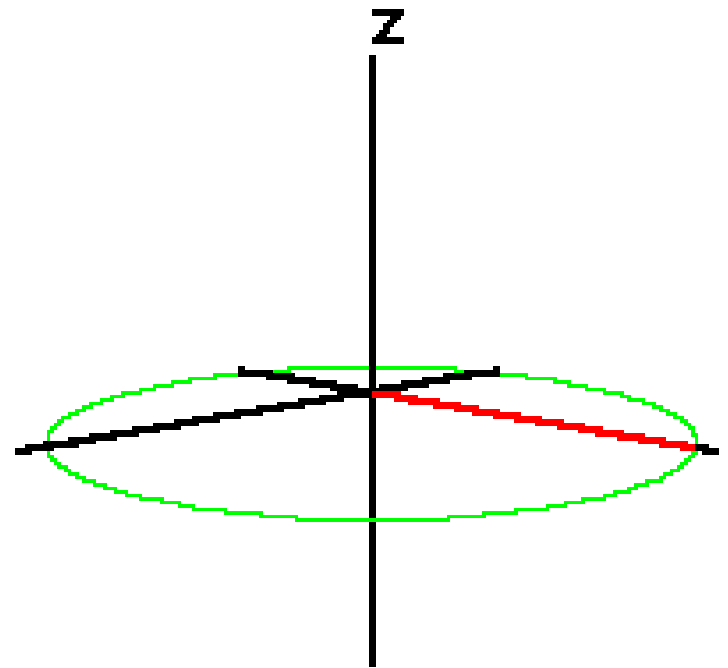


- In a sample there are spin packets traveling faster and slower than the rotating frame. As a consequence, when the mean frequency of the sample is equal to the rotating frame, the dephasing of $M_{X'Y'}$ looks like this.



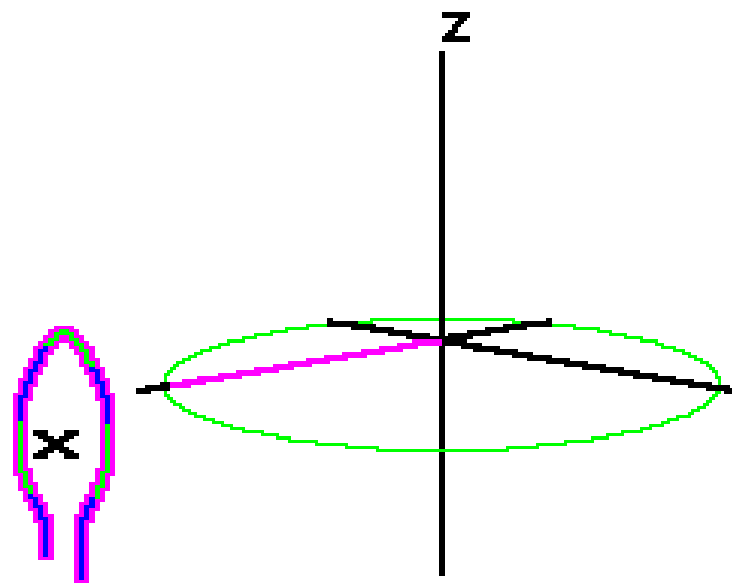
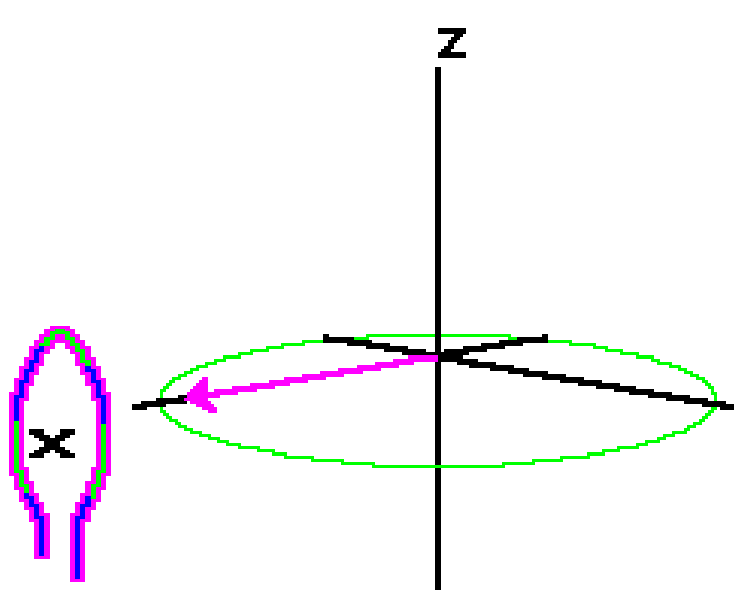


magnetization vector faster than the rotating frame
clockwise



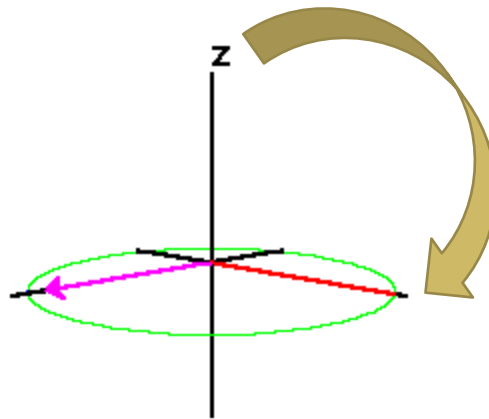
magnetization vector slower than the rotating frame
counter-clockwise

Pulsed Magnetic Fields

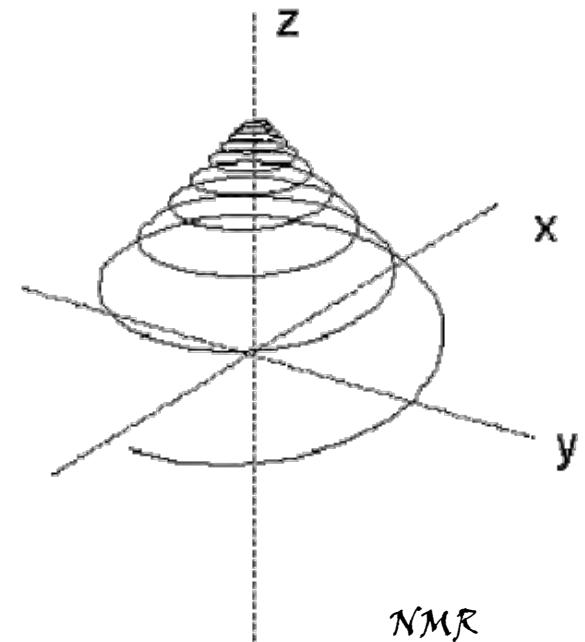
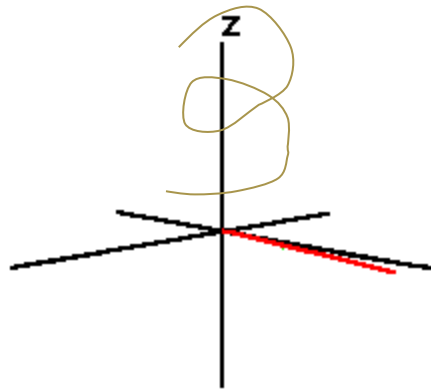


alternating current

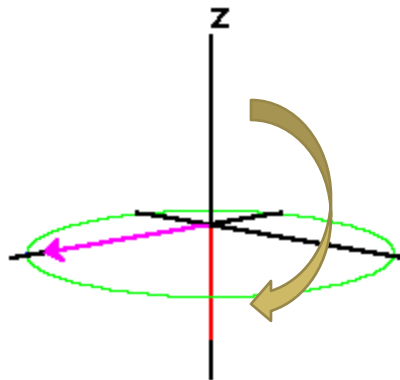
- A 90° pulse is one which rotates the magnetization vector clockwise by 90 degrees about the X' axis. A 90° pulse rotates the equilibrium magnetization down to the Y' axis.



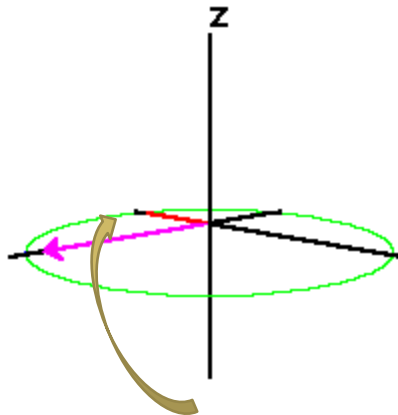
- In the laboratory frame the equilibrium magnetization **spirals down** around the Z axis to the XY plane. You can see why the rotating frame of reference is helpful in describing the behavior of magnetization in response to a pulsed magnetic field.



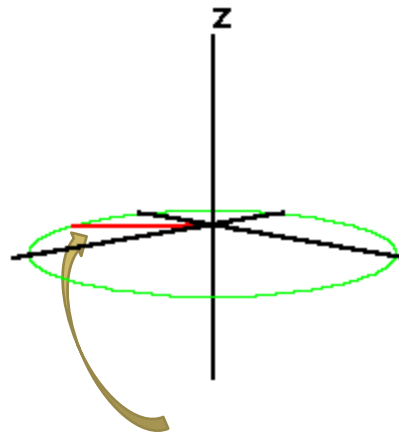
- A 180° pulse will rotate the magnetization vector by 180 degrees. A 180° pulse rotates the equilibrium magnetization down to along the $-Z$ axis.



- The net magnetization at any orientation will behave according to the rotation equation. For example, a net magnetization vector along the Y' axis will end up along the $-Y'$ axis when acted upon by a 180° pulse of B_1 along the X' axis.



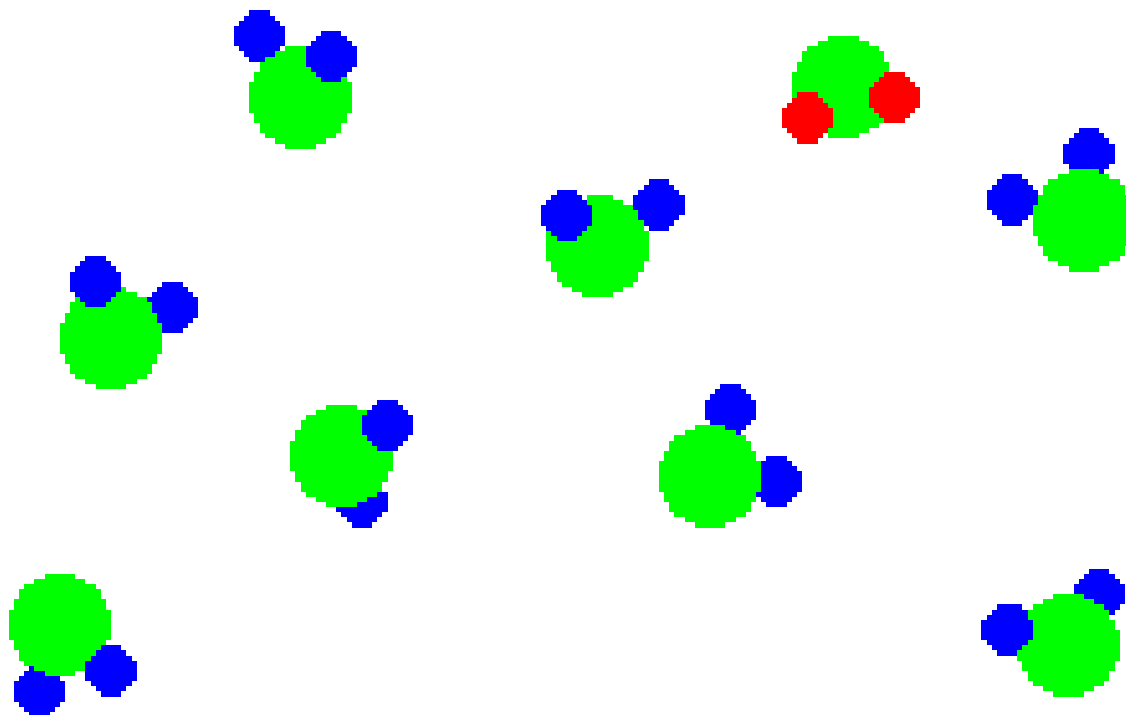
- A net magnetization vector between X' and Y' will end up between X' and $-Y'$ after the application of a 180° pulse of B_1 applied along the X' axis.



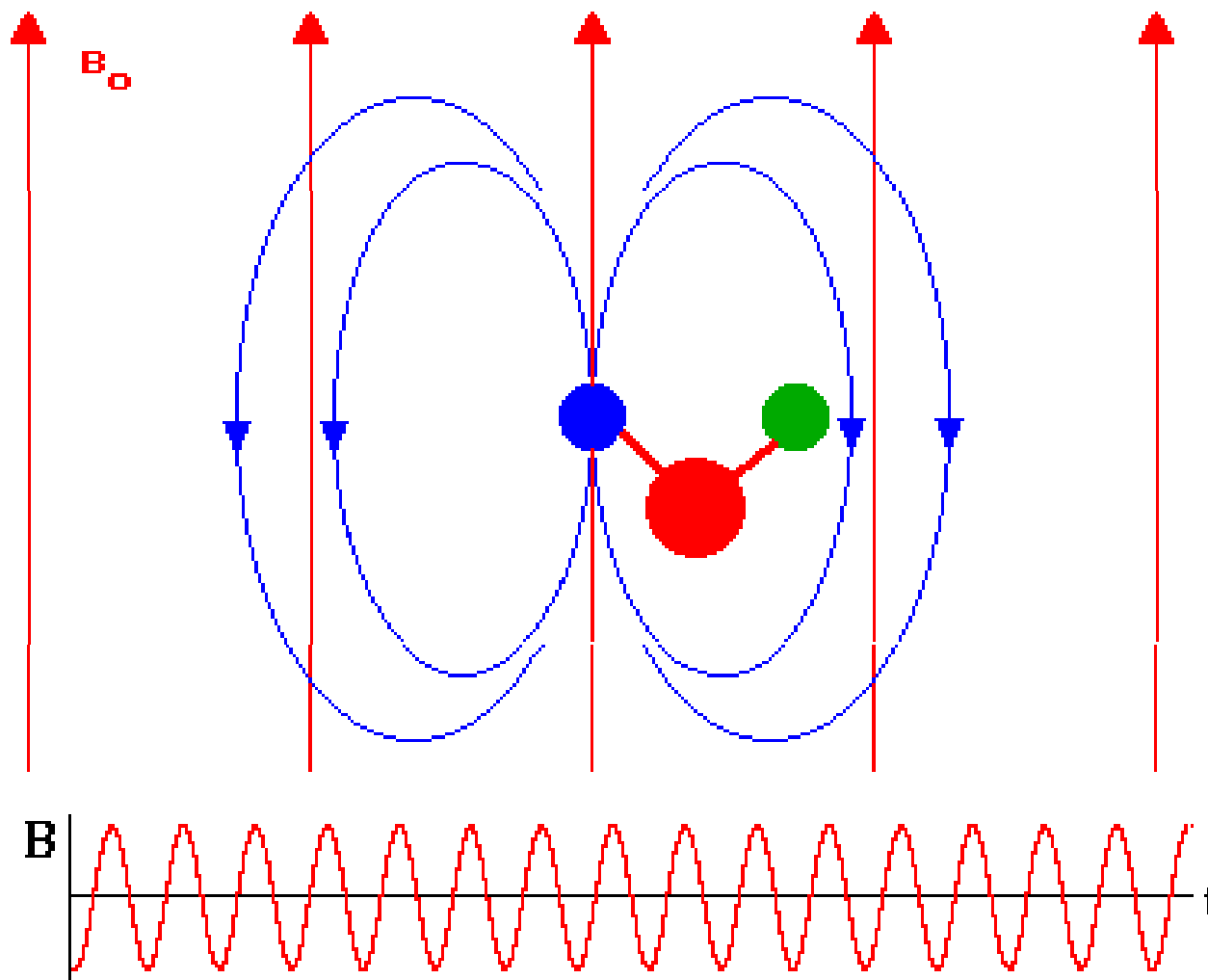
- The spins respond to this pulse in such a way as to cause the net magnetization vector to rotate about the direction of the applied B_1 field. The rotation angle depends on the length of time the field is on, τ , and its magnitude B_1 .

$$\theta = 2\pi \gamma \tau B_1$$

Spin Relaxation



Motions in solution which result in time varying magnetic fields cause spin relaxation

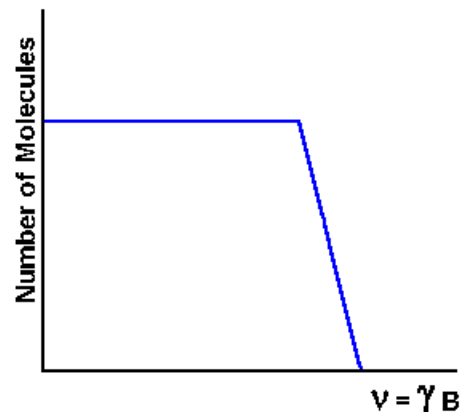


Time varying fields at the Larmor frequency cause transitions between the spin states and hence a change in M_z . This screen depicts the field at the green hydrogen on the water molecule as it rotates about the external field B_0 and a magnetic field from the blue hydrogen. ___ Note that the field experienced at the green hydrogen is sinusoidal.

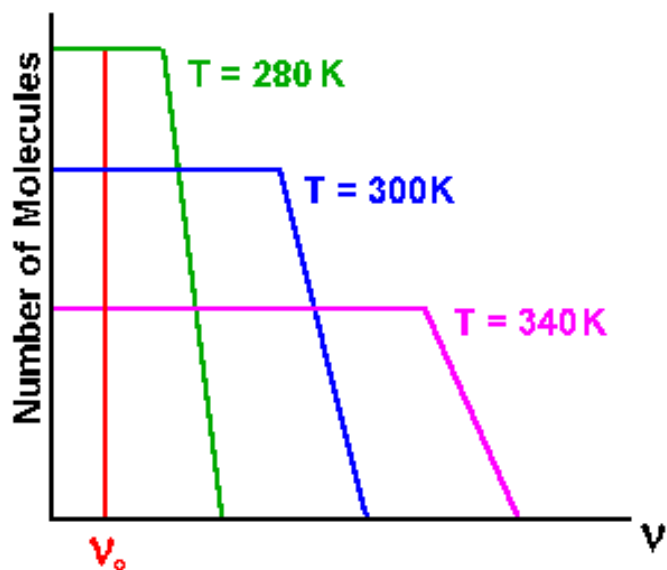
NMR

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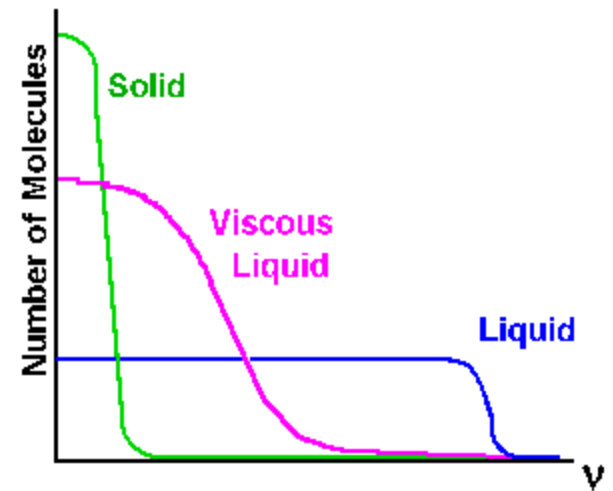
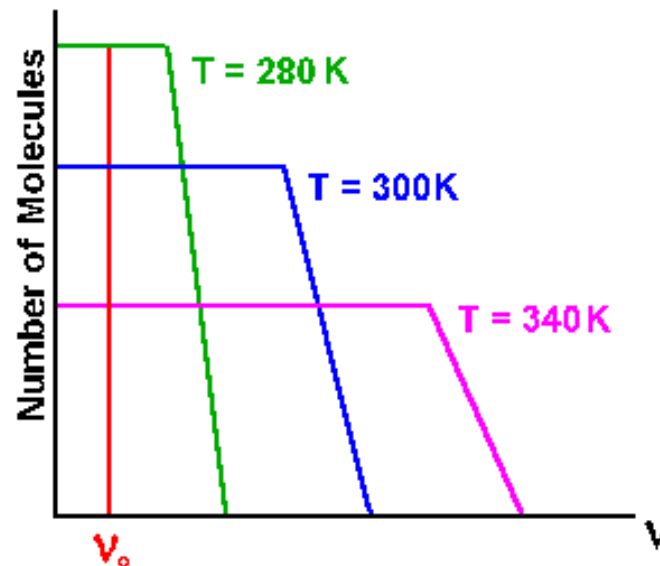
- There is a distribution of rotation frequencies in a sample of molecules. Only frequencies at the Larmor frequency affect T_1 . Since the Larmor frequency is proportional to B_0 , T_1 will therefore vary as a function of magnetic field strength. In general, T_1 is inversely proportional to the density of molecular motions at the Larmor frequency.



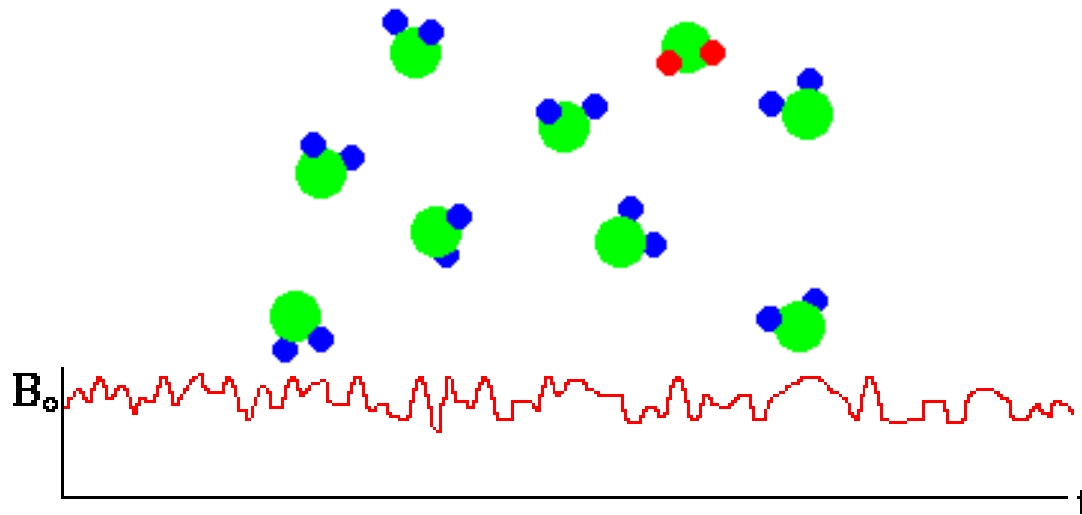
- The rotation frequency distribution depends on the temperature and viscosity of the solution. Therefore T_1 will vary as a function of temperature



- At the Larmor frequency indicated by ν_o , $T_1(280\text{ K}) < T_1(340\text{ K})$. The temperature of the human body does not vary by enough to cause a significant influence on T_1 . The viscosity does however vary significantly from tissue to tissue and influences T_1 as is seen in the following molecular motion plot

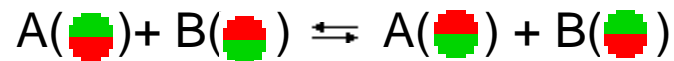


- Fluctuating fields which perturb the energy levels of the spin states cause the transverse magnetization to dephase. This can be seen by examining the plot of B_o experienced by the red hydrogens on the following water molecule. The number of molecular motions less than and equal to the Larmor frequency is inversely proportional to T_2 .



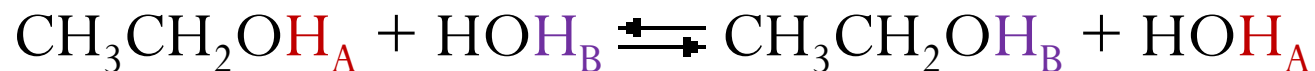
Spin Exchange

- Spin exchange is the exchange of spin state between two spins



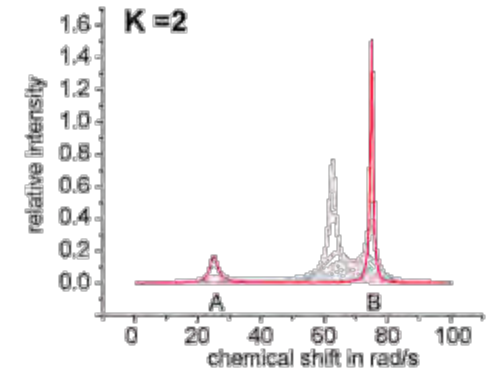
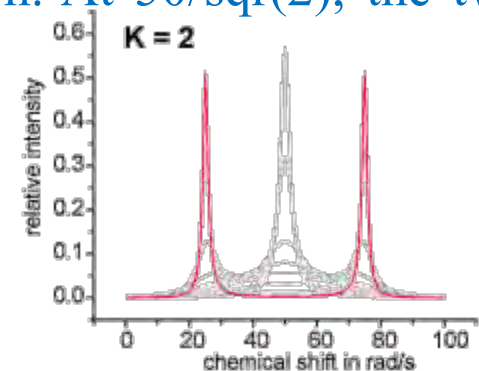
- Spin exchange will not affect T_1 but will affect T_2 . T_1 is not affected because the distribution of spins between the upper and lower states is not changed. T_2 will be affected because phase coherence of the transverse magnetization is lost during exchange.

- chemical exchange is a form of exchange
- In chemical exchange, the A and B nuclei are from different molecules. Consider the chemical exchange between water and ethanol.



Exchange

- When a nucleus experiences two or more states with different chemical properties, it is in exchange. The NMR signal(s) of the nucleus depend on the exchange rate (k), relative to the difference in the chemical shifts of the states. The animations below shows how the spectrum changes with k for a two state exchange with a chemical shift difference of 50 rad s^{-1} . The natural line width was neglected in this animation. At $50/\sqrt{2}$, the two peaks show coalescence.
- The states A and B are populated 1:1
- The states A and B are populated 1:3



NMR

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Bloch Equations

- The Bloch equations are a set of coupled differential equations which can be used to describe the behavior of a magnetization vector under any conditions. When properly integrated, the Bloch equations will yield the X', Y', and Z components of magnetization as a function of time.

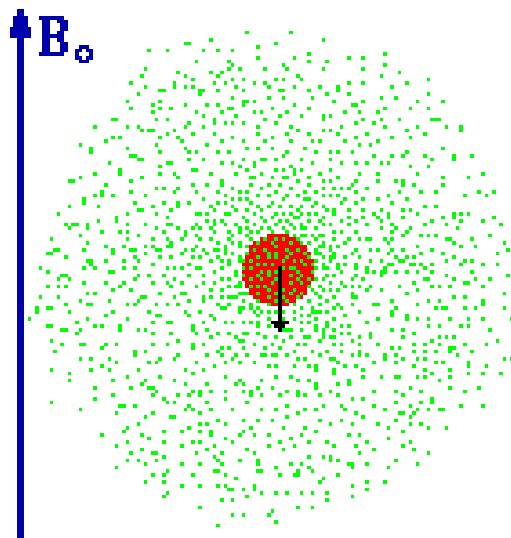
$$\frac{dM_{x'}}{dt} = (\omega_o - \omega)M_{y'} - \frac{M_{x'}}{T_2}$$

$$\frac{dM_{y'}}{dt} = -(\omega_o - \omega)M_{x'} + 2\pi\gamma B_1 M_z - \frac{M_{y'}}{T_2}$$

$$\frac{dM_z}{dt} = -2\pi\gamma B_1 M_{y'} - \frac{(M_z - M_{z_o})}{T_1}$$

Chemical Shift

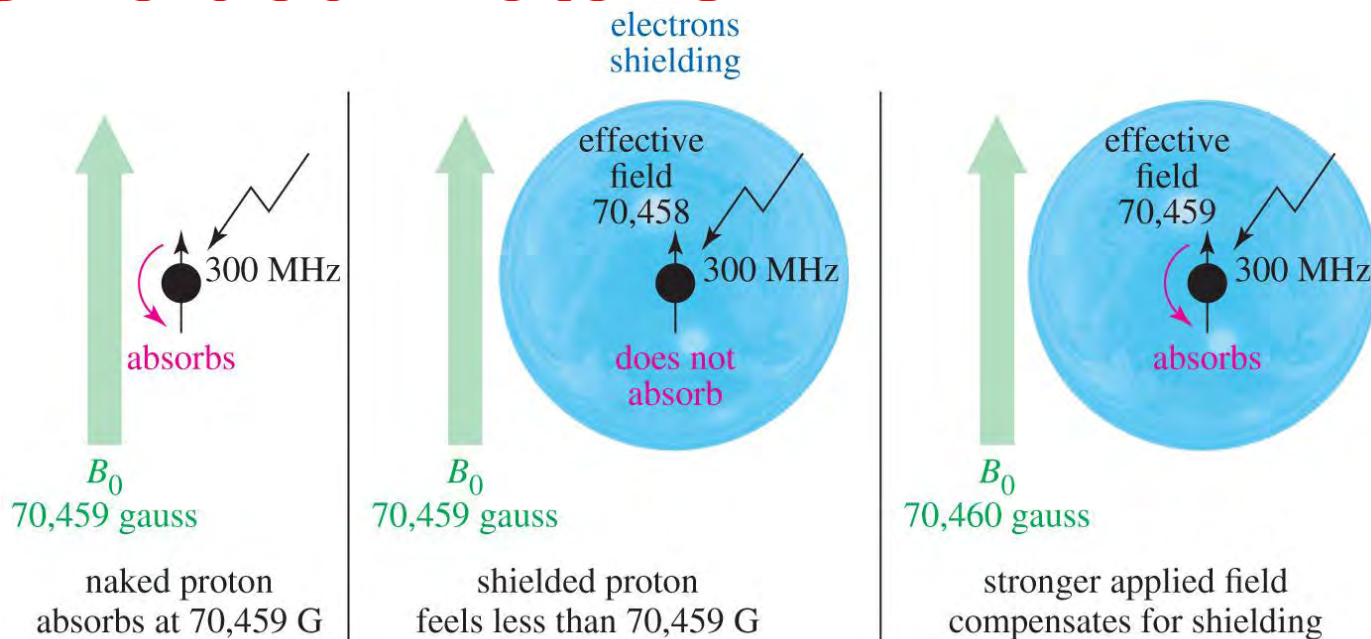
- When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field.



- The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction .

$$B = B_0 (1 - \sigma)$$

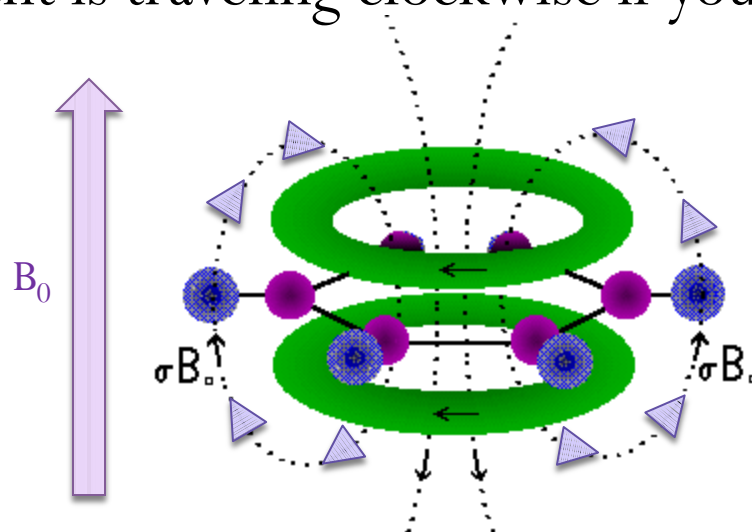
Shielded Protons



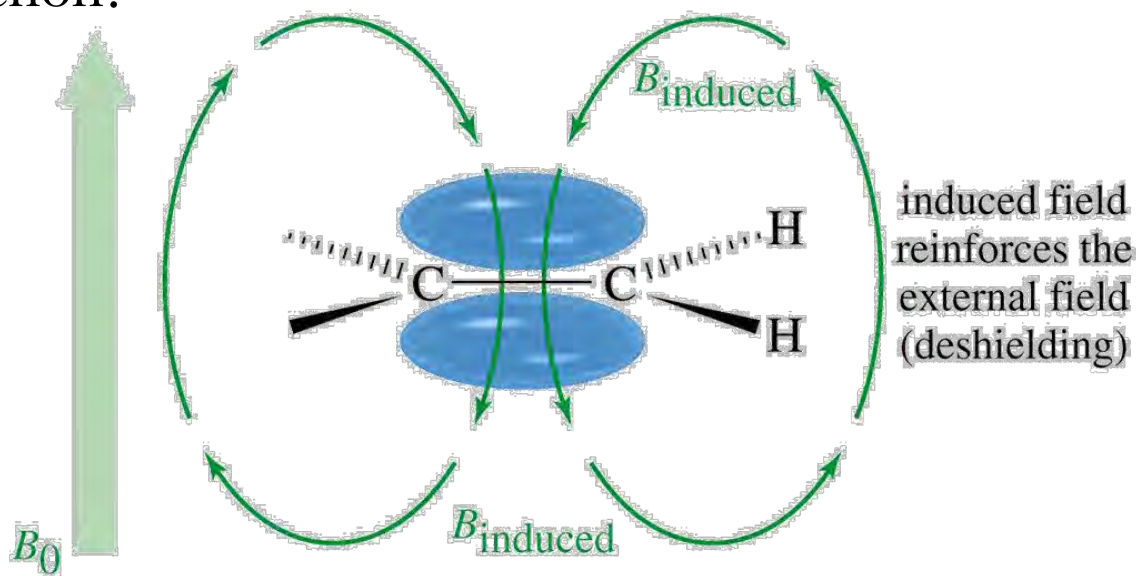
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- A naked proton will absorb at 70,459 gauss.
- A shielded proton will not absorb at 70,459 gauss so the magnetic field must be increased slightly to achieve resonance.

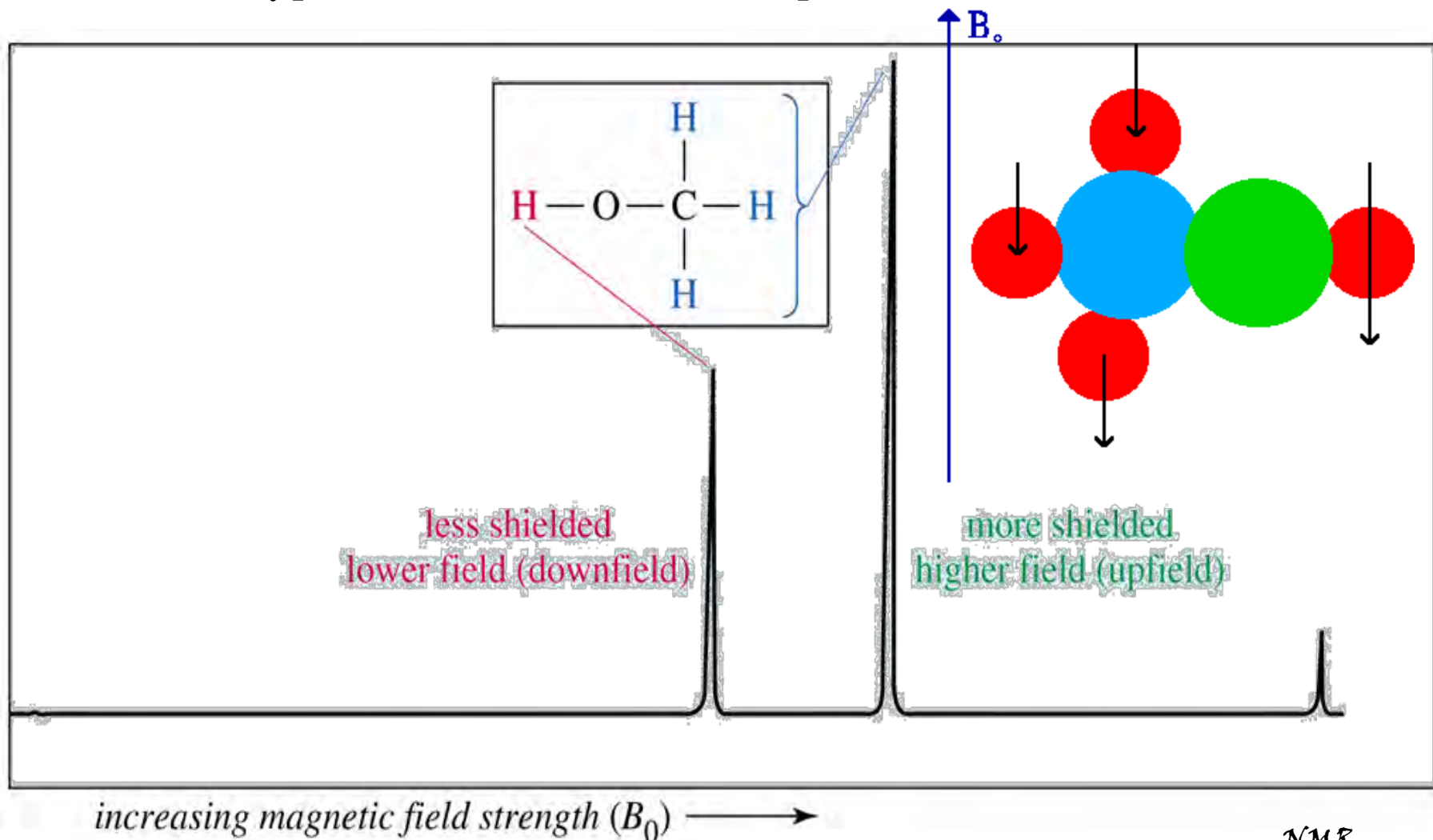
- In some cases, such as the benzene molecule, the circulation of the electrons in the aromatic orbitals creates a magnetic field at the hydrogen nuclei which enhances the B_0 field. This phenomenon is called deshielding. In this example, the B_0 field is applied perpendicular to the plane of the molecule. The ring current is traveling clockwise if you look down at the plane.



- The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon.



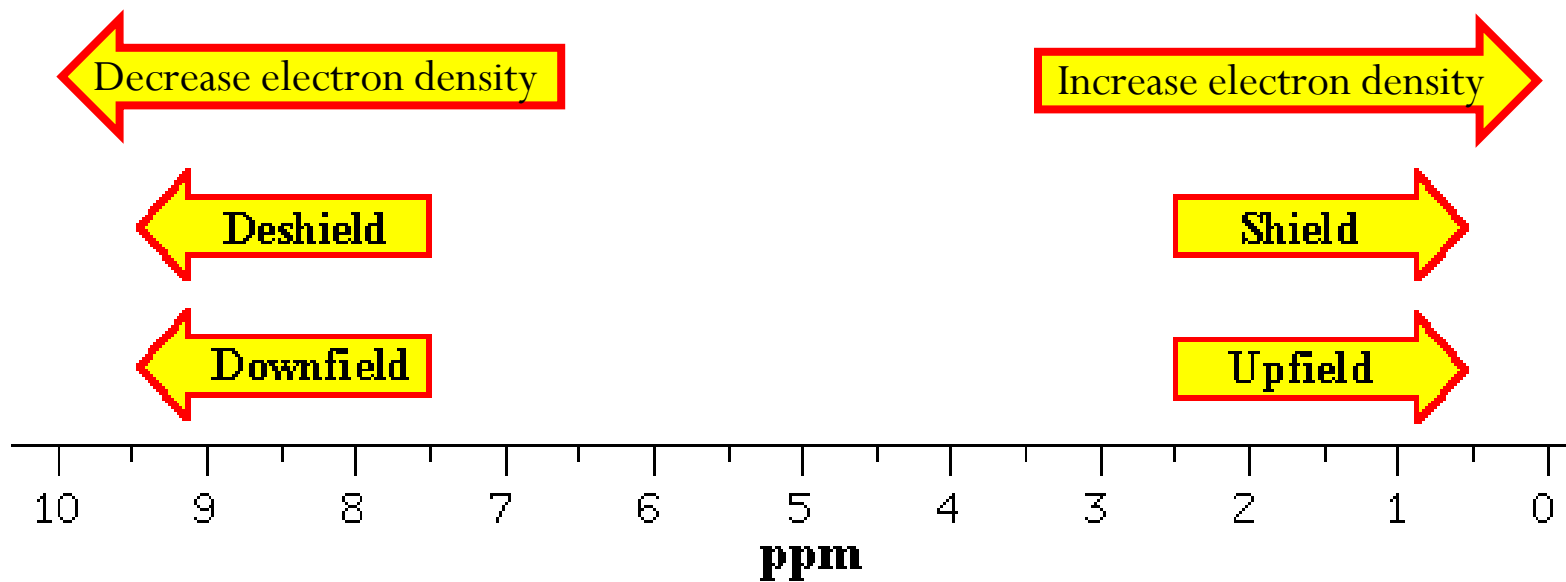
- Consider the methanol molecule. The resonance frequency of two types of nuclei in this example differ.



- The chemical shift of a nucleus is the difference between the **resonance frequency** of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol delta, .

$$\delta = (\nu - \nu_{\text{REF}}) \times 10^6 / \nu_{\text{REF}}$$

$$\text{chemical shift (ppm)} = \frac{\text{shift downfield from TMS (Hz)}}{\text{total spectrometer frequency (MHz)}}$$



- In NMR spectroscopy, this standard is often tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, abbreviated TMS. The chemical shift is a very precise metric of the chemical environment around a nucleus. For example, the hydrogen chemical shift of a CH_2 hydrogen next to a Cl will be different than that of a CH_3 next to the same Cl. It is therefore difficult to give a detailed list of chemical shifts in a limited space. The animation window displays a chart of selected hydrogen chemical shifts of pure liquids and some gasses.

