NMR SPECTROSCOPY

Spin States

- Nuclei with an odd mass, an odd number of protons, or both, are said to have spin angular momentum
- The number of allowed spin states is quantized, and is determined by its spin quantum number, I
- There are 2I+1 allowed spin states
- See table 3.1

Nuclei with I = 0 have only one spin state and are NMR inactive. These include ^{12}C and ^{16}O, two of the most common nuclei in organic compounds.

A spinning nucleus with a spin quantum number of ½ has 2 possible spin states.

$$2I+1 = 2\,(1/2) + 1 = 2$$

The Most Interesting Elements (to us) All Have 2 Allowed Spin States

These are

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

Deuterium ^{2}H is spin active with I = 1!

2 (1) + 1 = 3 spin states for deuterium

The spinning of the nuclei causes them to behave like magnets.

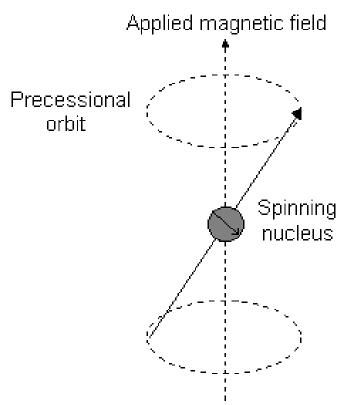
These nuclear magnets are influenced by other magnetic fields. These other magnetic fields may be externally applied or they can be generated by other nearby nuclei or electrons in the molecule.

Externally applied magnetic fields may result from the magnet that the sample is placed in or from irradiation by radio frequency light.

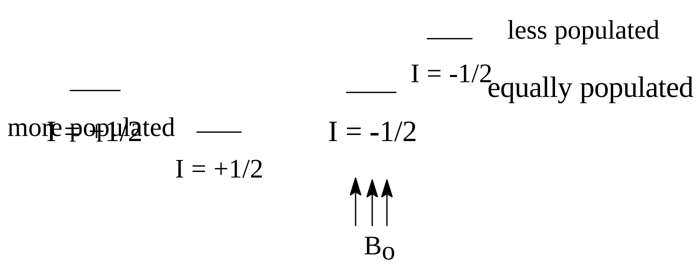
In an Applied Magnetic Field

- Nuclei with 2 allowed spin states can align either <u>with</u> or <u>against</u> the field, with slight excess of nuclei aligned with the field

The nuclei precess about an axis parallel to the applied magnetic field, with a frequency called the Larmor Frequency (ω)

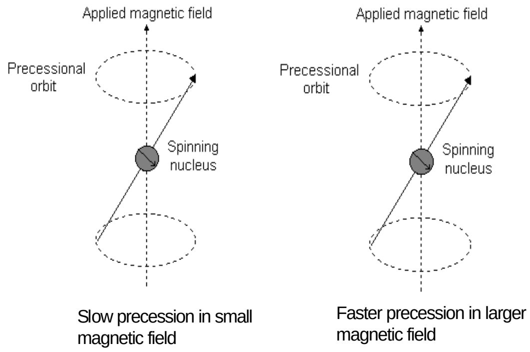


In an applied magnetic field the spin states have different energies and therefore different populations.

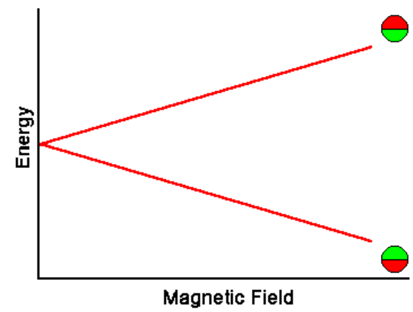


Transitions may occur between these energy states which allows NMR signals to be observed. The greater the difference in population, the stronger the NMR signal.

Larmor Frequency is Proportional to the Applied Magnetic Field

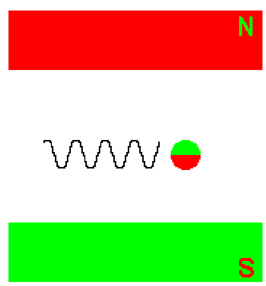


The difference in energy between the 2 spin states is proportional to the Larmor frequency



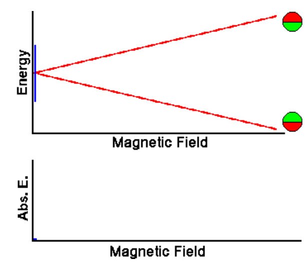
Rf Energy Can Be Absorbed

- Precessing nuclei generates an oscillating electric field of the same frequency
- Rf energy with the same frequency as the Larmor frequency can be applied to the system and absorbed by the nuclei



Old CW Instruments

- We held the Rf energy constant and varied the strength of the magnetic field. When they matched, energy was absorbed and that change was observed by the instrument.



How does our NMR observe the signals?

1) The sample tube is placed in a strong magnetic field to produce the primary splitting of the energy levels and create the necessary population imbalance.

2) The sample is irradiated with a range of radio frequency light to transfer nuclei from the lower to the higher energy state.

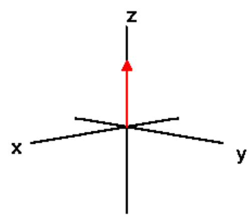
3) The oscillating magnetic fields produced by the nuclei are observed using the same coil that was used for the irradiation. A complex, decaying signal is observed that contains all of the information about the nuclei. This is called the free induction decay (FID)

4) A Fourier transform is performed on the FID to produce an NMR spectrum with each signal represented by a peak at its relative Larmar frequency which is the frequency with which it wobbles as it spins.

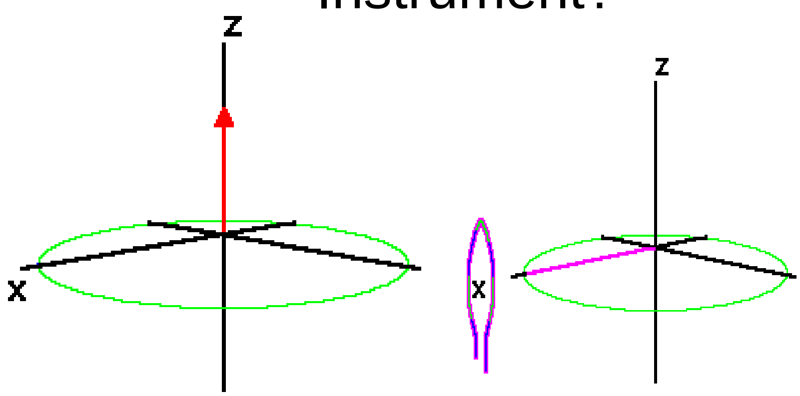
The nuclear spins can also be manipulated to produce many other types of spectra that provide a variety of information about the molecules

This can be pictured with vectors

- There are an assembly of nuclei, almost 50% in each spin state. There is a slight excess (1,000,048 vs 1,000,000 for protons in a 300 MHz instrument) in the lower energy state that causes a small net magnetization in the z direction.



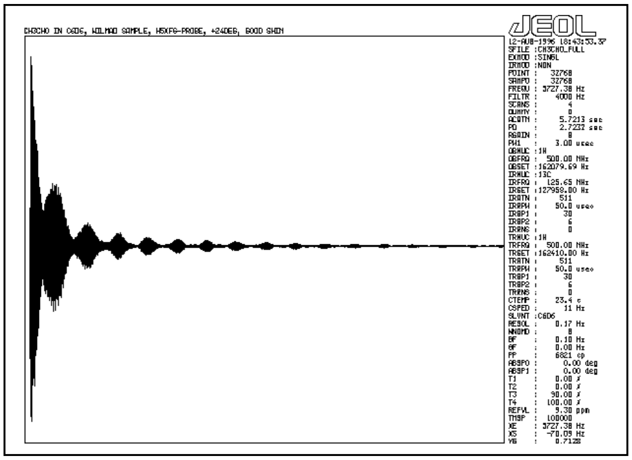
How Does this Happen in the Instrument?

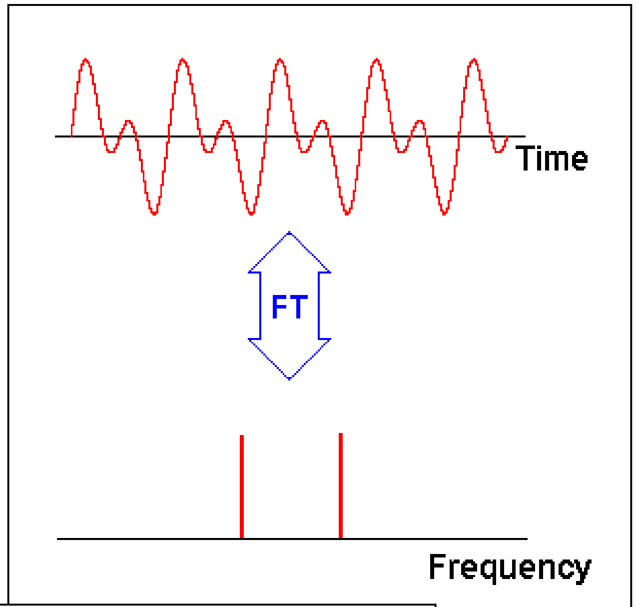


Red arrow represents net magnetization (there is an excess in the low spin state. The applied Rf energy causes the net magnetization for all types of the nuclei to tip to the x-y plane (90 degree pulse). It should be noted that all nuclei of a given type are in synch with one another.

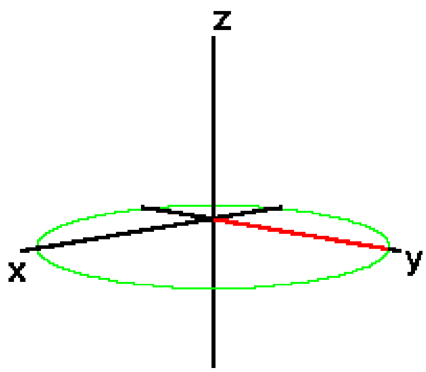
Nuclei relax back to their original state, emitting electromagnetic radiation at their original Larmor frequencies

The data we get can be complex: it is a superimposed combination of all the frequencies (Note: this is the *difference* between the applied frequency and the Larmor frequencies of the nuclei.





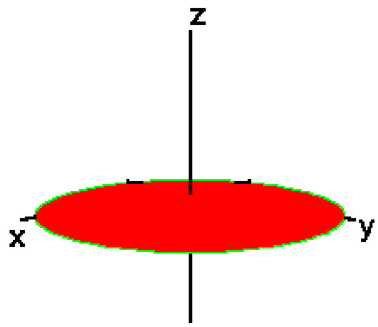
T1 Relaxation



T_1 relaxation is sometimes called spin-lattice relaxation.

In this type of relaxation the energy lost as the nucleus returns to the lower energy state is transferred to the molecule in the form of heat. This means that the total number of nuclei in the excited state decreases.

T2 Relaxation



T_2 relaxation is commonly refered as spin-spin relaxation.

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.