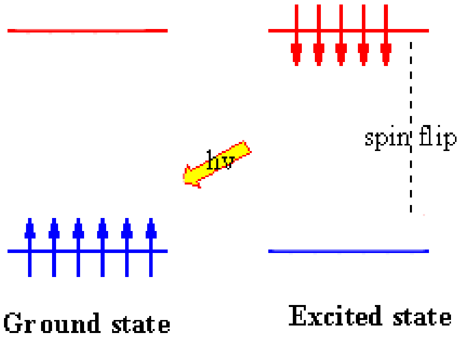
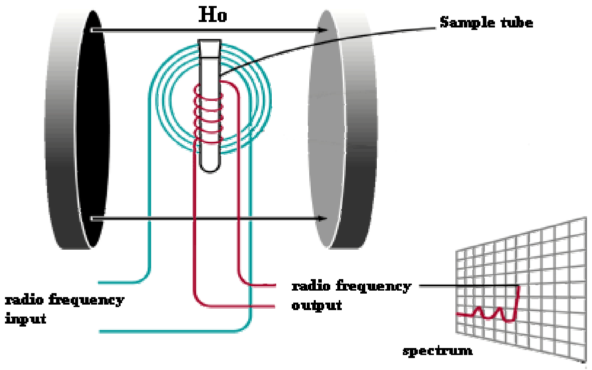
Lab 6: NMR Spectroscopy - Chemical Environments of Nuclei (^{1}H, ^{13}C) in Organic Molecule

Nuclei with an odd mass or odd atomic number have "nuclear spin" (in a similar fashion to the spin of an electron). ^{1}H and ^{13}C (but **not** ^{12}C) have a nuclear spin number equal to 1/2 just like an electron. The alignment of these magnetic poles in strong magnetic field create energy levels that are sufficiently different that NMR experiments can be sensitive enough for identifying the environments of different ^{1}H and ^{13}C nuclei in organic molecule. The NMR behavior of ^{1}H and ^{13}C nuclei has been exploited by organic chemist since they provide valuable information that can be used to deduce the structure of organic compounds.

Since a nucleus is a charged particle in motion, it will develop a magnetic field. In the absence of a magnetic field, these are randomly oriented but when a field is applied they line up parallel to the applied field, either spin aligned or spin opposed. The more highly populated state is the lower energy spin state spin aligned situation.





Sample Preparation

The NMR tube is 20.5 cm (8 inches) long. The sample volume fills the tube to a depth of 4.5 cm. The sample solution is clear and a single phase. For proton NMR spectra, samples should be prepared as follows:

A) weigh 5- 10 mg into an appropriate container (NOT the NMR tube!);
B) add 0.7 - 1.0 ml of <u>deutero</u>chloroform ($CDCl_3$) and stir or shake to dissolve any solids;
C) filter to remove any undissolved solids or alternatively, cleanly pipette off the clear (NO SOLIDS !) supernatant liquid;
D) D) pipette the solution into a 8 inch undamaged NMR tube; and
E) Label the NMR tube containing the sample and store in the proper sample rack location.

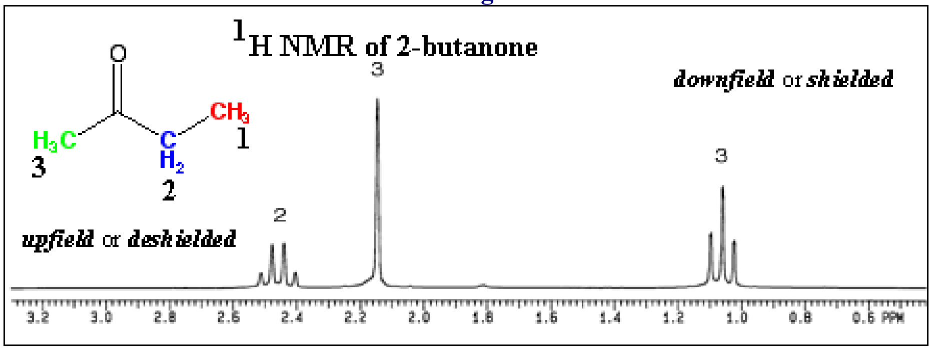
Chemical Shift (δ)

An NMR spectrum is a plot of the *radio frequency applied* against *absorption*.
A signal in the spectrum is referred to as a *resonance*.
The frequency of a signal is known as its *chemical shift*.
The **chemical shift** in absolute terms is defined by the frequency of the resonance expressed with reference to a standard compound which is *defined* to be at 0 ppm. The scale is made more manageable by expressing it in parts per million (**ppm**) and is **indepedent** of the spectrometer frequency.

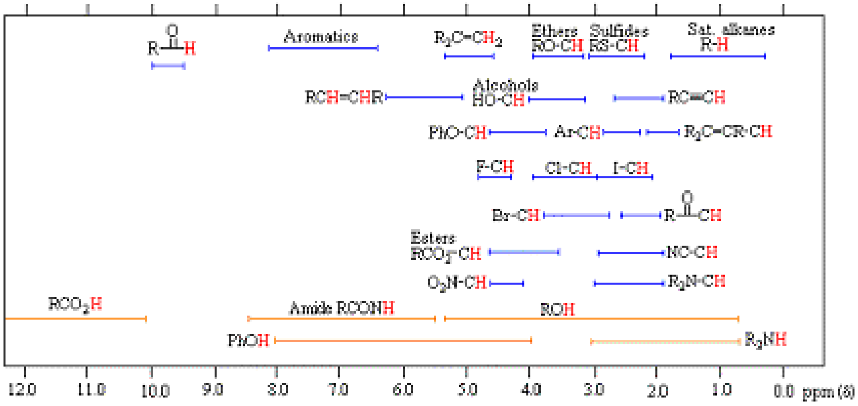
$$\text{Chemical shift, } \delta = \frac{\text{frequency of signal} - \text{frequency of reference}}{\text{spectrometer frequency}} \times 10^{6}$$

It is often convienient to describe the relative positions of the resonances in an NMR spectrum. For example, a peak at a chemical shift, δ, of 10 ppm is said to be ***downfield*** or ***shielded*** with respect to a peak at 5 ppm, or if you prefer, the peak at 5 ppm is ***upfield*** or ***deshielded*** with respect to the peak at 10 ppm.

^{1}H NMR **Eg. 2-butanone**

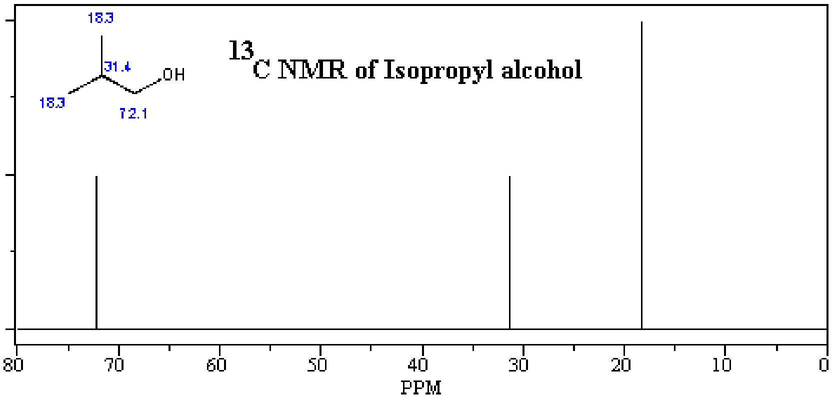


Proton Chemical Shift Ranges*

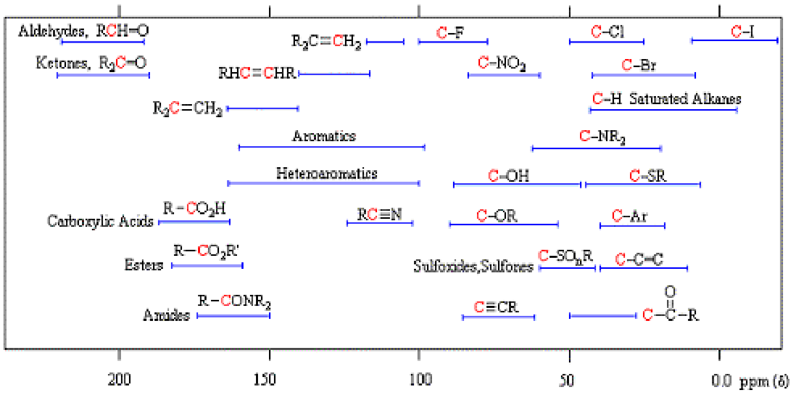


* For samples in $CDCl_3$ solution. The δ scale is relative to TMS at δ = 0.

Decoupled ^{13}C NMR **Eg. Isopropyl Alcohol**



^{13}C Chemical Shift Ranges*



* For samples in $CDCl_3$ solution. The δ scale is relative to TMS at δ=0.