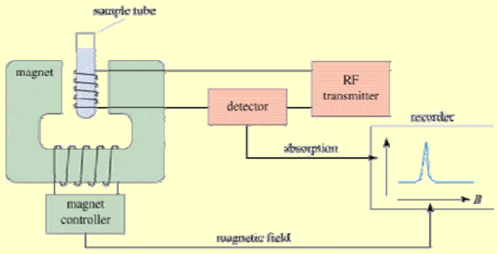
The NMR Spectrometer



The NMR Spectrometer

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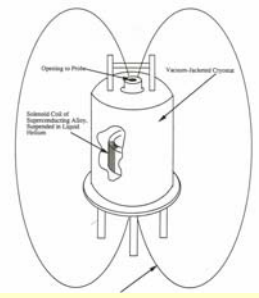
Sample Tube

Modern Superconducting NMR Magnets

Modern Superconducting NMR Magnets

- Older Magnets (1970s) had opposed pole faces. High voltages and currents demanded heroic temperature control. Field ran side to side through sample
- Supercon magnets have much larger fields, better homogeneity. Field runs up the axis of the sample.
- New technology! Built in auxilliary magnet with reversed current acts as "active" shield, partly eliminating the projection into the room.



Note: Special superconducting alloys Niobium-Tantalum. Search goes on for higher temperature superconductors.

Lines of force project several feet into the room. They concentrate at the top and bottom. Magnets can grab iron objects and accelerate them.

Modern Superconducting NMR Magnets

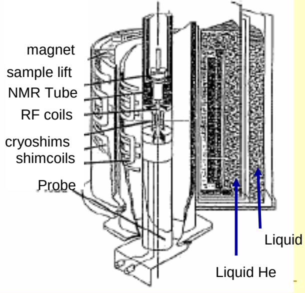
a) solenoid wound from superconducting niobium/tin or niobium/titanium wire

b) kept at liquid helium temperature (4K), outer liquid N_2 dewar

   1) near zero resistance → minimal current lose → magnet stays at field for years without external power source

Superconducting solenoid
Use up to 190 miles of wire!

Cross-section of magnet



MRI Magnet

The Interactions of NMR

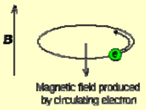
- Zeeman interaction (basic NMR phenomenon)
- Shifts (interactions that change NMR frequency)
  - Chemical shift
  - others (e.g. Knight shift, paramagnetic shifts)
- Couplings (interactions that split NMR signals)
  - *J* coupling
  - Dipolar coupling
  - Quadrupole coupling

Peak Position in an NMR Spectrum

- Nuclei in different chemical environments in a molecule will resonate at slightly different frequencies
- The position of the signals in the spectrum is called the “chemical shift”
- There are two reasons for differences in the magnetic environment for a proton
  - The magnetic field generated by electrons circulating around the nucleus giving the signal
  - Local magnetic fields generated by electrons elsewhere in the molecule

Magnetic Shielding

- If all protons absorbed the same amount of energy in a given magnetic field, not much information could be obtained.
- But protons are surrounded by electrons that shield them from the external field.
- Circulating electrons create an induced magnetic field that opposes the external magnetic field.



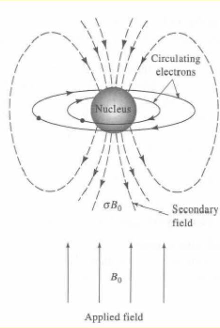
Magnetic Shielding

- Small local magnetic fields (B_{loc}) are generated by electrons as they circulate nuclei.
  - Current in a circular coil generates a magnetic field
- These local magnetic fields can either oppose or augment the external magnetic field
  - Typically oppose external magnetic field
  - Nuclei “see” an effective magnetic field (B_{eff}) **smaller** then the external field
  - σ – magnetic shielding or screening constant
    - Depends on electron density
    - Depends on the structure of the compound

$$B_{eff} = B_o - B_{loc} \quad --- \quad B_{eff} = B_o(1 - \sigma)$$

Magnetic Shielding

- Under the influence of the magnetic field, electrons bonding the proton tend to precess around the nucleus in a plane perpendicular to the magnetic field. This develops a secondary field that opposes the primary field.
- So nucleus experiences resultant field that is smaller (*I.e.,* shielded from full effect of primary field). As a consequence, external field must be increased to cause nuclear resonance.
- The frequency of the precession and the magnitude of the secondary field is a direct function of the external field.

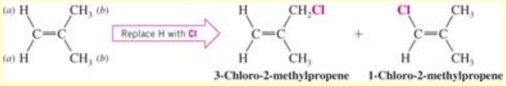


Shielding and Deshielding of Protons

- Protons in an external magnetic field absorb at different frequencies depending on the electron density around that proton
- High electron density around a nucleus *shields* the nucleus from the external magnetic field
  - Shielding causes absorption of energy at higher frequencies (more energy is required for this nucleus to flip between spin states) - the signals are upfield in the NMR spectrum
- Lower electron density around a nucleus *deshields* the nucleus from the external magnetic field
  - Deshielding causes absorption of energy at lower frequencies (less energy is required for this nucleus to flip between spin states) - the signals are downfield in the NMR spectrum

Equivalent and Nonequivalent Protons

- To predict the number of signals to expect in an NMR spectrum it is necessary to determine how many sets of protons are in unique environments
- *Chemically equivalent protons* are in the same environment and will produce only one signal
- Homotopic Hydrogens
  - Hydrogens are chemically equivalent or homotopic if replacing each one in turn by the same group would lead to an identical compound

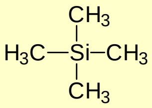


Chemical Shift and Resonance Frequency

- **Chemical shift** is defined as the difference in the resonance position of a signal with respect to a reference signal.
  - Ratio of shift downfield from TMS (Hz) to total spectrometer frequency (Hz).
  - Measured in parts per million.
  - It is independent of applied magnetic field strength. Same value for 60, 100, or 300 MHz machine.
  - Called the delta scale.
- The **Resonance Frequency** is defined as the frequency difference between the reference signal and a proton signal.

Tetramethylsilane

- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

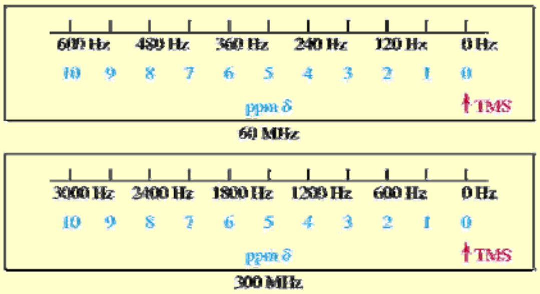


$$\mathrm{H_3C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}CH_3}$$

Chemical Shift

Delta Scale

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



Chemical Shift

- The δ scale for chemical shifts is independent of the magnetic field strength of the instrument (whereas the absolute frequency depends on field strength)

$$\delta = \frac{(\text{observed shift from TMS in hertz}) \times 10^6}{(\text{operating frequency of the instrument in hertz})}$$

- Thus, the chemical shift in δ units for protons on benzene is the same whether a 60 MHz or 300 MHz instrument is used

$$\delta = \frac{2181 \text{ Hz} \times 10^6}{300 \times 10^6 \text{ Hz}} = 7.27$$

$$\delta = \frac{436 \text{ Hz} \times 10^6}{60 \times 10^6 \text{ Hz}} = 7.27$$