Nuclear Magnetic Resonance

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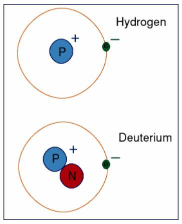
Which element isotopes are NMR active? The Nuclear Spin Quantum Number (I) has to be non-zero.

I = 0	no NMR signals	(i.e.: ^{12}C, ^{16}O)
I = ½	sharp NMR signals	(i.e.: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si)
I > ½	broad NMR signals	(i.e.: ^{2}H, ^{10}B, ^{11}B, ^{14}N, ^{17}O, ^{23}Na, ^{51}V)

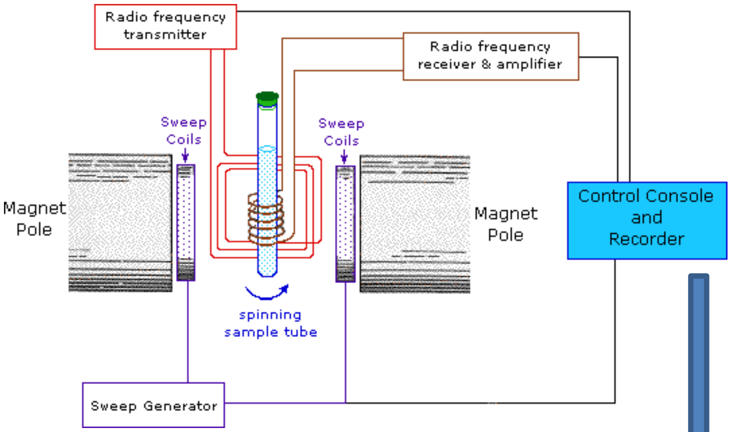


What types of magnets are used for NMR spectroscopy?

Permanent magnets: magnetic field strengths up to 2 Tesla, typically used in benchtop NMRs.
Electromagnets: higher fields, need high & stable electrical power, problematic field stability and uniformity
Superconducting magnets: very homogenous (uniform) magnetic fields up to 25 Tesla, $$$$$
Superconducting magnets are also called "cryomagnets" because of their need for cryogenic liquids (liquid Helium and liquid Nitrogen) to keep the magnet coil in a superconducting state.
Loss of cryogens will lead to a "magnet quench", a loss of the magnetic field, requiring very expensive repairs.

What is the difference between *Continuous Wave NMR* and *Pulsed Fourier Transform NMR*?

►CW NMR:

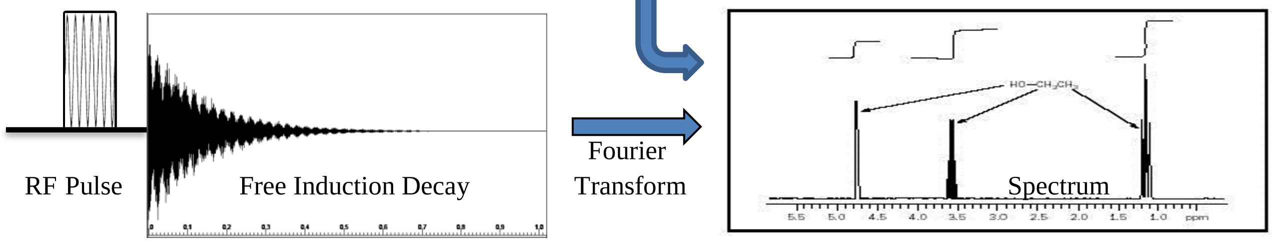


While the sample is continuously irradiated with a constant frequency the magnetic field is slowly increased. When field and frequency match, the resonance condition is met and energy is absorbed by the nucleus. The receiver detects a dip in the RF energy and the recorder prints the spectrum.

This experiment can also be performed by sweeping the frequency at a constant magnetic field.

In both cases a single sweep can take several minutes.

►Pulse-FT NMR:

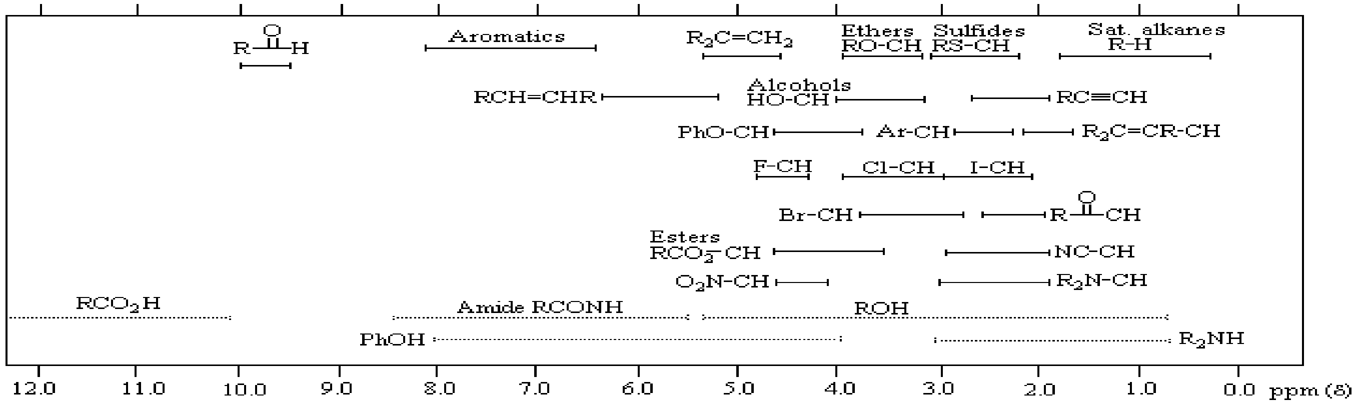


A brief, powerful RF pulse (microseconds) from the transmitter coil will excite all protons at once. The proton spins immediately begin to precess with their own resonance frequencies. This motion will induce a variable current in the receiver coil. The resulting FID can be transformed mathematically into the final NMR spectrum. A single scan only takes a few seconds and can be repeated many times to improve the signal-to-noise ratio.

What is NMR used for?

- Reaction monitoring, identification of reaction byproducts, degradation products, or other impurities.
- Structure determinations, i.e. stereochemistry, protein folding, protein/DNA/drug interactions.
- Solid State NMR: insoluble compounds, crystal structure, materials testing, battery research.

What are typical ^{1}H chemical shift ranges for organic molecules?



Why do we use "chemical shifts" instead of frequencies for NMR peak positions?

Distances between peaks are very small (hertz – kilohertz) compared to the resonance frequencies (megahertz). Further, the absolute resonance frequency (ν_0) of any nucleus depends on the strength of the magnetic field (B_0). Thus, the frequency of an NMR signal is different at different magnetic field values.

To be able to compare NMR spectra recorded on different platforms, regardless of the field strength, peak positions are reported relative to an internal reference compound (usually TMS, tetramethylsilane) and normalized to the reference compound's frequency. A scaling factor of 10^6 is applied. The unit is "ppm".

Chemical shift: $\delta = 10^6 * (\nu - \nu_{ref}) / \nu_{ref}$

<u>Example:</u>
Your forgetful NMR specialist hands you two spectra. Unfortunately he printed them with a frequency scale instead of a ppm scale. Each spectrum only has two signals but he cannot remember whether the two spectra were recorded from the same sample or from different samples.

Spectrum A	Spectrum B
B_0 = 2.35 T	B_0 = 7.05 T
ν_A = 100,000,480 Hz	ν_B = 300,001,440 Hz
ν_{ref} = 100,000,000 Hz	ν_{ref} = 300,000,000 Hz
δ_A = …….. ppm	δ_B = …….. ppm

Q: What are the chemical shifts for signals A and B?
Q: Are compounds A and B identical?
Q: Don't like Tesla? Try converting B_0 into Gauss.

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