

# **NUCLEAR MAGNETIC RESONANCE**

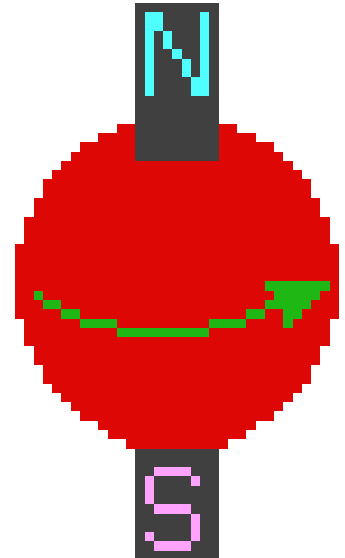
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# What is NMR?

- Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique to observe local magnetic fields around atomic nuclei.
- To be successful in using NMR as an analytical tool, it is necessary to understand the physical principles on which the methods are based.
- The nuclei of many elemental isotopes have a characteristic spin ( $I$ ). Some nuclei have integral spins (e.g.  $I = 1, 2, 3 \dots$ ), some have fractional spins (e.g.  $I = 1/2, 3/2, 5/2 \dots$ ), and a few have no spin,  $I = 0$  (e.g.  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{32}\text{S}$ , ....).
- Isotopes of particular interest and use to organic chemists are  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ , all of which have  $I = 1/2$ .

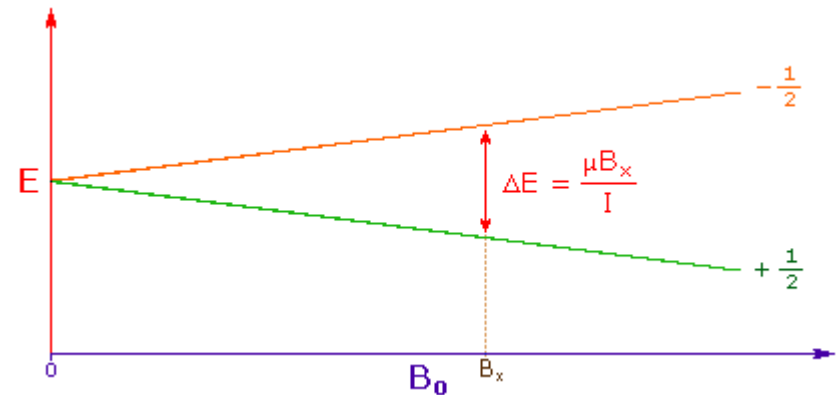
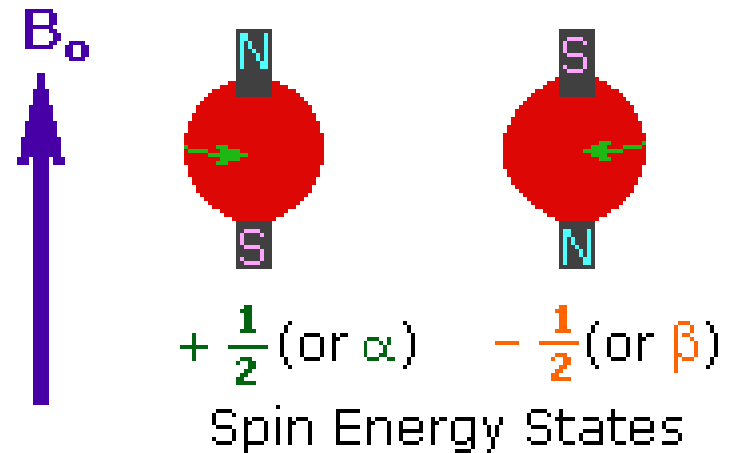
# Principle

1. A spinning charge generates a magnetic field.
  - The resulting spin-magnet has a magnetic moment ( $\mu$ ) proportional to the spin.
2. In the absence of an external magnetic field the direction of the spin of the nuclei will be randomly oriented.
  - However, when a sample of these nuclei is placed in an external magnetic field ( $B_0$ ), the nuclear spins will adopt specific orientations much as a compass needle responds to the Earth's magnetic field and aligns with it.
  - Two possible orientations are possible, with the external field (*i.e.* parallel to and in the same direction as the external field) or against the field (*i.e.* antiparallel to the external field).



# ... Principle

- If the ordered nuclei are now subjected to EM radiation of the proper frequency the nuclei aligned with the field will absorb energy and "spin-flip" to align themselves against the field, a higher energy state.
- When this spin-flip occurs the nuclei are said to be in "resonance" with the field, hence the name for the technique, **Nuclear Magnetic Resonance** or NMR.
- Note that the arrow representing the external field points North.
- 3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small.
- The two spin states have the same energy when the external field is zero, but diverge as the field increases.
- At a field equal to  $B_x$  a formula for the energy difference is given (remember  $I = 1/2$  and  $\mu$  is the magnetic moment of the nucleus in the field).



# ... Principle

- The reason NMR can differentiate between different elements and isotopes is due to the fact that each specific nuclide will only absorb at a very specific frequency.
- This specificity means that NMR can generally detect one isotope at a time, and this results in different types of NMR: such as  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{31}\text{P}$  NMR, to name only a few.
- The subsequent absorbed frequency of any type of nuclei is not always constant, since electrons surrounding a nucleus can result in an effect called nuclear shielding, where the magnetic field at the nucleus is changed (usually lowered) because of the surrounding electron environment.
- This differentiation of a particular nucleus based upon its electronic (chemical) environment allows NMR be used to identify structure.
- Since nuclei of the same type in different electron environments will be more or less shielded than another, the difference in their environment (as observed by a difference in the surrounding magnetic field) is defined as the **chemical shift**.

# Chemical Shift

- This is recorded as the chemical shift ( $\delta$ ) and is measured relative to an internal standard, which in most cases is tetramethylsilane (TMS;  $(\text{H}_3\text{C})_4\text{Si}$ ) because it contains 12 identical protons.
- The chemical shift arises from the applied field inducing secondary fields of about 0.15–0.2 mT at the proton by interacting with the adjacent bonding electrons.
- If the induced field opposes the applied field, the latter will have to be at a slightly higher value for resonance to occur. The nucleus is said to be shielded, the magnitude of the shielding being proportional to the electron-withdrawing power of proximal substituents.
- Alternatively, if the induced and applied fields are aligned, the latter is required to be at a lower value for resonance. The nucleus is then said to be deshielded.
- Usually, deuterated solvents such as  $\text{CDCl}_3$  are used for sample preparation of organic compounds. For peptides and proteins  $\text{D}_2\text{O}$  is the solvent of choice.

# $^{13}\text{C}$ - NMR

- Due to the low abundance of the  $^{13}\text{C}$  isotope, the chance of finding two such species next to each other in a molecule is very small.
- As a consequence,  $^{13}\text{C}$ – $^{13}\text{C}$  couplings (homonuclear couplings) do not arise. While  $^1\text{H}$ – $^{13}\text{C}$  interactions (heteronuclear coupling) are possible, one usually records decoupled  $^{13}\text{C}$  spectra where all bands represent carbon only.
- $^{13}\text{C}$  spectra are thus much simpler and cleaner when compared to  $^1\text{H}$  spectra.
- The main disadvantage though is the fact that multiplicities in these spectra cannot be observed, i.e. it cannot be decided whether a particular  $^{13}\text{C}$  is associated with a methyl ( $\text{H}_3\text{C}$ ), a methylene ( $\text{H}_2\text{C}$ ) or a methyne ( $\text{HC}$ ) group.

# Working of Nuclear Magnetic Resonance (NMR) Spectroscopy

- The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio waves into nuclear magnetic resonance, which is detected with sensitive radio receivers.
- The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups.
- As the fields are unique or highly characteristic to individual compounds, NMR spectroscopy is the definitive method to identify monomolecular organic compounds.
- Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.
- The most common types of NMR are proton and carbon-13 NMR spectroscopy, but it is applicable to any kind of sample that contains nuclei possessing spin.

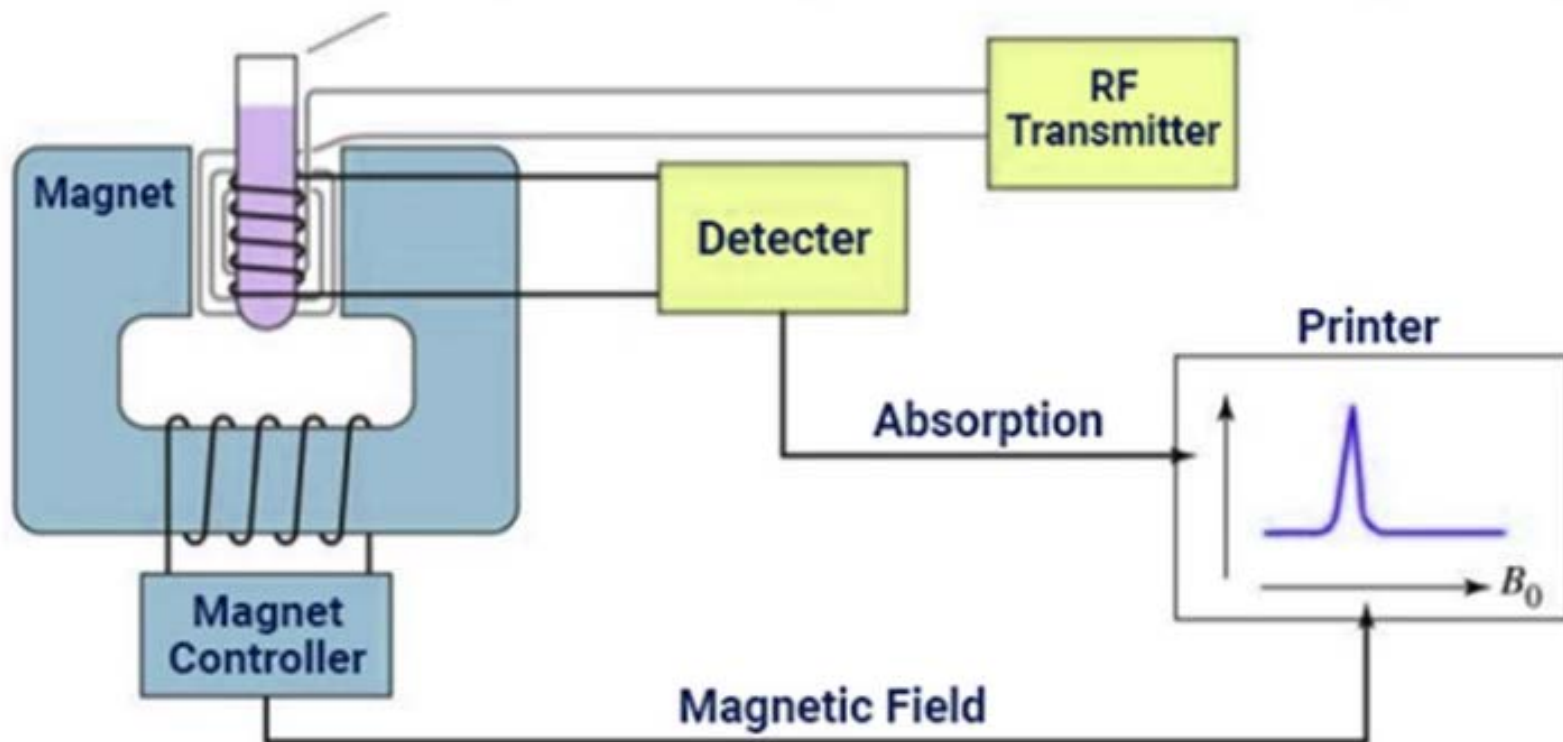


# Instrumentation

- **Sample holder**
- Glass tube with 8.5 cm long, 0.3 cm in diameter.
- **Permanent magnet**
- It provides a homogeneous magnetic field at 60-100 MHz
- **Magnetic coils**
- These coils induce a magnetic field when current flows through them
- **Sweep generator**
- To produce an equal amount of magnetic field pass through the sample
- **Radio frequency transmitter**
- A radio transmitter coil transmitter that produces a short powerful pulse of radio waves
- **Radio frequency receiver**
- A radio receiver coil that detects radio frequencies emitted as nuclei relax to a lower energy level
- **Read out systems**
- A computer that analyses and records the data.

Sample Tube

# Nuclear Magnetic Resonance (NMR) Spectroscopy



# Applications

- It is an analytical chemistry technique used in quality control.
- It is used in research for determining the content and purity of a sample as well as its molecular structure. For example, NMR can quantitatively analyze mixtures containing known compounds.
- NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules.
- These techniques are replacing x-ray crystallography for the determination of protein structure.
- Time domain NMR spectroscopy techniques are used to probe molecular dynamics in solution.
- Solid state NMR spectroscopy is used to determine the molecular structure of solids.
- Other scientists have developed NMR methods-of measuring diffusion coefficients.