MSE 310 Lecture 18

Nuclear Magnetic Resonance Spectroscopy, 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.
- It is a spectroscopy technique which is based on the absorption of electromagnetic radiation in the radio frequency region 4 to 900 MHz by nuclei of the atoms.
- Over the past fifty years, NMR has become the preeminent technique for determining the structure of organic compounds.
- Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected.

Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as 12C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.
2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*.

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*.

Nuclei possessing angular moment (also called spin) have an associated magnetic moment. A few examples of magnetic isotopes are 13C, 1H, 19F,14N, 17O, 31P, and 33S. Please note that not every isotope is magnetic. In particular, you should note that ^{12}C is not magnetic. If a nucleus is not magnetic, it can't be studied by nuclear magnetic resonance spectroscopy.

Principle

The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap). The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency.The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.

Alpha and Beta Orientation

Nuclear Magnetic Spectroscopy is based on the fact that when a population of magnetic nuclei is placed in an external magnetic field, the nuclei become aligned in a predictable and finite number of orientations. For ^1H there are two orientations. In one orientation the protons are aligned with the external magnetic field (north pole of the nucleus aligned with the south pole of the magnet and south pole of the nucleus with the north pole of the magnet) and in the other where the nuclei are aligned against the field (north with north, south with south). The alignment with the field is also called the "alpha" orientation and the alignment against the field is called the "beta" orientation.

Since the alpha orientation is preferred, more of the population of nuclei are aligned with the field than against the field. You might wonder why any spins would align against the field. Realize that we are talking about atomic magnets. These are very, very weak magnets. The energy difference between the alpha and beta orientations is not large. There is enough energy for nuclei to exchange between the two orientations at room temperature, though a slight excess on average is in the lower energy, alpha state.

The nuclear magnetic resonance (NMR) spectroscopy experiment involves using energy in the form of electromagnetic radiation to pump the excess alpha oriented nuclei into the beta state. When the energy is removed, the energized nuclei relax back to the alpha state. The fluctuation of the magnetic field associated with this relaxation process is called resonance and this resonance can be detected and converted into the peaks we see in an NMR spectrum.

What sort of electromagnetic radiation is appropriate for the low energy transition involved in NMR? Well believe it or not, radio waves do the trick. Radio waves are at the very low energy end of the electromagnetic spectrum and are sufficient to induce the desired transition. It is for this reason that NMR is considered to be a safe method of analysis.

Instrumentation and Working of NMR

1. **Sample holder**

Glass tube with 8.5 cm long, 0.3 cm in diameter.

2. **Permanent magnet**

It provides homogeneous magnetic field at 60-100 MHZ

3. **Magnetic coils**

These coils induce magnetic field when current flows through them

4. **Sweep generator**

To produce the equal amount of magnetic field pass through the sample

5. **Radio frequency transmitter**

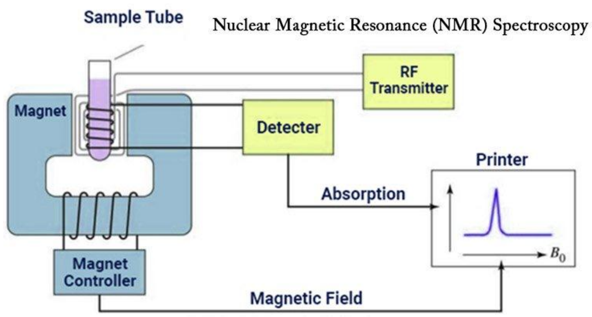
A radio transmitter coil transmitter that produces a short powerful pulse of radio waves

6. **Radio frequency receiver**

A radio receiver coil that detects radio frequencies emitted as nuclei relax to a lower energy level

7. **Read out systems**

A computer that analyses and record the data.



- 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.

Applications

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. NMR spectroscopy is the use of the NMR phenomenon to study physical, chemical and biological properties of matter.

- 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.