

# Nuclear Magnetic Resonance Spectroscopy

## Nuclear Magnetic Resonance

Over the past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as 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. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram.

NMR is a phenomenon which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon, and others do not, dependent upon whether they possess a property called spin. 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.  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{32}\text{S}$ ,  $\dots$ ). 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  $I = 1/2$ .

## Spectroscopy

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. In NMR spectroscopy, this electromagnetic radiation falls in the radio frequency region of the electromagnetic spectrum. NMR spectroscopy is therefore the energetically mildest probe used to examine the structure of molecules.

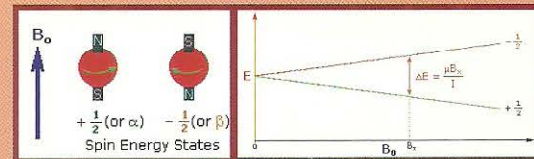
NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques. Two-dimensional techniques are used to determine the structure of more complicated molecules. These techniques are replacing x-ray crystallography for the determination of protein structure. Time domain NMR spectroscopic techniques are used to probe molecular dynamics in solutions. Solid state NMR spectroscopy is used to determine the molecular structure of solids. Other scientists have developed NMR methods of measuring diffusion coefficients.

The versatility of NMR makes it pervasive in the sciences. Scientists and students are discovering that knowledge of the science and technology of NMR is essential for applying, as well as developing, new applications for it.

1. A spinning charge generates a magnetic field, as shown (right). The resulting spin-magnet has a magnetic moment ( $\mu$ ) proportional to the spin.



2. In the presence of an external magnetic field ( $B_0$ ), two spin states exist,  $+1/2$  and  $-1/2$ . The magnetic moment of the lower energy  $+1/2$  state is aligned with the external field, but that of the higher energy  $-1/2$  spin state is opposed to the external field. (The arrow representing the external field points North.)



Strong magnetic fields are necessary for nmr spectroscopy. The international unit for magnetic flux is the tesla (T). The earth's magnetic field is not constant, but is approximately  $10^{-4}$  T at ground level. Modern nmr spectrometers use powerful magnets having fields of 1 to 20 T. Even with these high fields, the energy difference between the two spin states is less than 0.1 cal/mole. To put this in perspective, recall that infrared transitions involve 1 to 10 kcal/mole and electronic transitions are nearly 100 time greater.

For NMR purposes, this small energy difference ( $\Delta E$ ) is usually given as a frequency in units of MHz (10<sup>6</sup> Hz), ranging from 20 to 900 Mz, depending on the magnetic field strength and the specific nucleus being studied. Irradiation of a sample with radio frequency (rf) energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the  $+1/2$  state to the higher  $-1/2$  spin state.