

RADIO SPECTROSCOPY METHODS

Electron spin resonance (ESR), and Nuclear Magnetic Resonance (NMR) both record the absorption of radio frequency electromagnetic radiation by a sample placed in a magnetic field. The physical principles underlying NMR and ESR methods are similar. Both methods have many biomedical applications, but NMR plays an outstanding role in chemical applications and medical imaging.

Spin

Spin is the intrinsic angular momentum of elementary particles. It is one of the basic physical parameters of the particle, among other parameters such as mass or charge. Charged particles with non zero spin have an intrinsic magnetic momentum. The magnetic momentum (M_N) of the proton spin is:

$$M_N = g_N \cdot \mu_N \cdot \sqrt{S \cdot (S + 1)},$$

where g is the nuclear factor, μ_N is the Bohr magneton, $S=1/2$ is the spin of the proton. The value of the Bohr magneton can be calculated as:

$$\mu_N = \frac{e \cdot h}{4 \cdot \pi \cdot m_p},$$

where e is the elementary charge, h is Planck's constant, m_p is the mass of the proton.

Zeeman Splitting, Larmor Precession

In the presence of an external magnetic field, the interaction between the magnetic moment of the particle and the external magnetic field causes the energy level of the proton to split into two levels, one of which will correspond to the ground state of the particle, and the other to the excited state. This splitting is called Zeeman effect. Some protons will be parallel (α), while others opposite (β , antiparallel) to the H_0 magnetic field. The energy difference between the two states depends linearly on the strength of the applied external magnetic field (H_0):

$$\Delta E = g_N \cdot \mu_N \cdot H_0$$

In thermal equilibrium, the ratio of the populations of the two states is given by the Boltzmann distribution:

$$\frac{N_\beta}{N_\alpha} = e^{-\frac{\Delta E}{k \cdot T}}.$$

Here N_α , and N_β are the number of protons in the parallel and antiparallel states, respectively; k is Boltzmann's constant, T is the absolute temperature.

The condition for the absorption of a photon coupled to the transition between the two levels:

$$\Delta E = h \cdot f,$$

where h denotes Planck's constant, f the frequency of the electromagnetic radiation.

Larmor precession (named after Joseph Larmor) refers to the wobble (precession) of the magnetic moments of electrons or protons about the external magnetic field with a frequency f_L .

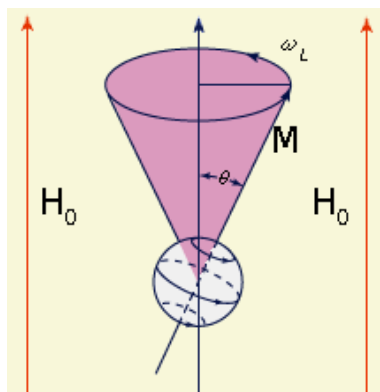
The resonant frequency of the Zeeman splitting (f) is equal to the frequency of the Larmor precession (f_L).

NMR Spectrum

The NMR spectrum is the frequency dependence of the absorbance for the radio frequency electromagnetic radiation of the sample placed in the magnetic field. The electron cloud surrounding the proton influences the external magnetic field H_0 . The nuclei will experience a local magnetic field, slightly different from H_0 . This is taken into account by the so-called screening factor (σ):

$$H_{local} = H_0 \cdot (1 - \sigma).$$

Because of this, the actual resonance frequency of the given nucleus will be slightly shifted. The shift of the frequency (spectrum line) depends on the chemical surroundings of the nucleus. The

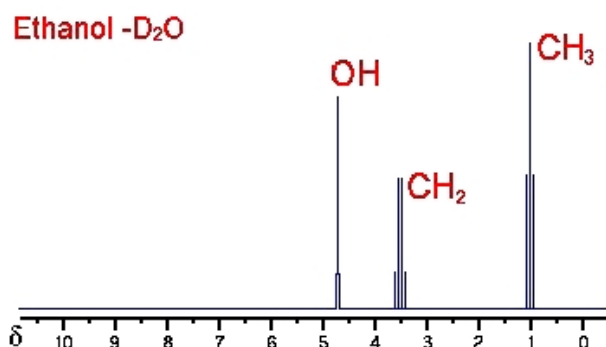


chemical shift of NMR lines is usually measured with respect to the signal of a reference compound (e.g. tetramethyl-silane) and is expressed in units of parts per million (ppm):

$$\delta = \frac{f - f_0}{f_0} \cdot 10^6 \text{ (ppm)},$$

where f and f_0 denote the resonant frequencies of the sample and of the reference, respectively.

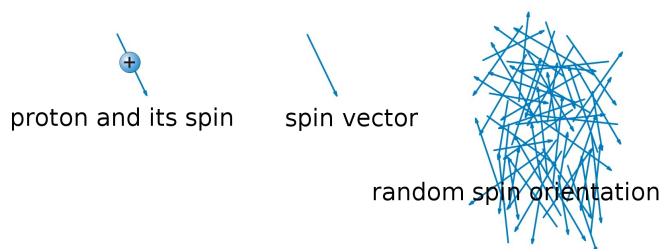
Analyzing the chemical shifts and shape of the spectra allows direct chemical identification of the sample.



Recording the NMR Spectrum

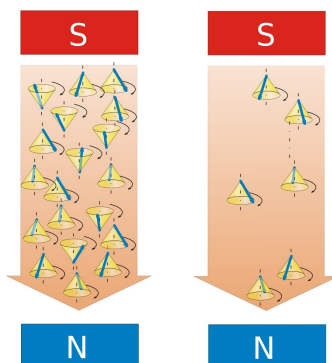
Before placing the sample in the magnetic field, the spins of the protons are randomly oriented. Figures in this section are the courtesy of Dr. István Derka.

No magnetic field



In the magnetic field the spins of the protons orient in parallel and antiparallel directions compared to the external magnetic field (first figure below). More protons will be in the parallel state than in the antiparallel state. The second figure below indicates only these extra protons.

The figure below shows the scheme of the NMR measurement. The net magnetization vector of the sample is parallel to the external magnetic field (vertical in our coordinate system), since the precession axes of the resonantly precessing spins are parallel to the axis z . If the sample is excited with a radio frequency pulse of resonance frequency, the magnetization vector of the sample will start to precess around the magnetic component of the radio frequency field. If we apply a pulse duration that exactly rotates the magnetization vector by 90° , the magnetization vector of the sample becomes



perpendicular to the H_0 field. After the 90° pulse is switched off, the magnetization vector which has been rotated into the x-y plane will induce changing electrical voltage in the detector coil. The signal will slowly become smaller and smaller as the system returns to thermal equilibrium. The observed signal is the so-called free induction decay (FID). After the FID has been recorded, the NMR spectrum can be calculated by using Fourier transform to extract the frequency components present in the signal, and their corresponding amplitudes.

