Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-5

Nuclear Magnetic Resonance Spectroscopy

3. High-Resolution Solution NMR Spectroscopy

Knowing the gyromagnetic ratio γ of a nucleus enables the resonance frequency from Equation (1) to be calculated for any magnetic field strength. Table 2 lists useful, commonly studied nuclei and their magnetic properties. The frequencies are for a 2.35 T applied magnetic field, i.e., relative to ^{1}H at 100 MHz. Table 2 gives the relative sensitivity for equal numbers of each nucleus and their relative receptivities, i.e., the product of the relative sensitivity and natural abundance.

The abundant nuclei, ^{1}H, ^{19}F, and ^{31}P, with $I = 1/2$ were the first to be studied by CW NMR. Owing to sensitivity problems, less abundant isotopes of important spin 1/2 nuclei such as ^{13}C and ^{15}N require FT techniques for observation in nat-

ural abundance. Nuclei with spin $I \geq 1$ have a quadrupole moment in addition to their magnetic moment. The interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus provides a very efficient process for nuclear relaxation. Often, the quadrupolar mechanism is dominant, the resulting relaxation times are very short, and the signals broad. In extreme cases (e.g., covalently bonded ^{35}Cl or ^{37}Cl), the signals are too broad to detect. However, nuclei with very small quadrupole moments such as ^{2}H and ^{11}B can be observed in the usual manner as the broadening is much less severe.

4. The NMR Experiment

The first successful NMR experiments were reported in 1945 by two independent groups in the USA [7], [8]. The discoveries by BLOCH at Stanford and by PURCELL at Harvard were awarded a Nobel Prize in Physics in 1952. Already in September 1952 the first commercial NMR spectrometer was installed. Early instruments used permanent magnets or electromagnets with fields from 0.94 up to 2.35 T, corresponding to 40 up to 100 MHz for proton resonance. Permanent magnets give very stable magnetic fields and are

often used without further stabilization. Electromagnets need additional control mechanisms to provide the necessary stability. The commonest

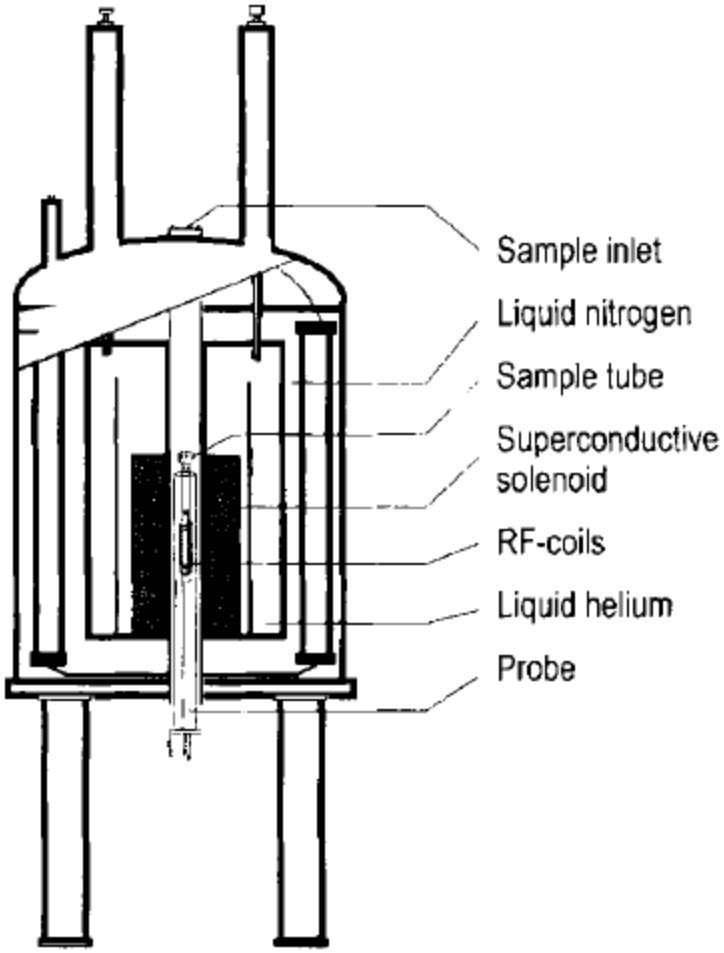

Figure . Schematic diagram of a cryomagnet. The superconducting coil is immersed in liquid helium. The sample tube is placed from above into the middle of the solenoid, where the field is strongest and has lhe best homogeneity. The lines of the static magnetic field are parallel to the long axis of the sample tube.

way to do this is to use the NMR signal of another nucleus in the sample to provide a field-frequency locking mechanism. The other nucleus may be the reference nucleus (homo-lock) or a different nucleus (hetero-lock), e.g., the deuterium resonance

of a deuterated solvent. The need for instruments with higher resolution and sensitivity has led to the development of commercially available systems operating at up to 900 MHz for protons. All instruments operating above 100 MHz use helium-cooled superconducting solenoids to provide the magnetic field. High-resolution NMR requires both the magnetic field and the RF source to be

homogeneous and stable to better than 1 part in 10^8. To achieve this performance, which allows to obtain the maximum information possible from an NMR experiment, the magnetic field profile has to be made extremely uniform in the region of the sample. The two parameters which quantify these performance characteristics are magnetic field "homogeneity" and field "drift". The magnets are designed to minimize any magnetic field variations in time. Inevitable imperfections are introduced during manufacture of the wire of the solenoid and also caused by different samples, temperature variations, etc. They are eliminated using correction coils and so-called shim coils to remove residual field gradients. Also the magnetic field stability is of major importance. In conventional magnets the superconducting wire is bathed in liquid helium under atmospheric pressure where

it has a boiling point of 4.2 K. By reducing the pressure the boiling point of helium can be lowered to 2.3 K. By doing this the performance of the superconducting wire is enhanced and higher magnetic fields can be achieved (cryostabilization). In Figure 5 a schematic diagram of a superconducting magnet is shown.

The sample, normally a solution in a deuterated solvent in a 5 or 10 mm glass tube (smaller tubes have been employed for specific applications for some years as well), is placed in the instrument probe between the poles of an electromagnet/permanent magnet or inside the solenoid of a superconducting magnet. The probe contains the RF transmitter and receiver coils and a spinner to spin the tube about its vertical axis. Sample spinning is used to average out magnetic field inhomogeneity across the sample. Multidimensional NMR spectra are measured in modern instruments without rotating.

The ideal NMR solvent should dissolve the sample, be inert, nonpolar, liquid over the temperature range of interest, inexpensive, and not give rise to large interfering peaks in the spectrum being recorded. Deuterated solvents such as deuterochloroform and deuterodimethyl sulfoxide are

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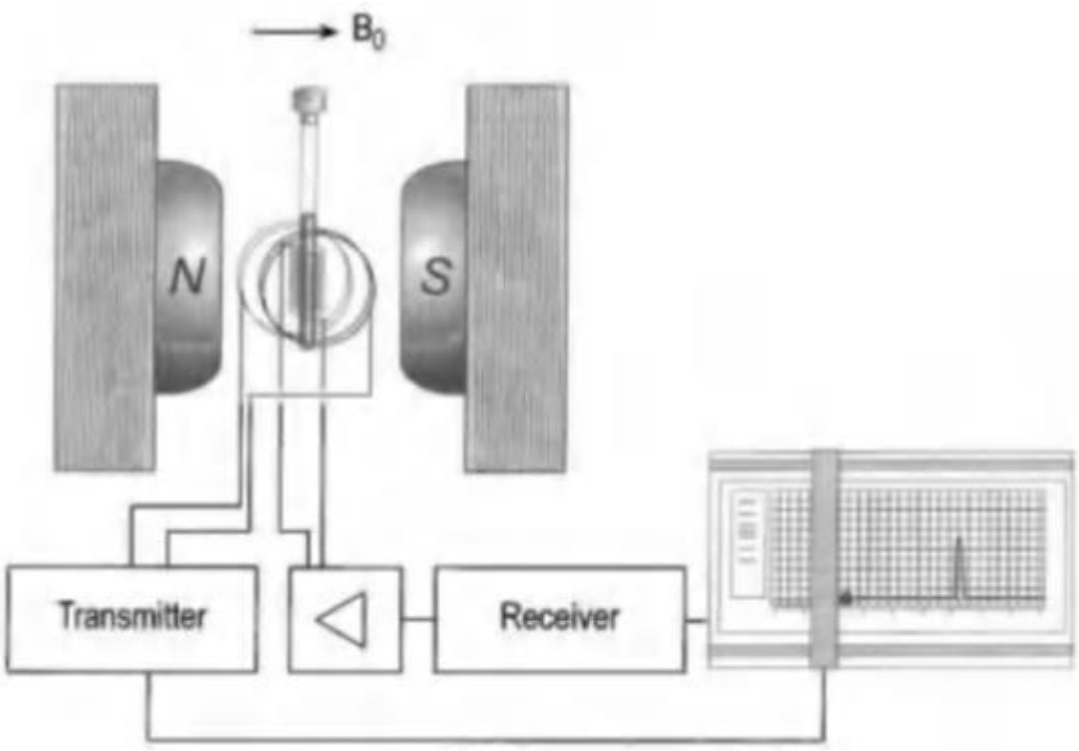

Figure 6. Block diagram of a CW NMR spectrometer.

most commonly used. They offer the advantage of being "transparent" in proton spectra and provide a deuterium signal which can be used to stabilize and lock the spectrometer system. A clear, mobile solution is required for a high-quality spectrum. Solid particles or viscous solutions degrade the resolution. Traces of paramagnetic impurities in a solution can dramatically reduce relaxation times and cause peak broadening. With increasing field strength the demands both on the sample and on the used NMR tubes are usually growing.

Spectra are recorded either by the CW scan or pulsed FT method. The amount of sample required depends on the method of detection (CW or FT) and the receptivity of the nucleus being studied. For most routine CW proton spectrometers 10 – 20 mg of compound of M_r 200 – 300, dissolved in 0.4 mL of solvent should give a reasonable spectrum. On a 500 MHz FT instrument it should be possible to obtain a proton spectrum from less than one milligram of such a compound. Even smaller amounts can be measured with specific techniques, e.g., special NMR tube inserts. For specially designed probes amounts of few nanograms are sufficient [110], [144].

To measure nuclei with low receptivity, such as ^{13}C, a more concentrated solution must be used, in order to obtain a spectrum in as short a time as possible. Larger diameter sample tubes (10 or 15 mm) and, consequently, larger sample volumes can be used to increase the amount of sample. Recently the so-called inverse detection techniques were used for observation of nuclei with small sensitivities (Section 18.3.6.4).