3. Principle

Nuclei with an odd number of protons and/or neutrons undertake nuclear spin with the nuclear magnetic moment μ proportional to the nuclear spin quantum number I, as:

$$\mu = g\mu_N I \tag{1}$$

where g is a dimensionless factor called g-factor (g=5.5851 for H-nuclei), and μ_N is a constant ($\mu_N = qhC/2m_p$) called Bohr nuclear magnetic moment, in which q is the charge of an electron, m_p is the mass of an electron, C is the speed of light, and h is the Planck's constant.

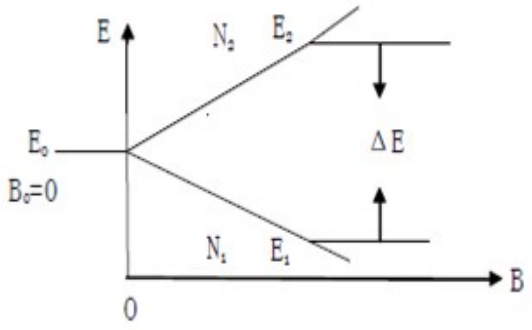

Figure 1 Zeeman splitting of an energy level in magnetic field

When a nuclear spin system is in a constant DC magnetic field B_0, the energy levels of the nucleus are split due to the Zeeman effect. For a sample with H-nuclei (I=1/2), the original energy level is split into upper and lower two energy levels, E_2 and E_1, as shown in Figure 1, whose energy difference is proportional to the product of g and B_0, as:

$$E_2 - E_1 = \Delta E = g\mu_N B_0 \tag{2}$$

If a sweeping magnetic field of $B_1\cos(wt)$ with an angular frequency (w) in the range of 10^6 to 10^9 Hz, is applied perpendicularly to a constant magnetic field B_0, two opposite processes, stimulated transition and spontaneous emission, would occur between the two energy levels if the RF quantum energy equals the energy difference between the two energy levels, as

$$\Delta E = g\mu_N B_0 = wh \tag{3}$$

These two processes have an equal probability, which is proportional to the square of B_1. As the nuclear spin system absorbs the energy from the RF magnetic field to create resonance absorption, it is in a non-equilibrium state. Equation (3) is referred to as the condition for nuclear magnetic resonance (NMR), which can be rewritten as

$$w_0 = B_0\gamma \tag{4}$$

where γ is called the gyromagnetic ratio. If the sweeping magnetic field is removed, the nuclear spin system will undertake a relaxation process through the interactions of lattice-to-spin and spin-to-spin to restore back to an equilibrium state.

The above discussions are the theory of NMR for a single nucleus in an external magnetic field. Experimental samples usually contain a large number of similar nuclei. If the nuclei number on the upper energy level is the same as that on the lower energy level, under the excitation of an

electromagnetic wave, both energy levels have the same transition probability, so the absorbed energy and the emitted energy are equal, thus no NMR signal can be observed. Only when the nuclei number on the lower level is greater than that of the upper level, the absorbed energy is more than the emitted energy, and hence NMR signals can be observed. In the state of thermal equilibrium, the relative distribution of nuclei number in the two energy levels is determined by the Boltzmann factor:

$$\frac{N_2}{N_1} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{g_N \mu_N B_0}{kT}\right) \tag{5}$$

where N_1 and N_2 are the nuclei numbers on the lower and upper levels, respectively, ΔE is the energy difference between the two levels, k is Boltzmann constant, T is absolute temperature. In the case of $g_N \mu_N B_0 << kT$, (5) can be approximated as

$$\frac{N_2}{N_1} = 1 - \frac{g_N \mu_N B_0}{kT} \tag{6}$$

Equation (6) indicates that the nuclei number on the lower energy is just slightly more than that on the upper level. For hydrogen nuclei, if temperature T=300 K, and magnetic field B_0=1 T, we get

$$\frac{N_2}{N_1} = 1 - 6.75 \times 10^{-6} \text{ or } \frac{N_1 - N_2}{N_1} \approx 7 \times 10^{-6} \tag{7}$$

Equation (7) shows the difference of nuclei numbers in lower and upper levels is very small, so the NMR signal is very weak demanding the use of a high quality detector. It is apparent from Equation (6) that a stronger external magnetic field is favorable for the observation of NMR signal. In addition, a highly uniform magnetic field is needed for a better NMR signal.

Actual NMR absorption does not occur only at a single frequency determined by Equation (4), but within a certain frequency range, so the NMR spectral line has a certain width. Usually the width of the frequency interval at the half height of the absorption curve is called the resonant line width. Line width due to relaxation processes is known as intrinsic line width, while the non-uniform distribution of an external magnetic field also extends the line width. In general, NMR line width can be derived as

$$w_0 - w = \frac{1}{T_2 (1 - \gamma^2 B_1^2 T_1 T_2^{1/2})} \tag{8}$$

where T_1 and T_2 are the longitudinal (lattice-to-spin) and transverse (spin-to-spin) relaxation time of the nuclei, respectively. It is apparent from Equation (8) that NMR line width is mainly affected by the transverse relaxation time.

4. Structure of Apparatus

This NMR apparatus consists of an electric unit, a magnet unit, a marginal oscillator with sample probe, a Tesla probe, and two optional apparatus (frequency counter and oscilloscope).

1) Marginal oscillator

A RF magnetic field (B_1) is provided by the NMR apparatus through a sample probe which also detects the magnetic field strength. A block diagram of the NMR controller unit is shown in Figure 2.

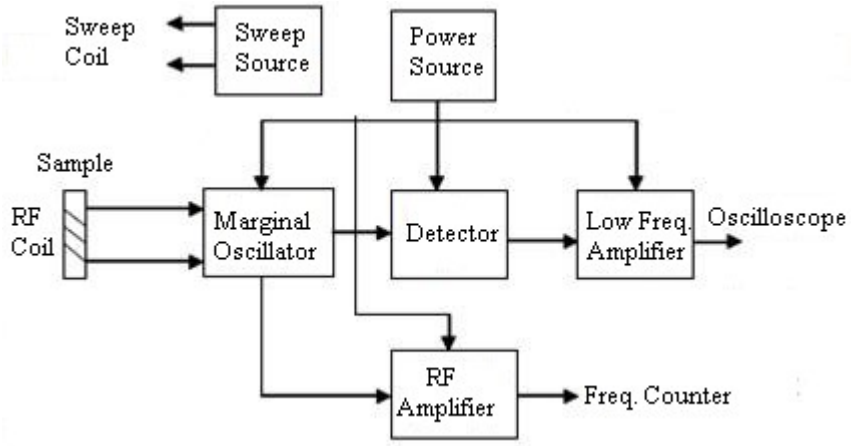

Figure 2 Block diagram of controller unit

In Figure 2, the marginal oscillator generates RF oscillations whose frequency is determined by the RF coil and a parallel capacitor. A marginal oscillator is normally tuned to work in the critical state to prevent NMR signal from saturation while offering higher detection sensitivity. In the absence of NMR, the oscillator generates equal-amplitude oscillations detected as a DC signal, seen as a straight line on the oscilloscope through the low frequency amplifier. In the presence of NMR, since the sample absorbs the RF energy, oscillation amplitude of the oscillator reduces. Thus, the envelope of the RF signal is amplitude-modulated by the resonant absorption signal. After demodulation and amplification, the resonant absorption signal can be detected and displayed, which reflects the change in oscillation amplitude.

2) Sweep coil

The magnet used in this apparatus is a permanent magnet with good homogeneity. The sweep coil produces a weak AC magnetic field (B_m) through the sweeping current at 50 Hz/60 Hz determined by the AC line frequency, which is superimposed to the constant magnetic field (B_0). Hence, within a period of the AC sweep signal, stable NMR absorption signal of ^{1}H nucleus in the sample can be observed on the oscilloscope.

It is apparent from Eq (4) that there is one-to-one relationship between magnetic field and RF frequency for resonance absorption. Because it is difficult to find the frequency for resonance absorption, a weak low-frequency AC magnetic field B_m is usually superposed to the constant magnetic field B_0, as shown in Figure 3, in which the upper trace is the superimposed magnetic field (B_0+B_m), and the lower trace is the amplitude change in oscillation voltage over time. B_0' is the resonance magnetic field at a specific RF frequency. Thus, the actual magnetic field at the sample location is B_0+B_m. Since the sweeping amplitude is small, the direction of the superimposed magnetic field remains unchanged. As the amplitude of the superimposed magnetic field varies periodically with the sweeping field, the Larmor precession angular frequency (ω_0) of the nuclear magnetic moment also varies periodically, as

$$w_0 = \gamma(B_0 + B_m) \tag{9}$$

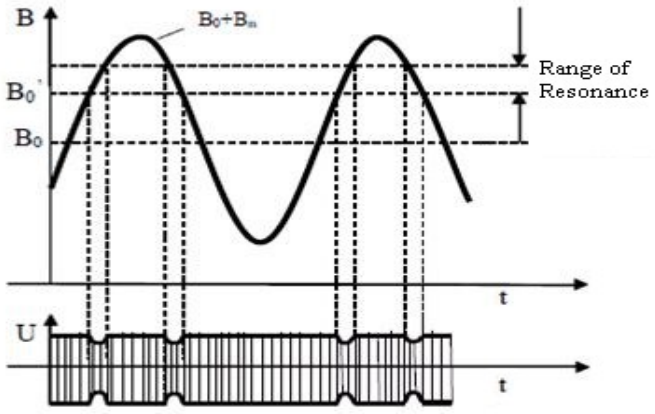

Figure 3 Magnetic field and resonance absorption

If the angular frequency (ω') of the sweeping field falls within the variation range of ω_0' and the valley-to-peak value of the sweeping field exceeds the range of the resonance field, NMR occurs. Resonance absorption signal can be observed on an oscilloscope, when the resonance magnetic field, B_0', is passed by the superimposed magnetic field (B_0+B_m). As otherwise, no NMR signal will be observed. Within one period, the resonance magnetic field is passed twice by the superimposed magnetic field, so two resonance absorption signals can be observed.

If the time or frequency interval between adjacent resonance absorption signals varies from period to period as shown in Figure 4 (a), this is caused by the fact that the resonance magnetic field (B_0') is not equal to the constant magnetic field (B_0). By changing the constant magnetic field (B_0) or the frequency of the RF field, the relative positions of the resonance signals will shift. When the interval between adjacent resonance absorption signals remains constant from period to period as shown in Figure 4 (b), the relative positions of the resonance absorption signals are independent of the amplitude of the sweep magnetic field (B_m), and the width of the resonance absorption signals increases with a decrease in sweep magnetic field (B_m) as shown in Figure 4 (c), at this time, B_0' and B_0 are equal.

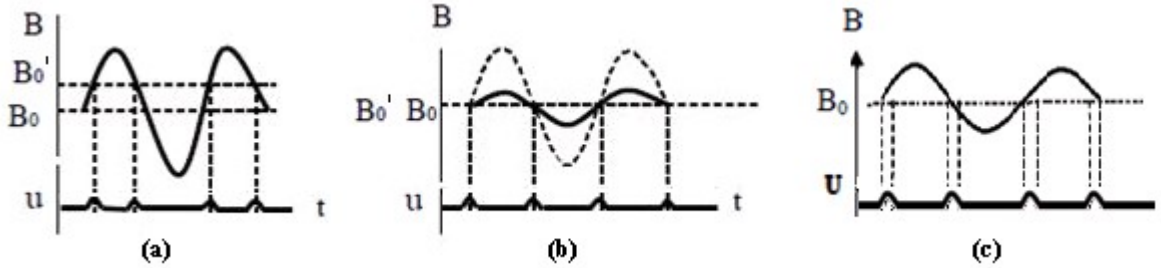

Figure 4 Relationship between resonance absorption signal waveform and magnetic field