Electronics And Instrumentation

8ᵗʰ Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-5

Nuclear Magnetic Resonance Spectroscopy

3.1.1. Continuous Wave Methodology

Until the late 1960s all NMR instruments were of the CW type. Figure 6 shows a block diagram of such a spectrometer. To obtain a spectrum from a sample, either the magnetic field or the RF frequency is slowly varied. When the resonance condition (Eq. 1) is met for the nuclei being observed, the sample absorbs RF energy and the resulting signal is detected by the receiver coils, amplified, and recorded. Spectra are recorded on precalibrated charts relative to a reference compound.

The CW method is suitable for recording spectra of abundant nuclei from relatively large amounts of sample. As a result, early NMR work was essentially limited to the ^{1}H, ^{19}F, and ^{31}P nuclei. Nowadays the use of CW instruments, which are relatively inexpensive, is mainly limited

to ^{1}H observation. Such instrumentation is usually to be found in university teaching or synthetic organic chemical laboratories rather than specialist NMR facilities.

One of the main limitations of NMR spectroscopy is its inherent lack of sensitivity. As a result, the CW method is unsuitable for recording spectra from nuclei of low natural abundance or even from abundant nuclei in solutions of very low concentration. One way of improving the signal-to-noise (S/N) ratio is to record several spectra from a sample and add them together. The noise averages
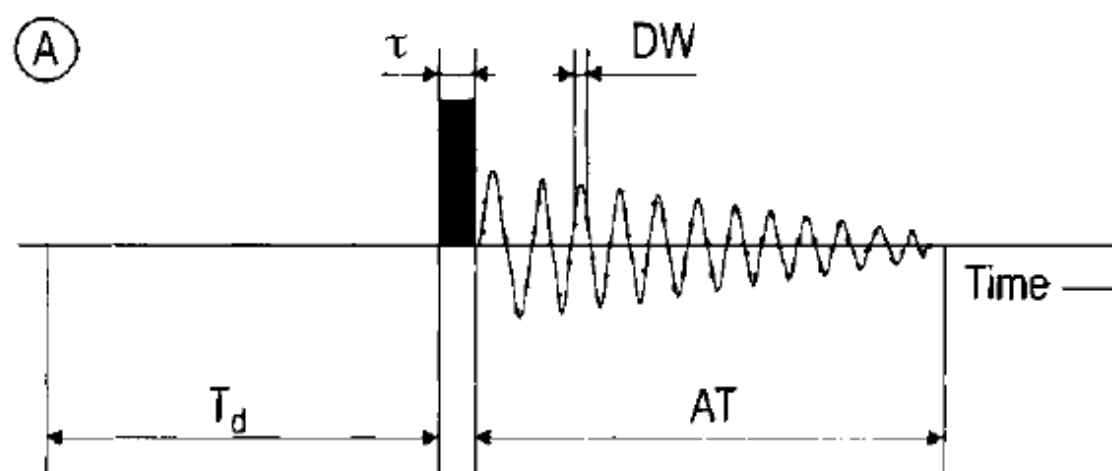

Figure 7. Schematic presentation of a pulse or FT NMR experiment (A); the free induction decay (FID) (B); and the appendant Fourier-transformed signal (NMR spectrum) (C). In A the FID is shown in a simplified manner also in the digital form, which will be generated by an analog-to-digital converter (ADC).

out, and the S/N ratio increases by a factor equal to the square root of the number of spectra accumulated. Using a computer to store and add the spectra allows many thousands of spectra to be accumulated in this way. The main drawback to this method on a CW instrument is the time to acquire each spectrum, typically ca. 4 min, resulting in excessive and often prohibitive total experiment times. A technique was required which could simultaneously excite the whole spectral region of interest. The pulsed FT technique, which first became available on commercial instruments in the late 1960s, provided the answer.

3.1.2. Fourier Transform Methodology

In 1966 ERNST and ANDERSON discovered that the sensitivity of NMR spectra could be increased dramatically if the sample was not exposed to the slow radio frequency sweep but to short and intense radio frequency pulses. The intensity of the signal was measured as a function of time after this pulse. The next pulse and signal acquisition were started after a few seconds, and the signals after each pulse were summed in a computer. If the RF frequency ν is turned on and off very rapidly to obtain a pulse τ seconds long, this is

equivalent to irradiating the sample with a range of frequencies centered about v over a frequency range $v \pm 1/\tau$. Thus if $\tau = 50\,\mu s$ a range of $v \pm 20\,000\,Hz$ is covered.

If an RF pulse, at the resonant frequency v_0, is applied along the x-axis in the laboratory frame, this is equivalent to applying a static field $\boldsymbol{B}_1$ along the x'-axis of the rotating frame. This drives the sample magnetization about the x'-axis by an angle θ, as shown in Figure 4. Spectrometers are normally designed to detect signals along the y'-axis. The component of magnetization along this direc-

tion is given by $M_0 \sin \theta$, and the maximum signal is obtained when $\theta = 90°$. A pulse producing this effect is known as a $90°$ pulse, and the time for which the pulse must be applied to achieve this is known as the $90°$ pulse time. On modern FT spectrometers $90°$ pulse times are usually significantly less than $50\,\mu s$. Since the pulse applied is very short it must be powerful enough to excite nuclei in the time available across the whole spectral region of interest. To do this it must satisfy the condition:

$$\gamma \boldsymbol{B}_1 \geq 2\pi(SW)$$

where SW is the spectral width required.

At the end of the RF pulse, the spin system begins to relax back towards its equilibrium condition by means of the two relaxation mechanisms described in Section 18.2.4. After a time $5\,T_1$ the magnetization along y' — the signal detection axis — has decayed essentially to zero. For the remainder of this article the rotating frame is assumed and the axes are referred to simply as x, y, and z.

In the CW experiment, descibed in Section 18.3.1.1, the intensity of the NMR signal is recorded as function of frequency. However, in the pulsed experiment, the intensity of the decaying signal, following the RF pulse, is detected and recorded as a function of time. The signal is known as the free induction decay (FID) and it is not amenable to a simple interpretation. In Figure 7 a pulse experiment is represented as diagram in the usual notation. After the delay period T_d the excitation occurs through a pulse with the pulse width (length) τ and the subsequent acquisition. The resultant FID is also illustrated in Figure 7 together with the conventional NMR spectrum, for a sample which gives a spectrum with a single peak. For a spectrum containing more than one peak, the FID is an interference pattern resulting from the frequencies corresponding to all the individual peaks in the spectrum. The FID is often

referred to as the time domain signal, whereas the corresponding NMR spectrum provides a frequency domain signal.

Time and frequency domain data can be interconverted by the mathematical process of Fourier transformation (FT), which can be performed rapidly by the computer. The intensity of the FID is measured at n intervals equally spaced by the so-called dwell time DW and stored in digital form. In other words, the dwell time is the time used to produce a particular data point. The total time to acquire the data is referred to as the acquisition time AT. In order to obtain a spectral width SW the following equation must be satisfied:

$$AT = \frac{n}{2\,(SW)} = n \cdot DW$$

Thus, typical values for obtaining a 100 MHz ^{13}C NMR spectrum would be:

SW   = 20 000 Hz (equivalent to 200 ppm)
N   = 16 384 (stored in 16 K computer words)
DW   = 25 μs
AT   = 0.41 s

Fourier transformation of the 16 K data points gives a spectrum with 8 K points since the transform contains both real and imaginary components, the real component being identical to the conventional CW spectrum.

The principal advantage of the FT method is that full spectral data can be obtained in a few seconds acquisition time as compared with minutes for the CW method. Signal averaging, by adding together the FIDs obtained after each of a series of RF pulses is therefore a much more efficient process than its CW analogue. The introduction of FT instruments made the routine study of less abundant isotopes. and in particular ^{13}C. possible.

FT instruments are available today with magnetic fields from 1.9 to 21.1 T. i.e., 80 to 900 MHz for ^{1}H observation. Most such instruments are available with a range of probeheads for studying different nuclei. Some probeheads are selectively tuned for observation of a single nucleus at maximum sensitivity. Dual- and trial-tuned probeheads for the convenient observation of ^{1}H and other fixed nuclei (e.g.. ^{13}C, ^{15}N. ^{31}P) on a single probehead are now widely used. as are tunable probeheads which enable a wide range of nuclei to be studied. However, the most extensive development occurred in the case of the pulse sequences. Several hundred pulse sequences were described in the last twenty years and it is impossible to know all. A very good overview of the 150 most important ones is given in [109]. Furthermore, numerous information about basics and new developments are to be found in the Internet. Some of the most impressive web pages are listed in [111], [112].