

# Electronics And Instrumentation

## 8<sup>th</sup> Semester

**Subject: Analytical Instrumentation**

**Subject code: BT 808**

### **Unit-5**

## **Nuclear Magnetic Resonance Spectroscopy**

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### **3.3 NMR and Structure**

In this section the relationship between chemical structure and the NMR parameters of chemical shift and spin–spin coupling are discussed for some of the more commonly studied nuclei.

#### **3.3.1. Hydrogen**

The two naturally occurring isotopes of hydrogen are the proton and the deuteron with natural abundances of 99.985 % and 0.015 %, respectively. Whilst the former with  $I = 1/2$  is the most commonly studied of all magnetic nuclei, the latter with  $I = 1$  is rarely studied in natural abundance and then only for a few specialist applications. One such application, the determination of deuterium levels in samples, is discussed in Section 18.3.8.2. If small isotope effects are disregarded,

corresponding  $^1\text{H}$  and  $^2\text{H}$  chemical shifts are the same.  $^2\text{H}$  spectra are less well dispersed than the corresponding  $^1\text{H}$  spectra by a factor of 6.51, the ratio of the magnetogyric ratios. The smaller magnetogyric ratio also results in correspondingly smaller coupling constants. Whilst the following discussion is exemplified by reference to the proton, most of the content is equally applicable to the deuteron. However, since deuterium homonuclear coupling constants are very small,  $^2\text{H}$  spectra with broadband  $^1\text{H}$  decoupling give a single peak from each chemically inequivalent deuteron even for deuterium enriched samples.

### 3.3.2. Carbon

Although present in natural abundance at only 1.1 %, the  $^{13}\text{C}$  nucleus has, since the advent of FT methodology, been extensively studied. Only the approximately 5700 times more sensitive  $^1\text{H}$  NMR is more widely used. In organic chemistry the information obtained from the two nuclei is often complementary for solving structural problems. The large  $^{13}\text{C}$  chemical shift range and the small line width of the  $^{13}\text{C}$  signals increases spectral resolution effectively. So,  $^{13}\text{C}$  NMR is the method

of choice for structural investigations of complex organic molecules, of complex mixtures of compounds, as well as biological oligomers and macromolecules.

### 3.3.3. Fluorine

With 100 % natural abundance and  $I = 1/2$ ,  $^{19}\text{F}$  is ideally suited to NMR investigations. Since the earliest days of NMR spectroscopy  $^{19}\text{F}$  applications in organic, inorganic, and organometallic chemistry have been widespread. As in the case of the  $^{13}\text{C}$  nucleus broadband proton decoupling is often used to simplify spectra.

### 3.3.4. Phosphorus

The  $^{31}\text{P}$  nucleus has 100 % natural abundance and  $I = 1/2$ . However, a relatively small magnetogyric ratio results in the sensitivity of the  $^{31}\text{P}$  nucleus being only 0.066 that of the proton. Nevertheless, with Fourier transform methodology, the nucleus is easy to detect even at low levels. There is much data in the literature covering applications involving inorganic compounds and complexes, organophosphorus chemistry, and biological and medical studies. In addition to these, even the

correlation between  $^{31}\text{P}$  and  $^{13}\text{C}$  is observable with modern spectrometers in 2D correlation experiments [118].

### 3.3.5. Nitrogen

There are two magnetic isotopes of nitrogen,  $^{14}\text{N}$  and  $^{15}\text{N}$ , with natural abundances of 99.63 % and 0.36 %, respectively. In a magnetic field of 9.4 T the  $^{14}\text{N}$  resonance frequency is 28.9 MHz, while that for  $^{15}\text{N}$  is 40.5 MHz. There are problems associated with observing both nuclei. The  $^{14}\text{N}$  nucleus possesses a quadrupole moment since  $I = 1$ . As a result, although  $^{14}\text{N}$  signals can often be detected easily, the lines can be very broad with widths often between 100 and 1000 Hz. With a 9.4 T applied magnetic field this is equivalent to 3.5 – 34.6 ppm. This can cause resolution problems when a molecule contains more than one type of nitrogen atom.

### 3.3.6. Oxygen

The only magnetic isotope of oxygen is  $^{17}\text{O}$ . With a natural abundance of only 0.037 %, a receptivity that is 0.61 that of  $^{13}\text{C}$ , and a quadrupole moment ( $I = 5/2$ ),  $^{17}\text{O}$  is difficult to study. Nevertheless, because of the importance of oxygen in

both inorganic and organic chemistry as well as biology, the  $^{17}\text{O}$  nucleus has been quite widely studied both in natural abundance and in isotopically enriched samples. For small molecules linewidths are typically in the range of several tens to several hundreds of hertz. With large molecules or viscous solutions much larger linewidths may be encountered.

### 3.3.7. Silicon

$^{29}\text{Si}$ , with an abundance of 4.7 %, is the only naturally occurring isotope of silicon with nonzero spin ( $I = 1/2$ ). Whilst its receptivity is 2.1 times that of the  $^{13}\text{C}$  nucleus there are problems associated with its detection. In common with the  $^{15}\text{N}$  nucleus a negative magnetogyric ratio results in negative NOEs when broadband proton decoupling is employed, as is usually the case. Inverse-gated decoupling and relaxation reagents are used to circumvent the problem. Broad signals from the glass in the NMR probehead or tube can also cause problems. The glass can be replaced by alternative materials such as teflon or the spectrum obtained from a blank run (i.e., without sample) can be subtracted from the spectrum of the sample.  $^{29}\text{Si}$  is very important for solid state NMR, e.g., for analysis of glasses and zeolites [128].