Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
Subject code: BT 808

Unit-5

Nuclear Magnetic Resonance Spectroscopy

4. NMR of Solids and Heterogeneous Systems

Solids give very broad NMR signals devoid of the fine structure which provides detailed information about chemical structures. The restriction of NMR spectroscopy to the liquid, solution, or gas phase, however, imposes considerable limitations on its applicability since some compounds are insoluble or have very low solubility. Moreover, a compound may experience a change in molecular structure on dissolution (e.g., by tautomerism). Studying samples as solids should provide some insight about how molecules pack as well as about molecular structure. Since the 1970s developments in experimental design and spectrometer hardware have made it possible in some situations to obtain spectra from solids in which the resolution approaches that obtainable in a solution experiment.

This section provides a brief explanation of the origins of the broadening effects, followed by an overview of the techniques employed to obtain high-resolution NMR spectra from solids and examples of their applications. Only spin 1/2 nuclei are considered. There are two principal factors which cause broadening in the NMR spectra of spin 1/2 nuclei obtained from solid samples. The first is chemical shift anisotropy: the chemical shifts are orientation dependent and the different crystallites in a sample have a range of orientations to the applied magnetic field. Broadening resulting from dipole–dipole interactions is the second factor. Both of these interactions are present in solution but are usually averaged out by molecular tumbling. A further problem results from the fact that nuclei in solids generally have very long relaxation times. This means that they take a long time to relax back to the equilibrium magnetization, which in turn affects the amount of time required to obtain a spectrum with a reasonable signal-to-noise ratio.

4.1. High-Resolution NMR of Solids

The study of "dilute" nuclear spin systems such as ^{13}C has been more amenable to obtaining high-resolution solid-state spectra than that of abundant nuclei such as the proton. The reason for this is that the problems associated with homonuclear dipolar interactions are essentially eliminated in a dilute spin system. Dilution may be the result of low natural abundance, as in the case of ^{13}C, or of abundant isotopes present in low concentration (e.g., ^{31}P in organophosphates). In either case homonuclear dipolar interactions are negligible, since dipolar interaction has a $1/r^3$ dependence. Heteronuclear dipolar interactions, usually to protons, remain but these can be removed effectively by the use of high-power proton decoupling. A technique known as magic angle spinning (MAS) is used to remove the effects of chemical shift anisotropy. This involves spinning the sample at an angle of 54°44′ to the applied magnetic field. To be effective the rate of rotation must be comparable to the frequency range being observed (i.e., several kilohertz). To overcome the problems associated with low sensitivity a technique known as cross-polarization (CP) is used. This involves the transfer of magnetization from highly polarizable abundant spins such as protons to dilute spins such as ^{13}C.

The combined application of CP, MAS, and high-power proton decoupling can give high-resolution spectra from powders and amorphous solids, comparable in quality to those obtained in solution. The ^{13}C, ^{29}Si, ^{15}N, and ^{31}P nuclei have been widely studied in this way in the last 20 years [128], [146], [147] . There are two principal reasons for obtaining a high-resolution NMR spectrum from a solid. Either it is insoluble or information is being sought about the solid-state structure. In the latter case crystallographic information is sought either because a single-crystal X-ray structure is not available or to enable a comparison of solid and solution state structures/conformations to be made when spectra are available in both phases. Crystallographic effects frequently give rise to splitting of lines in spectra of solids when compared with those obtained in solution. For a particular type of atom to yield a single line in a spectrum obtained from a solid, all the carbons of that type must be related by symmetry in the crystal. Nonequivalence is not an uncommon occurrence and may be intramolecular or intermolecular. Figure 30 shows the solid-state and solution spectra of 4,4′-dimethoxybiphenyl (**4**).

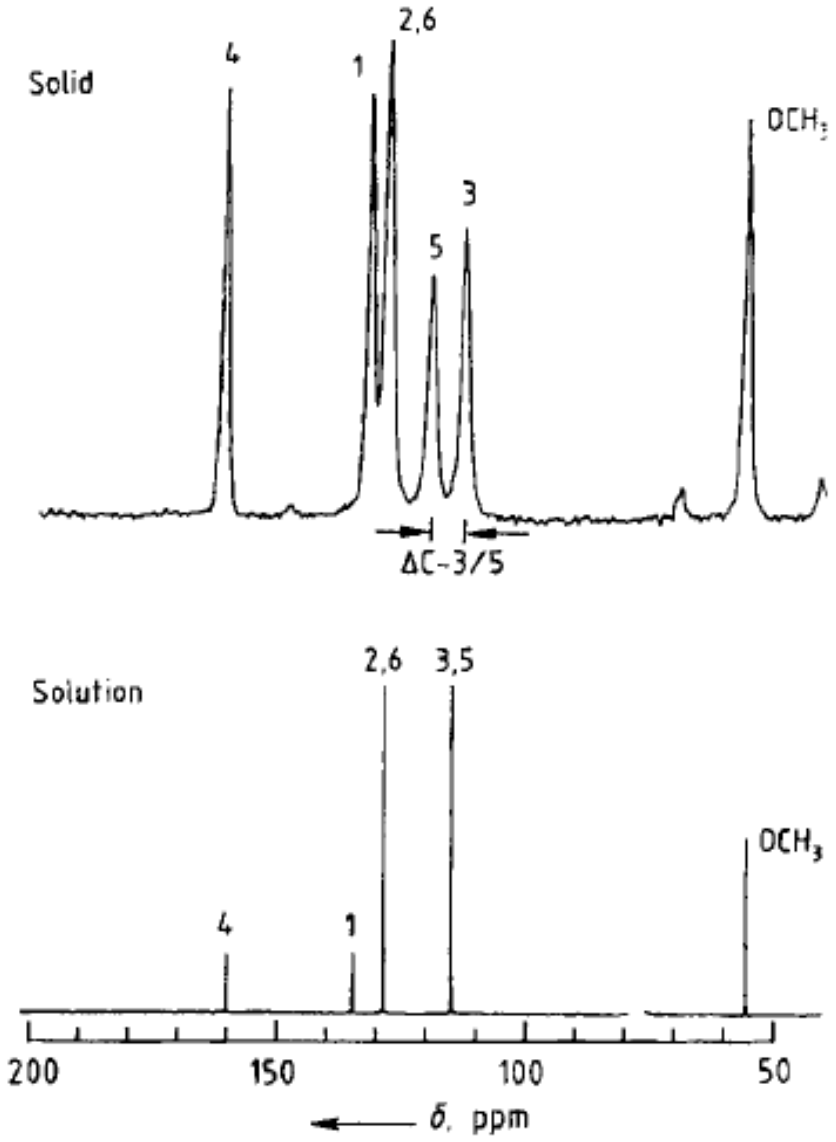

Figure 30. ^{13}C NMR spectra of 4,4'-dimethoxybiphenyl (**4**)

5. NMR Imaging

Since 1970 a technique known as magnetic resonance imaging (MRI) has been developed which has revolutionized diagnostic medicine. The technique produces an NMR picture or image. In addition to the NMR methodology described

above, MRI also uses magnetic field gradients in the x, y, and z directions to make the resonance frequency a function of the spatial origin of the signal. First, a slice at height z and thickness dz of the object is selected. This is done by means of a selective RF pulse, combined with a field gradient in z direction. Next, the spatial coding for the x direction is obtained by means of an x-gradient. Finally, the spatial coding for the second direction, i.e., the y direction, is obtained by means of a y-gradient. In medical imaging the protons in water are usually detected. While the water content in different types of tissue may show little variation, the T_1 and T_2 relaxation times are different. Pulse sequences are therefore used which produce contrast that reflects the different relaxation times. The technique has become particularly important in the diagnosis of cancer, since cancerous tissue has a longer relaxation time than healthy tissue. In recent years this method acquired special importance in neurochemistry [152].

Equipment is available for a range of applications from whole human body imagers operating at field strengths of up to ca. 8 T to equipment for imaging small samples up to 11.7 T. The achievable resolution depends on the magnitude and duration of the field gradients applied. For small

objects the best resolution which has been achieved is of the order of $5-10\,\mu m$. For whole body in-vivo applications it is much lower.

The techniques developed for biomedical applications to study the liquid state have also been used in materials science. Such applications include the study of solvents ingressed into polymers, liquids absorbed onto porous media, and polymerization reactions [51], all of which can be studied as a function of space and time.

6. ESR Spectroscopy

Electron spin resonance (ESR) spectroscopy is also known as electron paramagnetic resonance (EPR) spectroscopy or electron magnetic resonance (EMR) spectroscopy. The main requirement for observation of an ESR response is the presence of unpaired electrons. Organic and inorganic free radicals and many transition metal compounds fulfil this condition, as do electronic triplet state molecules and biradicals, semicon-ductor impurities, electrons in unfilled conduction bands, and electrons trapped in radiation-damaged sites and crystal defect sites.

The principles of ESR and general applications are covered in various monographs [52]–[57]. Reviews of technique developments and applications have been published [58], [59]; industrial applications have been reviewed [60]; and dosimetry [61] and biological applications described [62]–[66].

6.1. The ESR Experiment

The resonance condition for ESR, for a system having a spin value of 1/2, is:

$$\Delta E = h\nu = g\beta B \tag{3}$$

where ΔE is the separation of energy levels produced by the application of an external magnetic field B, and β is the Bohr magneton (9.274×10^{24} J/K). Most ESR spectrometers operate at a fixed frequency ν and record an ESR spectrum by sweeping the external field B. The most convenient frequency is ca. 9 GHz, which is in the microwave region. It corresponds to a wavelength of ca. 3 cm and is known as X-band. Spectrometers have been built which operate at other microwave frequencies: L-band (1.0–1.2 GHz),

S-band (3.8 – 4.2 GHz), K-band (24 GHz), and Q-band (34 GHz); and some even operate at a few megahertz in the earth's field. The lower frequencies are used when "lossy" samples, that is those with high dielectric constants such as aqueous or biological samples, are examined. The higher frequencies are used when greater dispersion is required, e.g., when improved separation of anisotropic g components in solid samples is required to reduce overlap of lines. Unfortunately, at the higher frequencies the sample size is restricted and noisier spectra often result.

6.1.1. Continuous Wave ESR

The basic components of a continuous wave (CW) ESR spectrometer are a frequency source (klystron or Gunn diode), an electromagnet (having a field of ca. 350 mT for X-band) and a resonant cavity (or loop gap resonator) in which the sample is placed (Fig. 31). To improve the signal-to-noise ratio, it is customary to modulate the microwave frequency at 100 kHz (other frequencies are also used) and to detect at this frequency by using a phase sensitive detector. This results in the usual recorder tracing from the spectrometer being the first-derivative instead of absorption as found in NMR spectrometers. A simple ESR spectrum is shown in Figure 32.

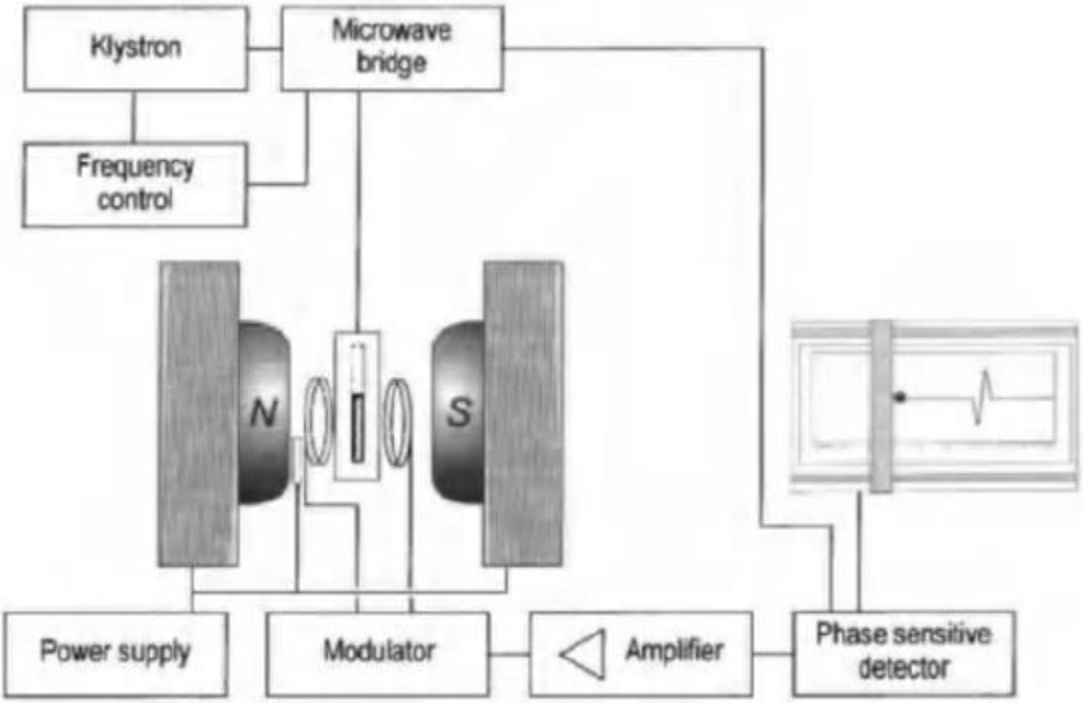

Figure 31. Block diagram of a CW ESR spectrometer

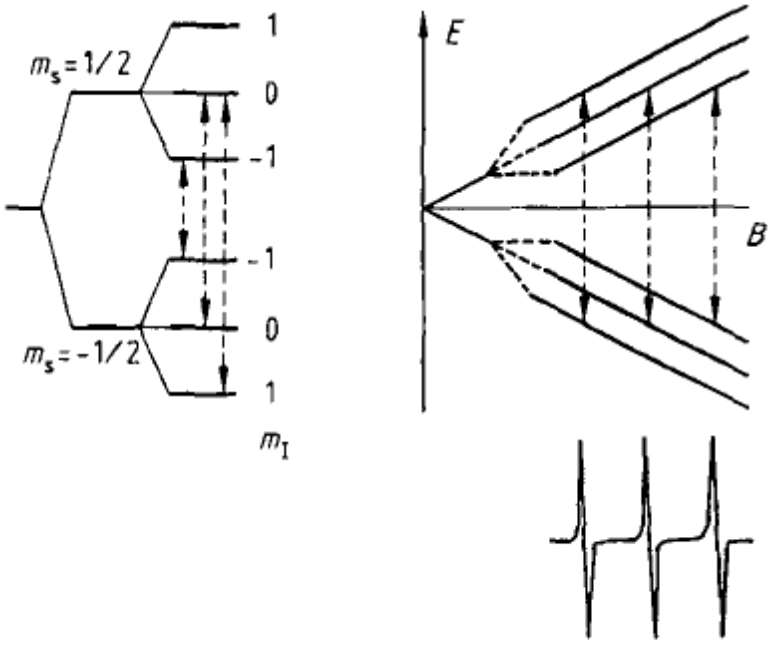

Figure 32. Simple ESR spectrum
P. L. Nordio in [64] (with permission)