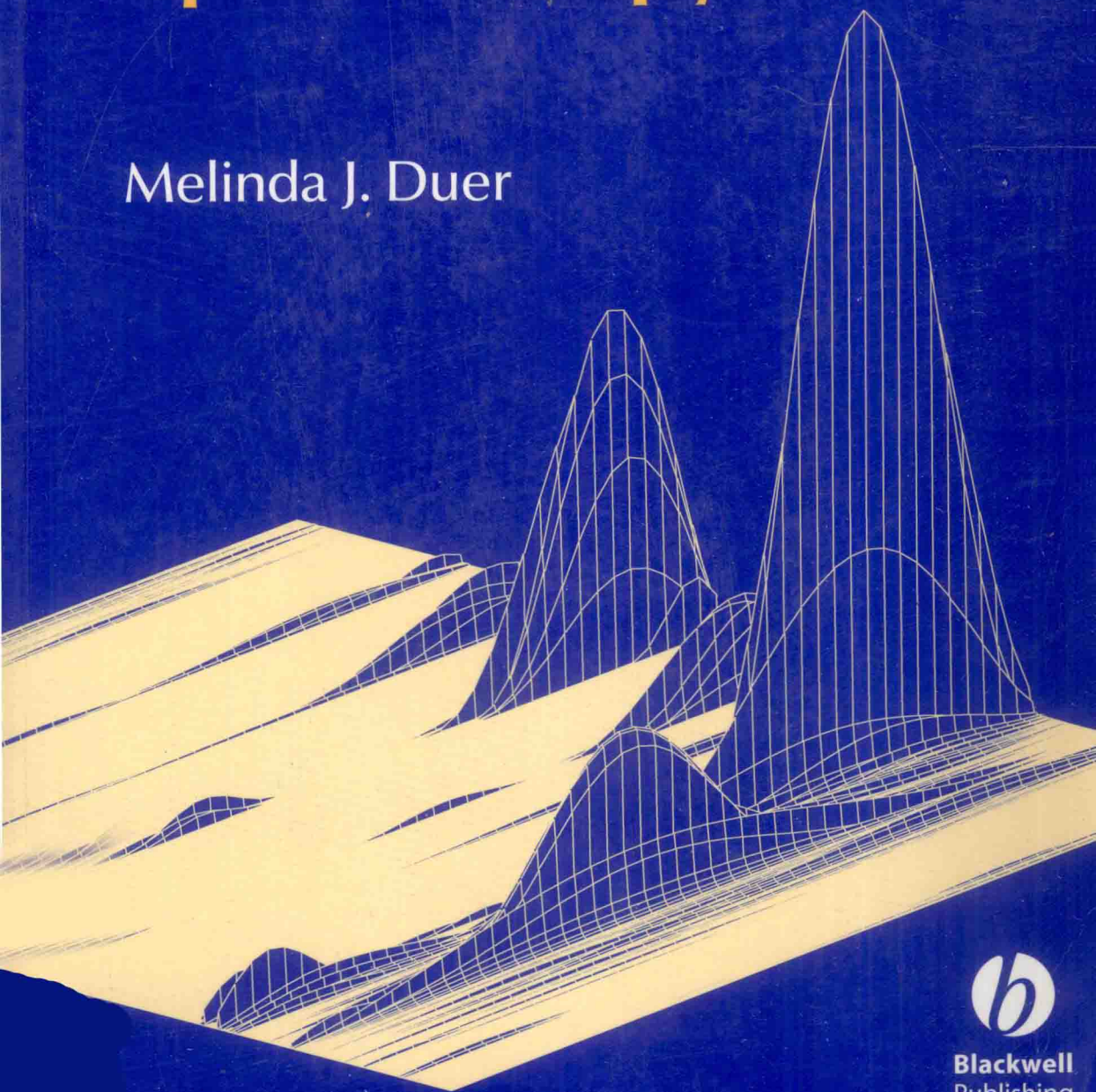


Introduction to
**Solid-State NMR
Spectroscopy**

Melinda J. Duer



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Introduction to Solid-State NMR Spectroscopy

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Preface

The days when nuclear magnetic resonance (NMR) was a technique applicable only to solution-state samples have long since gone. In the last thirty years, NMR spectroscopists have striven to make solid-state NMR a truly useful method, applicable to a very wide range of samples. In this, they have succeeded admirably, and today NMR spectroscopists have at their disposal a huge battery of solid-state NMR experiments that allow features of molecular structure and molecular dynamics to be determined.

Spectral resolution used to be a problem for solid-state NMR. It is no longer. The resolution routinely obtainable in solid-state NMR spectroscopy is now largely limited by the homogeneity (or lack of it!) of the samples being investigated, and not by the solid-state NMR technique. Consequently, the kind of resolution typically seen in solution-state NMR spectra is now realistically achievable for the solid state.

But solid-state NMR can do so much more than simply repeat the experiments of its solution-state counterpart. Solid-state NMR experiments can be set up such that the anisotropic nuclear spin interactions, which vanish in solution-state NMR experiments, remain in force. Thus, the anisotropy of nuclear spin interactions, such as chemical shielding (giving rise to the chemical shift in the NMR spectrum), can be measured and, more to the point, *utilized*, by chemists.

Chemical shift anisotropy, dipole-dipole coupling and quadrupole coupling can all be used by the chemist to give *quantitative* information on molecular structure, conformation and dynamics. One of the huge advances in solid-state NMR in the last twenty years is the spectroscopist's ability to, in effect, switch on and off these anisotropic interactions (at least as far as the resulting NMR spectrum is concerned). This is what has enable us to measure accurately the strengths of these anisotropic interactions for use in chemistry.

So what kinds of problems can solid-state NMR solve? The short answer

is many. The detailed answer is what prompted me to write this book. It can be used, for instance, to measure internuclear distances, quantitatively, which might enable one to determine the conformation of a molecule, or the length of a hydrogen bond, or determine a significant bond angle. Of course, diffraction techniques have been traditionally used to do this job but diffraction techniques require a crystalline lattice, on a relatively long length scale, before they can give useful results on structural problems. The excellent feature of solid-state NMR is that solid-state NMR can be used effectively even in inhomogeneous or amorphous systems.

The chemistry of today, and probably of the future, has a lot to do with heterogeneous (solid) systems. Polymers are an obvious example. Beyond simple polymers, there are polymer blends where two or more polymers are mixed on a molecular scale. New polymer materials involve the mixing of polymers with inorganic components, such as clays to improve the desired material properties. None of these systems can be usefully studied by traditional diffraction techniques. Solid-state NMR on the other hand can give huge amounts of information on such systems, ranging from features of molecular structure, to the length scale of mixing in blends, to information on the nature of the interaction between the components in organic-inorganic composites. Moreover, solid-state NMR can give very useful information on the molecular dynamics in such systems. Molecular dynamics are very important in determining material properties. For example, in molecular solids, stresses are generally dissipated by deformation or displacement (temporary or otherwise) of the molecules. The least damaging way of dissipating a stress is by a distortion of the molecular conformation, possibly with concomitant (small) displacements of surrounding molecules. This route requires molecules to have certain degrees of freedom in their molecular conformation, preferably with some mechanism for restoring the original structure. One of the few ways we can study the molecular degrees of freedom is with solid-state NMR.

Many catalytic systems consist of the active catalyst material mounted on a solid support – an intrinsically heterogeneous, solid system. Again, solid-state NMR, being a technique which probes local environments, can give information about the structure and siting of catalytic species, *in situ*. Similarly, it can give useful structural information on glasses, or so-called amorphous materials, and on microcrystalline materials, where crystals suitable for diffraction methods are not obtainable.

In a completely different area, biology has always dealt with heterogeneous systems. Solid proteins in particular, are receiving increasingly large amounts of interest, especially with the linking of debilitating diseases such as Alzheimer's, CJD and Type II diabetes with solid protein deposits in vital organs of the body. Proteins are notoriously difficult to crystallize, and a

great deal of useful information on the structure of amyloid proteins, amongst others, is now being accumulated through solid-state NMR methods.

This book is intended to provide the necessary background for those wishing to use solid-state NMR to solve problems in chemistry, biochemistry, materials, geology and engineering. As such, it is suitable for undergraduates embarking on a specialist NMR course and graduate students, as well as potential solid-state NMR spectroscopists. I hope that it will give a useful starting point from which to embark into this very interesting and exciting branch of spectroscopy.

Melinda Duer

Acknowledgements

No book can be written in isolation, and this one is no exception. The discussions I have had with numerous colleagues over the years have all contributed to this book; they have been invaluable and long may scientists go on talking to each other.

One never comes to really understand a subject until one has had to teach it. I should acknowledge here the many students, both undergraduate and postgraduate, who by their insistent questioning, and their own striving to understand the principles of NMR, have surely deepened my own understanding.

There are several people who deserve special thanks: Dr James Keeler and Dr Sharon Ashbrook for discussion and their perceptive comments; Francesca Wood, Nick Groom, Peter Gierth, Robin Stein, Robin Orr and Dr Oleg Antzutkin for their painstaking work in proof reading and gently pointing out the more incomprehensible sentences. Finally, my husband Dr Neil Piercy has, as ever, kept my computer working and borne my bad tempers with patience and even a little humour.

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The Basics of NMR 1

This chapter is primarily concerned with the basics of how to describe nuclear spin systems in NMR experiments. To this end, we first consider the classical vector model, which in many cases provides a sufficient description of an uncoupled spin system. As soon as there are interactions between the spins, such as dipolar coupling, we must use a quantum mechanical model to describe the dynamics of the spin system. We will use the *density operator* approach, which combines a quantum mechanical modelling of individual spins or sets of coupled spins with an ensemble averaging over all the spins (or sets of spins) in the sample.

The latter sections of the chapter deal with the essentials of recording Fourier transform (FT) NMR spectra. This is essential as it affects the way in which we view the spins in the sample and thus must influence our theoretical description of the spin system. Throughout, each topic is dealt with in such a way as to introduce the nomenclature which will be used in the rest of the book and to remind readers of the salient points. Those requiring a more in-depth discussion of these points are strongly recommended to read the superb book by Levitt [1].

1.1 The vector model of pulsed NMR

In the semi-classical model of NMR, only the net magnetization arising from the nuclei in the sample and its behaviour in magnetic fields is considered. It is a suitable model with which to consider the NMR properties of isolated spin- $\frac{1}{2}$ nuclei, i.e. those which are not coupled to other nuclei. This model also provides a convenient picture of the effects of radiofrequency pulses on such a system. Only a brief description is given here in order to define the terms and concepts that will be used throughout this book.

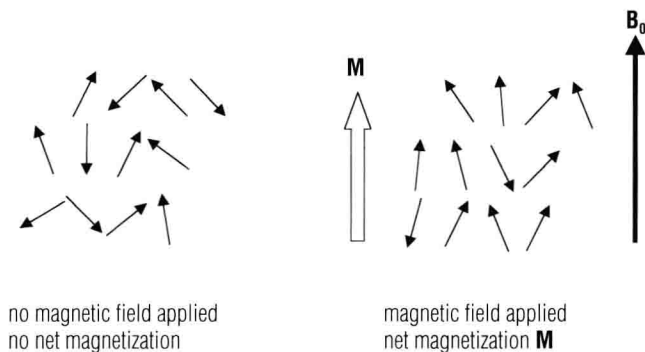


Fig. 1.1 The classical model of the formation of net nuclear magnetization in a sample. In the absence of a magnetic field, the individual nuclear magnetic moments (represented by vector arrows here) have random orientation so that there is no net magnetization. In the presence of an applied magnetic field, however, the nuclear magnetic moments are aligned preferentially with the applied field, except that thermal effects cause a distribution of orientations rather than perfect alignment. Nevertheless, there is in this case a net nuclear magnetization.

1.1.1 Nuclei in a static, uniform magnetic field

The net magnetization (which is equivalent to a bulk magnetic moment) arising from the nuclei in a sample is \mathbf{M} and is the vectorial sum of all the individual magnetic moments associated with all the nuclei (Fig. 1.1):

$$\mathbf{M} = \sum_i \mu_i \quad (1.1)$$

where μ_i is the magnetic moment associated with the i th nucleus. In turn, each nuclear magnetic moment is related to the *nuclear spin* \mathbf{I}_i of the nucleus by

$$\mu_i = \gamma \mathbf{I}_i \quad (1.2)$$

where γ is the magnetogyric ratio, a constant for a given type of nucleus. Thus we can write the net magnetization of the sample as

$$\mathbf{M} = \gamma \mathbf{J} \quad (1.3)$$

where \mathbf{J} is the net nuclear spin angular momentum of the sample giving rise to the magnetization \mathbf{M} . If the nuclei are placed in a uniform magnetic field \mathbf{B} as in the NMR experiment, a torque \mathbf{T} is exerted on the magnetization vector:

$$\mathbf{T} = \frac{d}{dt} \mathbf{J} \quad (1.4)$$

In turn, the torque in this situation is given by

$$\mathbf{T} = \mathbf{M} \times \mathbf{B} \quad (1.5)$$

Combining Equations (1.3) to (1.5), we can write

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \quad (1.6)$$

which describes the motion of the magnetization vector \mathbf{M} in the field \mathbf{B} . It can be shown that Equation (1.6) predicts that \mathbf{M} precesses about a fixed \mathbf{B} at a constant rate $\omega = \gamma B$.

In NMR, the applied magnetic field is generally labelled \mathbf{B}_0 and is taken to be along z of the laboratory frame of reference, i.e. $\mathbf{B} = (0, 0, B_0)$ in the above equations. The frequency with which the magnetization precesses about this field is defined as ω_0 , the *Larmor frequency*:

$$\omega_0 = -\gamma B_0 \quad (1.7)$$

1.1.2 The effect of rf pulses

An electromagnetic wave, such as a radiofrequency (rf) wave, has associated with it an oscillating magnetic field, and it is this field which interacts with the nuclei in addition to the static field in the NMR experiment. The rf wave is arranged in the NMR experiment so that its magnetic field oscillates along a direction perpendicular to z and the \mathbf{B}_0 field. Such an oscillating field can be thought of as a vector which can be written as the sum of two components rotating about \mathbf{B}_0 in opposite directions. The frequencies of these two components can be written as $\pm\omega_{\text{rf}}$, where ω_{rf} is the frequency of the rf pulse. Furthermore, it can be shown that only the component which rotates in the same sense as the precession of the magnetization vector \mathbf{M} about \mathbf{B}_0 has any significant effect on \mathbf{M} ; we will henceforth label this component $\mathbf{B}_1(t)$. The effect of this field is most easily seen by transforming the whole problem into a rotating frame of reference which rotates at frequency ω_{rf} around \mathbf{B}_0 ; in this frame \mathbf{B}_1 appears static, i.e. its time dependence is removed.

We can see what happens to the \mathbf{B}_0 field in this frame by examining the effect of a similar rotating frame in the absence of an rf pulse, i.e. the case of the static, uniform magnetic field considered previously. We concluded that in the presence of a field \mathbf{B}_0 the magnetization vector \mathbf{M} would precess around \mathbf{B}_0 at frequency ω_0 . If the pulse is *on resonance*, i.e. $\omega_0 = \omega_{\text{rf}}$, then the magnetization vector appears stationary in the rotating frame. In effect, then, the \mathbf{B}_0 field is removed in this frame; the effective static field parallel to z is zero and hence the magnetization \mathbf{M} is stationary. So, in the presence

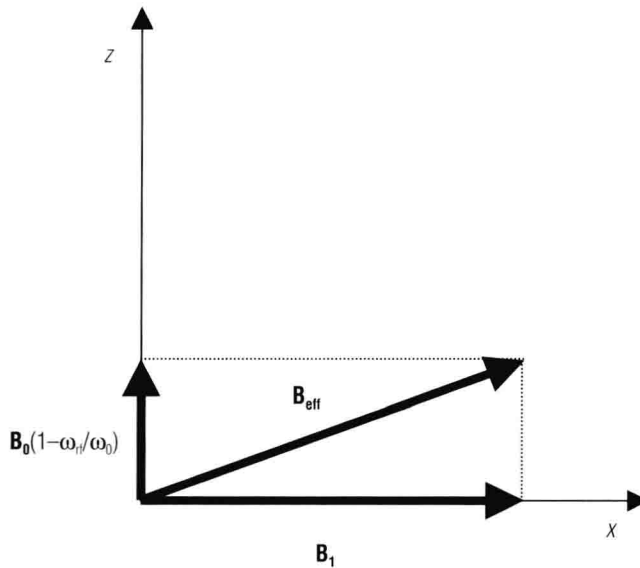


Fig. 1.2 The magnetic fields present in the rotating frame of reference. The rotating frame rotates about the laboratory z -axis at the frequency of the rf pulse, ω_{rf} . The rf irradiation is applied such that its oscillating magnetic field is along the laboratory x -axis – in common parlance, we say that the pulse is applied along x . The field due to the pulse appears static in the rotating frame, and the static field \mathbf{B}_0 appears to be reduced by a factor of ω_{rf}/ω_0 , where ω_0 is the Larmor frequency, $\omega_0 = -\gamma B_0$. The net effective field in the rotating frame is the vectorial sum of the components along x and z , \mathbf{B}_{eff} . It is this field that the nuclear spin magnetization precesses around.

of a pulse, the only field remaining in the rotating frame is the \mathbf{B}_1 field. As in the case of the magnetization experiencing the static field \mathbf{B}_0 in the laboratory frame, the result of this interaction is that the magnetization vector \mathbf{M} precesses about the resultant field, which is now \mathbf{B}_1 , at frequency $-\gamma B_1$. We define this *nutational frequency* $-\gamma B_1$ as ω_1 .

The direction of the magnetic field due to the rf pulse can be anywhere in the xy plane of the rotating frame. The *phase* of a pulse, ϕ_{rf} , is defined as the angle \mathbf{B}_1 makes to the x -axis in the rotating frame. The pulse does not have to be applied on resonance; indeed there will be many, many cases in solid-state NMR experiments when the pulse will be off resonance at least for part of the total spectrum available. In a frame rotating at ω_{rf} about \mathbf{B}_0 , in the absence of a pulse, the Larmor precession frequency is reduced from ω_0 to $\omega_0 - \omega_{rf}$ about \mathbf{B}_0 . We can infer from this that there is an effective static field along z in this frame of $(\omega_0 - \omega_{rf})/\gamma$, rather than zero as in the on-resonance case. The magnetic fields present in the rotating frame are then those shown in Fig. 1.2; there is a field of magnitude $(\omega_0 - \omega_{rf})/\gamma$ along z and B_1 along x (for a pulse with phase 0°). The nuclear magnetization precesses around the resultant field \mathbf{B}_{eff} shown in Fig. 1.2.

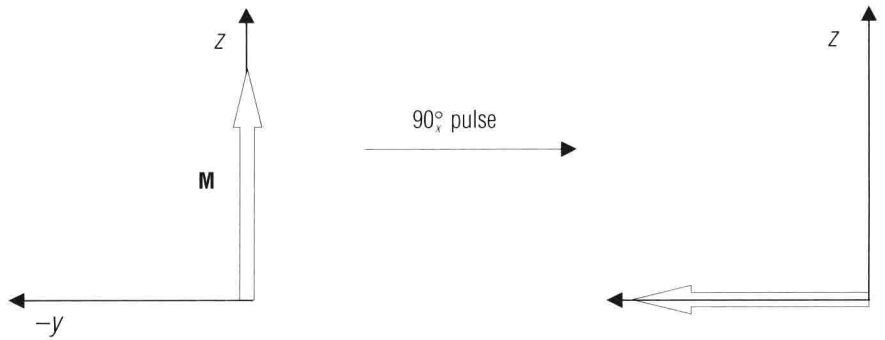


Fig. 1.3 The effect of a 90° on-resonance pulse on equilibrium magnetization in the rotating frame. The equilibrium magnetization rotates by 90° about x and ends up along $-y$.

NMR spectroscopists talk generally of an rf pulse ‘flipping’ the magnetization. The *flip angle* or *nututation angle*, θ_{rf} , of an on-resonance pulse is the angle that the pulse field B_1 turns the magnetization during time τ_{rf} :

$$\theta_{\text{rf}} = \omega_1 \tau_{\text{rf}} = \gamma B_1 \tau_{\text{rf}} \quad (1.8)$$

Thus, a 90° pulse is simply one which has a flip angle of $\theta_{\text{rf}} = \pi/2$ radians or 90° . The corresponding pulse length is referred to as the 90° pulse length. Rf pulses along x in the rotating frame are referred to as ‘ x -pulses’, those along y as ‘ y -pulses’, and so on.

By definition, positive rotations are anticlockwise about the given axis. So, after a 90° x -pulse (for shorthand labelled 90_x°), nuclear magnetization M , which started along z , is left lying along $-y$ (Fig. 1.3). From the point at which the rf pulse is turned off, the magnetization acts under the only magnetic field remaining, which is the effective field along z , of magnitude $(\omega_0 - \omega_{\text{rf}})/\gamma$, i.e. zero if the rotating frame frequency ω_{rf} is the same as the Larmor frequency, ω_0 . If the effective field along z is zero, then the magnetization is stationary in the rotating frame after the pulse is switched off; if non-zero, the magnetization precesses around z from the position it was in at the end of the pulse at frequency $\omega_0 - \omega_{\text{rf}}$.

1.2 The quantum mechanical picture: hamiltonians and the Schrödinger equation

In the quantum mechanical picture, we start from a consideration of individual nuclei and, from this, generate a picture for the whole collection of nuclei in a sample. This is called the *ensemble average*. We will often refer to the *spin system* by which we mean a nuclear spin or collection of inter-