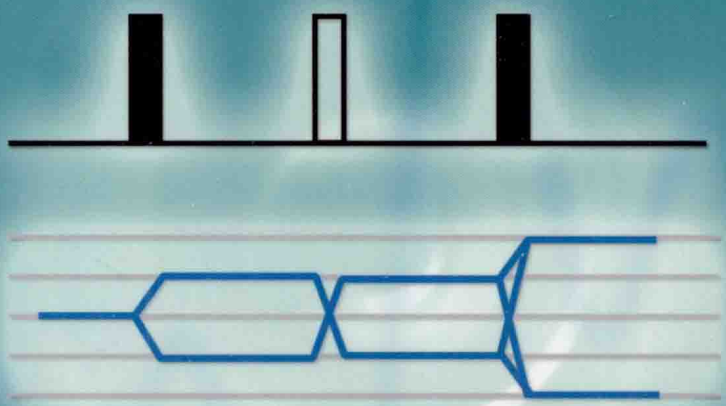
Understanding NMR Spectroscopy

SECOND EDITION



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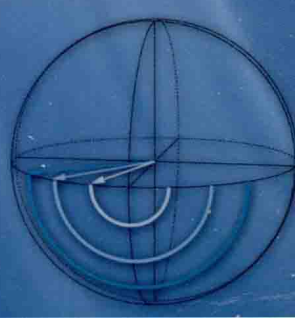

Understanding NMR Spectroscopy – Second Edition

James Keeler

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Preface

I am very pleased to have the opportunity to produce a second edition of *Understanding NMR Spectroscopy*, not least as I have been encouraged by the many kind comments that I have received by users of the first edition. For all its undoubted flaws, the book has clearly been found to be useful in helping people to get to grips with the theory of NMR.

I have resisted the temptation to add a great deal of additional material or to make the discussion more technical. However, I have included a new chapter which covers two topics which, in retrospect, seemed to be serious omissions from the first edition. The first topic is how product operators can be extended to describe experiments in AX_2 and AX_3 spin systems, thus making it possible to discuss the important APT, INEPT and DEPT experiments often used in ^{13}C spectroscopy.

The second topic is spin system analysis i.e. how shifts and couplings can be extracted from strongly coupled (second-order) spectra. In the early days of NMR this kind of analysis was all but essential since the low field strengths then available meant that spectra were often strongly coupled. The current use of much higher fields means that strong-coupling effects are less common, but they have not gone away completely. It therefore remains important to be aware of such effects and their consequences for the appearance of spectra. In a related topic, I also discuss how the presence of chemically equivalent spins leads to spectral features which are somewhat unusual and possibly misleading. In contrast to strong-coupling effects, these features are independent of the field strength and so are not mitigated by the move to higher fields.

The chapter on relaxation has been reorganised, and a discussion of chemical exchange effects has been introduced in order to help with the explanation of transverse relaxation. Finally, I have added a short section on double-quantum spectroscopy to Chapter 10.

The use of two-colour printing will, I hope, both improve the clarity of many of the diagrams and improve the appearance of the printed pages.

I am very much indebted to Dr Andrew Pell (now at the École Normale Supérieure de Lyon) who found time between completing his PhD and starting a postdoctoral position to help me in the preparation of this edition. Andy worked on adding colour to the figures, produced some additional simulations for Chapter 9, recorded all of the experimental spectra and commented on the new sections. I am also grateful to Dr Daniel Nietlispach (Department of Biochemistry, University of Cambridge) for once again providing very useful and perceptive comments on the new material.

Cambridge, January 2010

Preface to the first edition

I owe a huge debt of gratitude to Dr Daniel Nietlispach and Dr Katherine Stott (both from the Department of Biochemistry, University of Cambridge) who have read, corrected and commented on drafts of the entire book. Their careful and painstaking work has contributed a great deal to the final form of the text and has, in my view, improved it enormously. I am also grateful to them for their constant enthusiasm, which sustained and encouraged me throughout the project. I could not have wanted for two more constructive and helpful readers.

Special thanks are also due to Professor Nikolaus Loening (Lewis and Clark College, Portland, Oregon) who, at short notice and with great skill, provided all of the experimental spectra in the book. His good humoured response to my pernickety requirements is much appreciated. Andrew Pell (Selwyn College, Cambridge) also deserves special mention and thanks for his skilled assistance in producing the solutions manual for the exercises.

I would like to acknowledge the support and advice from my collaborator and colleague Dr Peter Wothers (Department of Chemistry, University of Cambridge): he remains both my sternest critic and greatest source of encouragement. I am also grateful to Professor Jeremy Sanders (Department of Chemistry, University of Cambridge) for his much valued support and advice.

My appreciation and understanding of NMR, such that it is, has been very much influenced by those I have been fortunate enough to work alongside, both as research students and collaborators; I thank them for their insights. I would also like to thank Professor Malcolm Levitt (Department of Chemistry, University of Southampton), Professor Art Palmer (Columbia University, New York) and Dr David Neuhaus (MRC LMB, Cambridge) for tirelessly answering my many questions.

This book grew out of a series of lecture notes which, over a number of years, I prepared for various summer schools and graduate courses. On the initiative of Dr Rainer Haessner (Technische Universität, Munich), the notes were made available on the web, and since then I have received a great deal of positive feedback about how useful people have found them. It was this, above all, which encouraged me to expand the notes into a book.

The book has been typeset by the author using LaTeX, in the particular implementation distributed as MiKTeX (`www.miktex.org`). I wish to express my thanks to the many people who develop and maintain the LaTeX system. All of the diagrams have been prepared using *Adobe Illustrator* (Adobe Systems Inc., San Jose, California), sometimes in combination with *Mathematica* (Wolfram Research Inc., Champaign, Illinois).

Finally, I am delighted to be able to dedicate this book to Professor Ray Freeman. I was lucky enough to have started my NMR career in Ray's group, and what I learnt there, both from Ray and my fellow students, has stood me in good stead ever since. My appreciation for Ray has continued as strong as ever since those early days, and I am pleased to have this opportunity to acknowledge the debt I owe him.

Cambridge, July 2005

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Dedicated to

Professor Ray Freeman FRS

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What this book is about and who should read it

This book is aimed at people who are familiar with the use of routine NMR for structure determination and who wish to deepen their understanding of just exactly how NMR experiments 'work'. It is one of the great virtues of NMR spectroscopy that one can use it, and indeed use it to quite a high level, without having the least idea of how the technique works. For example, we can be taught how to interpret two-dimensional spectra, such as COSY, in a few minutes, and similarly it does not take long to get to grips with the interpretation of NOE (nuclear Overhauser effect) difference spectra. In addition, modern spectrometers can now run quite sophisticated NMR experiments with the minimum of intervention, further obviating the need for any particular understanding on the part of the operator.

You should reach for this book when you feel that the time has come to understand just exactly what is going on. It may be that this is simply out of curiosity, or it may be that for your work you need to employ a less common technique, modify an existing experiment to a new situation or need to understand more fully the limitations of a particular technique. A study of this book should give you the confidence to deal with such problems and also extend your range as an NMR spectroscopist.

One of the difficulties with NMR is that the language and theoretical techniques needed to describe it are rather different from those used for just about all other kinds of spectroscopy. This creates a barrier to understanding, but it is the aim of this book to show you that the barrier is not too difficult to overcome. Indeed, in contrast to other kinds of spectroscopy, we shall see that in NMR it is possible, quite literally on the back of an envelope, to make exact predictions of the outcome of quite sophisticated experiments. Further, once you have got to grips with the theory, you should find it possible not only to analyse existing experiments but also dream up new possibilities.

There is no getting away from the fact that we need quantum mechanics in order to understand NMR spectroscopy. Developing the necessary quantum mechanical ideas from scratch would make this book rather a

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hard read. Luckily, it is not really necessary to introduce such a high level of formality provided we are prepared to accept, on trust, certain quantum mechanical ideas and are prepared to use these techniques more or less as a recipe. A good analogy for this approach is to remember that it is perfectly possible to learn to add up and multiply without appreciating the finer points of number theory.

One of the nice features we will discover is that, despite being rigorous, the quantum mechanical approach still retains many features of the simpler *vector model* often used to describe simple NMR experiments. Once you get used to using the quantum mechanical approach, you will find that it does work in quite an intuitive way and gives you a way of 'thinking' about experiments without always having to make detailed calculations.

Quantum mechanics is, of course, expressed in mathematical language, but the mathematics we will need is not very sophisticated. The only topic which we will need which is perhaps not so familiar is that of complex numbers and the complex exponential. These will be introduced as we go along, and the ideas are also summarized in an appendix.

1.1 How this book is organized

Optional sections are marked like this:

Optional section ⇒

The ideas we need to describe NMR experiments are built up chapter by chapter, and so the text will make most sense if it read from the beginning. Certain sections are not crucial to the development of the argument and so can be safely omitted at a first reading; these sections are clearly marked as such in the margin.

Chapter 6, which explains how quantum mechanics is formulated in a way useful for NMR, is also entirely optional. It provides the background to the product operator formalism, which is described in Chapter 7, but this latter chapter is written in such a way that it does not rely on anything from Chapter 6. At some point, I hope that you will want to find out about what is written in Chapter 6, but if you decide not to tackle it, rest assured that you will still be able to follow what goes on in the rest of the book.

The main sequence of the book really ends with Chapter 8, which is devoted to two-dimensional NMR. You should dip into Chapters 9–13 as and when you feel the need to further your understanding of the topics they cover. This applies particularly to Chapter 10 which discusses a selection of more advanced ideas in two-dimensional NMR, and Chapter 11 which is concerned with the rather 'technical' topic of how to write phase cycles and how field gradient pulses are used.

Quite deliberately, this book starts off at a gentle pace, working through some more-or-less familiar ideas to start with, and then elaborating these as we follow our theme. This means that you might find parts of the discussion rather pedestrian at times, but the aim is always to be clear about what is going on, and not to jump over steps in calculations or arguments. The same philosophy is followed when it comes to the more difficult and/or less familiar topics which are introduced in the later chapters. If you are already familiar with the vector model of pulsed NMR, and are happy with thinking about multiplets in terms of energy levels, then you might wish to jump in at Chapter 6 or Chapter 7.

Each chapter ends with some exercises which are designed to help your understanding of the ideas presented in that chapter. Tackling the exercises will undoubtedly help you to come to grips with the underlying ideas.

1.2 Scope and limitations

In this book we are going to discuss the high-resolution NMR of liquid samples and we will concentrate, almost exclusively, on spin-half nuclei (mainly ^{1}H and ^{13}C). The NMR of solids is an important and fast-developing field, but one which lies outside the scope of this book.

The experiments we will choose to describe are likely to be encountered in the routine NMR of small to medium-sized molecules. Many of the experiments are also applicable to the study of large biomolecules, such as proteins and nucleic acids. The special multi-dimensional experiments which have been devised for the study of proteins will not be described here, but we note that such experiments are built up using the repertoire of pulsed techniques which we are going to look at in detail.

The existence of the chemical shift and scalar coupling is, of course, crucial to the utility of NMR spectroscopy. However, we will simply treat the values of shifts and coupling constants as experimentally derived parameters; we will have nothing to say about their calculation or interpretation – topics which are very well covered elsewhere.

1.3 Context and further reading

This is not a 'how to' book: you will find no advice here on how to select and run a particular experiment, nor on how to interpret the result in terms of a chemical structure. What this book is concerned with is how the experiments work. However, it is not a book of NMR theory for its own sake: rather, the ideas presented, and the theories introduced, have been chosen carefully as those most useful for understanding the kinds of NMR experiments which are actually used.

There are many books which describe how modern NMR spectroscopy is applied in structural studies, and you may wish to consult these alongside this text in order to see how a particular experiment is used in practice. Two useful texts are: J. K. M. Sanders and B. K. Hunter, *Modern NMR Spectroscopy* (2nd edition, OUP, 1993), and T. D. W. Claridge, *High-Resolution NMR Techniques in Organic Chemistry* (Elsevier Science, 1999).

There are also a number of books which are at roughly the same level as this text and which you may wish to consult for further information or an alternative view. Amongst these, R. Freeman, *Spin Choreography* (Spektrum, 1997) and F. J. M. van de Ven, *Multidimensional NMR in Liquids* (VCH, 1995) are particularly useful. If you wish to go further and deeper into the theory of NMR, M. H. Levitt, *Spin Dynamics* (2nd edition, John Wiley & Sons, Ltd, 2008) is an excellent place to start.

The application of NMR to structural studies of biomolecules is a vast area which we will only touch on from time to time. A detailed account of this important area, covering both theoretical and practical matters, can be

found in J. Cavanagh, W. J. Fairbrother, A. G. Palmer III, M. Rance and N. J. Skelton, *Protein NMR Spectroscopy* (2nd edition, Academic Press, 2007).

At the end of each chapter you will also find suggestions for further reading. Many of these are directions to particular chapters of the books we have already mentioned.

1.4 On-line resources

A solutions manual for the exercises at the end of each chapter is available on-line via the *spectroscopyNOW* website:

`http://www.spectroscopynow.com/nmr`
follow the 'Education' link from this page

A list of corrections and amendments will also be available on this site, as well as other additional material. It will also be possible to download all of the figures (in 'jpeg' format) from this book.

1.5 Abbreviations and acronyms

ADC	analogue to digital converter
APT	attached proton test
COSY	correlation spectroscopy
CTP	coherence transfer pathway
DEPT	distortionless enhancement by polarization transfer
DQF COSY	double-quantum filtered COSY
FID	free induction decay
HETCOR	heteronuclear correlation
HMBC	heteronuclear multiple-bond correlation
HMQC	heteronuclear multiple-quantum correlation
HSQC	heteronuclear single-quantum correlation
INEPT	insensitive nuclei enhanced by polarization transfer
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
RF	radiofrequency
rx	receiver
ROESY	rotating frame Overhauser effect spectroscopy
SHR	States–Haberkorn–Ruben
SNR	signal-to-noise ratio
TOCSY	total correlation spectroscopy
TPPI	time proportional phase incrementation
TROSY	transverse relaxation optimized spectroscopy
tx	transmitter

2

Setting the scene

You will probably find that much of this chapter covers topics you are familiar with or have at least come across before. The point of the chapter is, as the title says, to set the scene for what follows by reminding you of the basic language of NMR, how we describe NMR spectra and how some important quantities are defined. There is also a section on oscillations and rotations, explaining how these are described and represented mathematically. These are key ideas which we will use extensively in the rest of the book.

2.1 NMR frequencies and chemical shifts

Like all forms of spectroscopy, an NMR spectrum is a plot of the intensity of absorption (or emission) on the vertical axis against frequency on the horizontal axis. NMR spectra are unusual in that they appear at rather low frequencies, typically in the range 10 to 800 MHz, corresponding to wavelengths from 30 m down to 40 cm. This is the radiofrequency (RF) part of the electromagnetic spectrum which is used for radio and TV broadcasts, mobile phones etc.

It is usual in spectroscopy to quote the frequency or wavelength of the observed absorptions; in contrast, in NMR we give the positions of the lines in 'ppm' using the chemical shift scale. The reason for using a shift scale is that it is found that the frequencies of NMR lines are directly proportional to the magnetic field strength. So doubling the field strength doubles the frequency, as shown in Fig. 2.1 on the following page. This field dependence makes it difficult to compare absorption frequencies between spectrometers which operate at different field strengths, and it is to get round this problem that the chemical shift scale is introduced. On this scale, the positions of the peaks are *independent of the field strength*. In this section we will explore the way in which the scale is defined, and also how to convert back and forth between frequencies and ppm – something we will need to do quite often.

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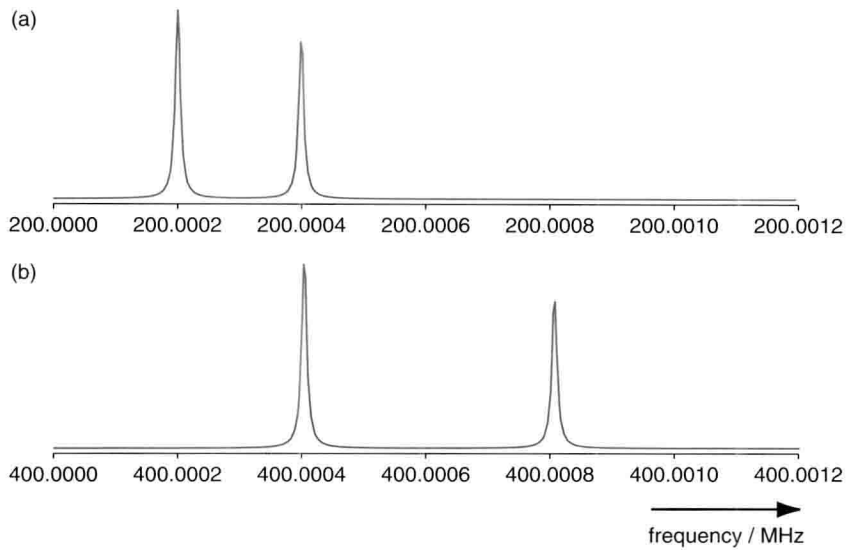

Fig. 2.1 Schematic NMR spectra consisting of two lines. In (a) the magnetic field is such that the two lines appear at 200.0002 and 200.0004 MHz, respectively; their separation is 200 Hz. The spectrum shown in (b) is that expected when the applied magnetic field is doubled. The frequency of each peak is doubled and, as a consequence, the separation between the two peaks has now also doubled to 400 Hz.

Before we look at the definition of the chemical shift it is worthwhile pointing out that the frequency at which an NMR signal appears also depends on the nuclear isotope (e.g. ^{1}H, ^{13}C, ^{15}N etc.) being studied. Also, for a given field, the NMR absorptions for a particular isotope cover rather a small range of frequencies relative to the absolute frequency of the absorption. In an experiment it is therefore usual only to measure the NMR spectrum from one particular isotope at a time.

2.1.1 Chemical shift scales

The chemical shift scale is set up first by agreeing a simple *reference compound*, a line from which is taken to define zero on the chemical shift scale. For ^{1}H and ^{13}C this reference compound is TMS. The choice of reference compound is arbitrary, but subject to careful international agreement so as to make sure everyone is using the same compound and hence the same origin on their shift scales.

The position of a peak in the spectrum is specified by measuring its frequency separation from the reference peak, and then dividing this difference by the frequency of the reference peak. As we are taking the *ratio* of two frequencies, the field dependence cancels out. The ratio thus specifies the position of a line in a way which is *independent* of the applied field, which is what we require.

Expressed mathematically, the chemical shift δ is given by

$$\delta(\text{ppm}) = 10^6 \times \frac{\upsilon - \upsilon_{\text{ref}}}{\upsilon_{\text{ref}}}, \tag{2.1}$$

where υ is the frequency of the NMR line in question and υ_{ref} is the frequency of the line from the agreed reference compound. Clearly, the line from the reference compound will appear at $\delta = 0$.

It is usual to quote chemical shifts in 'parts per million' (ppm) in order to make the numbers more convenient, and this is why in the definition of

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