

Ursula Weber,
Herbert Thiele

**NMR Spectroscopy:
Modern
Spectral Analysis**

 **WILEY-VCH**

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Modern
Spectral Analysis**

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Ursula Weber,
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D-28359 Bremen
Germany

A CD-ROM containing teaching versions of several WIN-NMR programs (© Bruker Analytik GmbH) is included with this book. Readers can obtain further information on this software by contacting:
Bruker Analytik GmbH, Silberstreifen, D-76287 Rheinstetten, Germany.

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Preface

In recent years Nuclear Magnetic Resonance spectroscopy has become one of the most popular and elegant methods for the elucidation of chemical structures. The rapid development in FOURIER transform techniques such as n-dimensional and imaging experiments has established NMR spectroscopy as the primary analytical method, not only in chemistry but also in the realms of biology, physics, medicine and related sciences.

The masses of raw data *acquired* with the NMR spectrometer need to be *processed, analyzed, interpreted* and *archived* for use in future structural problems.

| <i>Action</i> | <i>Tool</i> | <i>Result</i> | <i>Volume</i> |
|----------------|-------------|---------------|---------------|
| Acquisition | ⇒ | FID | 2 |
| ↓ | | ↕ | |
| Processing | ⇒ | Spectrum | 1 |
| ↓ | | ↕ | |
| Analysis | ⇒ | Parameter | 3 |
| ↓ | | ↕ | |
| Interpretation | ⇒ | Structure | 1,3,4 |
| ↓ | | ↕ | |
| Archiving | ⇒ | Knowledge | 4 |

Fig. 1: Flow scheme of data preparation in NMR spectroscopy.

In Fig. 1, the vertical black arrows (↓) on the left hand side symbolize the steps required in the analysis to obtain the information listed on the same row in the *Result* column, e.g. to obtain a spectrum (*Result*), it is first necessary to acquire and process (*Action*) the raw data. The horizontal white arrows (⇒) symbolize the software tools (*Tool*) required to obtain the desired *Result*. The strategy necessary to successfully perform the appropriate *Action* is described in the corresponding *Volume* in the series *Spectroscopic Techniques: An Interactive Course*. Thus the present volume, *NMR Spectroscopy: Modern Spectral Analysis* will discuss the various software tools and techniques required to perform the spectrum *Analysis* to obtain the correct NMR *Parameters*. Finally, the bi-directional vertical black arrows in the *Result* column symbolize the strong relationships between the different types of data that can be obtained which are discussed in detail in the various books in this series.

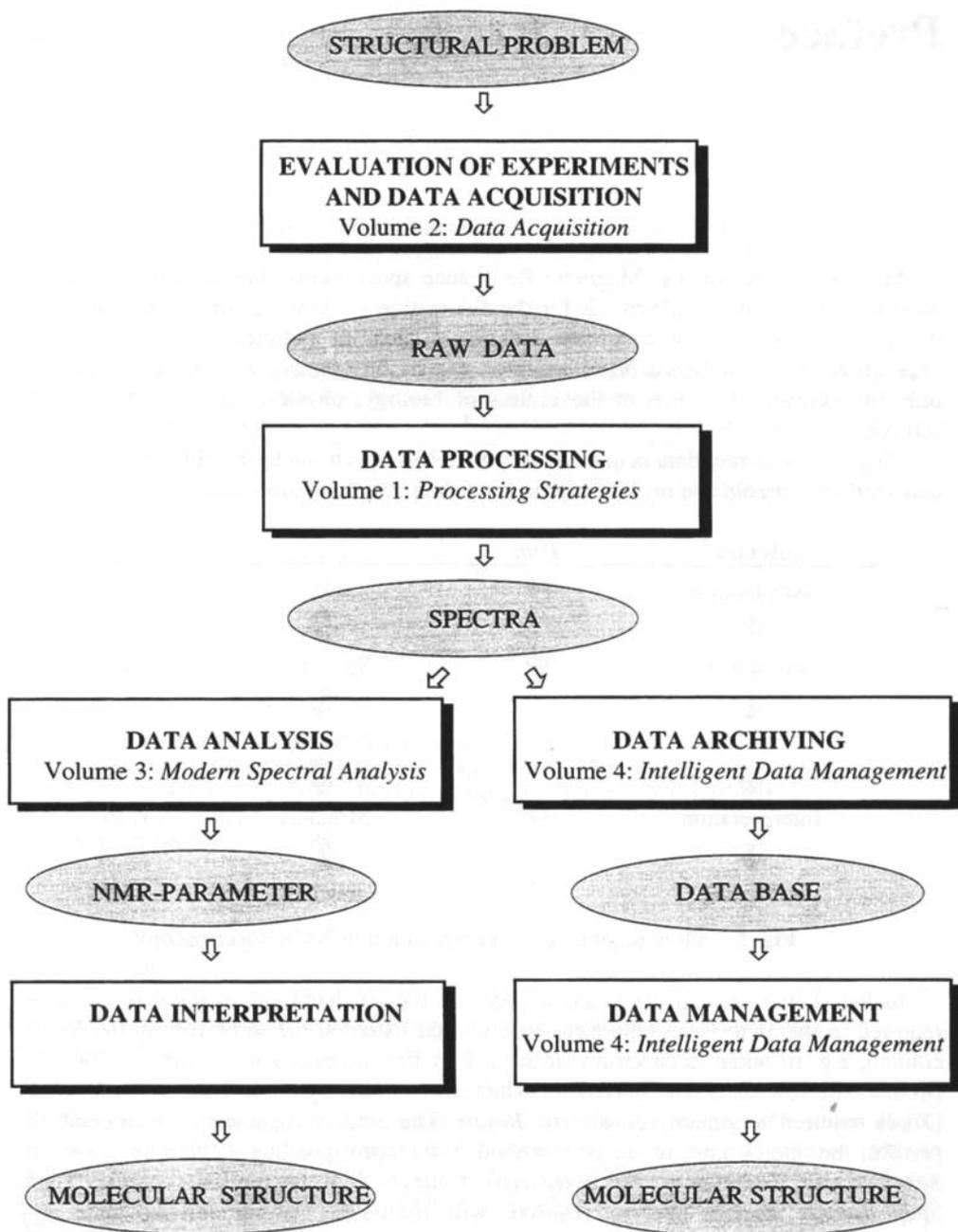


Fig. 2: Concept in the series of the interactive course: NMR Spectroscopy.

- Volume 1 – Processing Strategies
- Volume 2 – Data Acquisition
- Volume 3 – Modern Spectral Analysis
- Volume 4 – Intelligent Data Management

The concept of the series is visualized in Fig. 2, and the contents of volumes 1–4 may be summarized as follows:

Volume 1: *Processing Strategies*

Processing NMR data transforms the acquired time domain signal(s) – depending on the experiment – into 1D or 2D spectra. This is certainly the most central and important step in the whole NMR analysis and is probably the part, which is of interest to the vast majority of NMR users. Not everyone has direct access to an NMR spectrometer, but most have access to some remote computer and would prefer to process their own data according to their special needs with respect to their spectroscopic or structural problem and their ideas concerning the graphical layout *i.e.* for presentation of reports, papers or thesis. It is essential for the reliability of the extracted information and subsequent conclusions with respect to molecular structure, that a few general rules are followed when processing NMR data. It is of great advantage that the user is informed about the many possibilities for data manipulation so they can make the best use of their NMR data. This is especially true in more demanding situations when dealing with subtle, but nevertheless important spectral effects. Modern NMR data processing is not simply a FOURIER transformation in one or two dimensions, it consists of a series of additional steps in both the time and the frequency domain designed to improve and enhance the quality of the spectra.

Processing Strategies gives the theoretical background for all these individual processing steps and demonstrates the effects of the various manipulations on suitable examples. The powerful BRUKER 1D WIN-NMR, 2D WIN-NMR and GETFILE software tools, together with a set of experimental data for two carbohydrate compounds allow you to carry out the processing steps on your own remote computer, which behaves in some sense as a personal “NMR processing station”. You will learn how the quality of NMR spectra may be improved, experience the advantages and limitations of the various processing possibilities and most important, as you work through the text, become an expert in this field. The unknown structure of one of the carbohydrate compounds should stimulate you to exercise and apply what you have learnt. The elucidation of this unknown structure should demonstrate, how powerful the combined application of several modern NMR experiments can be and what an enormous and unexpected amount of structural information can thereby be obtained and extracted by appropriate data processing. It is this unknown structure which should remind you throughout this whole educational series that NMR data processing is neither just “playing around” on a computer nor some kind of scientific “l’art pour l’art”. The main

goal for measuring and processing NMR data and for extracting the structural information contained in it, is to get an insight into how molecules behave.

Furthermore, working through *Processing Strategies* should encourage you to study other topics covered by related volumes in this series. This is particularly important if you intend to operate a NMR spectrometer yourself, or want to become familiar with additional powerful software tools to make the best of your NMR data.

Volume 2: *Data Acquisition*

Any NMR analysis of a structural problem usually starts with the selection of the most appropriate pulse experiment(s). Understanding the basic principles of the most common experiments and being aware of the dependence of spectral quality on the various experimental parameters are the main prerequisites for the successful application of any NMR experiment. Spectral quality on the other hand strongly determines the reliability of the structural information extracted in subsequent steps of the NMR analysis. Even if you do not intend to operate a spectrometer yourself, it would be beneficial to acquire some familiarity with the interdependence of various experimental parameters e.g. acquisition time and resolution, repetition rate, relaxation times and signal intensities. Many mistakes made with the application of modern NMR spectroscopy arise because of a lack of understanding of these basic principles. *Data Acquisition* covers these various aspects and exploits them in an interactive way using the Bruker software package NMRSIM. Together with 1D WIN-NMR and 2D WIN-NMR, NMRSIM allows you to simulate routine NMR experiments and to study the interdependence of a number of NMR parameters and to get an insight into how modern multiple pulse NMR experiments work.

Volume 3: *Modern Spectral Analysis*

Following the strategy of spectral analysis, the evaluation of a whole unknown structure, of the local stereochemistry in a molecular fragment or of a molecules dynamic properties, depends on NMR parameters. Structural informations are obtained in subsequent steps from chemical shifts, homo- and heteronuclear spin-spin connectivities and corresponding coupling constants and from relaxation data such as NOEs, ROEs, T_{1s} or T_{2s} and assumes that the user is aware of the typical ranges of these NMR parameters and of the numerous correlations between NMR and structural parameters, i.e. between coupling constants, NOE enhancements or line widths and dihedral angles, internuclear distances and exchange rates respectively. However, the extraction of these NMR parameters from the corresponding spectra is not always straightforward,

- The spectrum may exhibit extensive signal overlap, a problem common with biomolecules.
- The spectrum may contain strongly coupled spin systems.
- The molecule under investigation may be undergoing dynamic or chemical exchange.

Modern Spectral Analysis discusses the strategies needed to efficiently and competently extract NMR parameters from the corresponding spectra. You will be shown how to use the spectrum simulation package WIN-DAISY to extract chemical shifts, coupling constants and individual line widths from even highly complex NMR spectra. In addition, the determination of T_1 s, T_2 s or NOEs using the special analysis tools of 1D WIN-NMR will be explained. The simulation of double resonance spectra are shown using the program WIN-DR and the calculation of dynamic NMR spectra with WIN-DYNAMICS is trained. Sets of spectral data for a series of representative compounds, including the two carbohydrates mentioned in volume 1 are used as instructive examples and for problem solving. NMR analysis often stops with the plotting of the spectrum thereby renouncing a wealth of structural data. This part of the series should encourage you to go further and fully exploit the valuable information "hidden" in the carefully determined NMR parameters of your molecule.

Volume 4: *Intelligent Data Management*

The evaluation and interpretation of NMR parameters to establish molecular structures is usually a tedious task. An alternative way to elucidate a molecular structure is to directly compare its measured NMR spectrum – serving here as a fingerprint of the investigated molecule – with the corresponding spectra of known compounds. An expert system combining a comprehensive data base of NMR spectra with associated structures, NMR spectra prediction and structure generators not only facilitates this part of the NMR analysis but makes structure elucidation more reliable and efficient.

In *Intelligent Data Management*, an introduction to the computer-assisted interpretation of molecular spectra of organic compounds using the Bruker WIN-SPECEDIT software package is given. This expert system together with the Bruker STRUKED software tool is designed to follow up the traditional processing of NMR spectra using 1D- and 2D WIN-NMR in terms of structure-oriented spectral interpretation and signal assignments. WIN-SPECEDIT offers not only various tools for automatic interpretation of spectra and for structure elucidation, including the prediction of spectra, but also a number of functions for so-called "authentic" archiving of spectra in a database, which links molecular structures, shift information and assignments with original spectroscopic data. You will learn to exploit several interactive functions such as the simple assignment of individual resonances to specific atoms in a structure and about a number of automated functions such as the recognition of signal groups (multiplets) in ^1H NMR spectra. In addition, you will also learn how to calculate and predict chemical shifts and how to generate a local database dedicated to your own purposes. Several examples and exercises, including the two carbohydrate compounds, serve to apply all these tools and to give you the necessary practice for your daily spectroscopic work.

The concept of the series is the complementary self-teaching method of textbook and interactive data treatment using the *Teaching Versions* of the WIN-NMR family of programs stored on your own personal computer (PC). Each book is delivered with a CD-ROM which includes all the appropriate software tools and the corresponding data base to enable you to perform all the "Check it" exercises in the textbook.

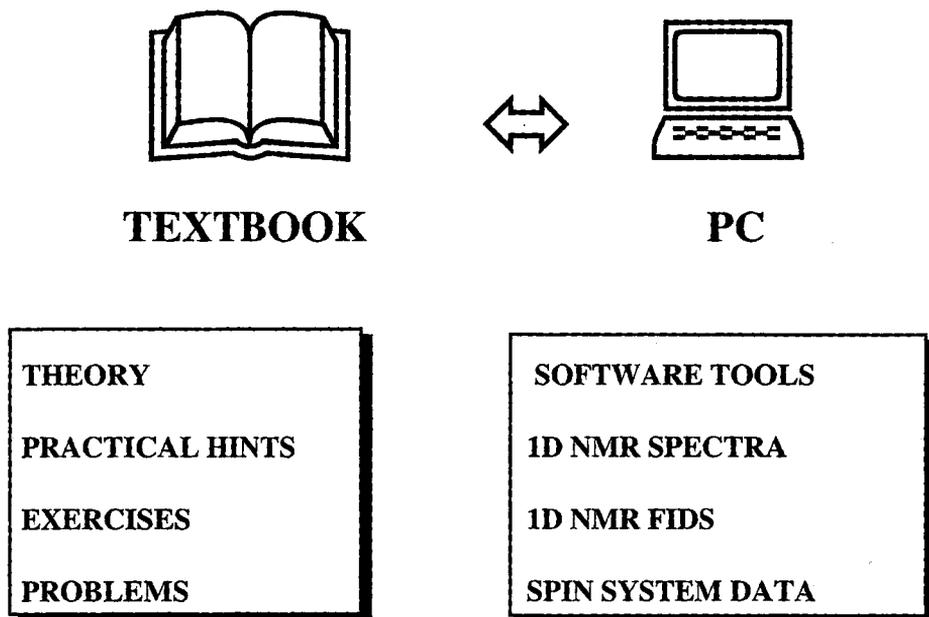


Fig. 3: Mutual interaction between textbook and PC.

The textbook contains a brief theoretical background description stressing the practical aspects of *why* things are done in a particular manner. The “Check it” exercises in the textbook describe the treatment of the NMR data using the software tools and initiate the switching from the textbook to the software tools loaded on your PC (Fig. 3). The way *how* to solve the problems with respect to the theoretical descriptions is explained in the “Check it” text. The results may be verified by comparing your own results either with the comments made in the text or by using the solutions delivered with the data base. Using this “learning-by-doing” method with its complementary *why-and-how* approach you will be shown the most effective way to solve problems and at the same time you will also become familiar with the software tools that make up the WIN-NMR family of programs.

The Teaching Versions are identical with the full program versions, but they can only process the special NMR data sets delivered on the CD-ROM. To order the full program version, contact your local BRUKER office, or send your order to:

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 Silberstreifen
 D-76287 Rheinstetten/Karlsruhe
 FRG

Tel.: +49 (0)721 5161 0
 Fax: +49 (0)721 5161 297

When you begin this text, it is assumed that you are already skilled in the processing of NMR data, which is the subject of the first volume of this series, *NMR Spectroscopy: Processing Strategies*. The present volume, *NMR Spectroscopy: Modern Spectral Analysis*, deals with the analysis of one-dimensional NMR spectra. Methods to determine NMR parameters such as chemical shifts, scalar coupling constants, half-height line widths, relaxation times and rate constants are described. Special emphasis is laid on the understanding of coupled spin systems and on the abstract concept of spin systems but the aim is always to use this information in a *practical* way to obtain structural information. The book contains many examples and discusses in detail the interpretation of NMR parameters in order either to verify a model structure or to determine an unknown structure and simultaneously teaches you how to analyze your own 1D NMR data in the most effective manner.

It is the primary aim of the series to teach the user how NMR spectra may be obtained from the data acquired on a spectrometer and how these spectra may be used to establish a molecular structure following one of the two strategies outlined before. The series of volumes therefore emphasizes the methodical aspect of NMR spectroscopy, rather than the more usual analytical aspects *i.e.* the description of the various NMR parameters and of how they depend on structural features, presented in numerous text books.

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Bremen, September 1997

U. Weber
H. Thiele

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1 Introduction

1.1 Scope and Audience

From the discovery of the magnetic resonance effect in 1945 [1.1], [1.2] up to the present day Nuclear Magnetic Resonance (NMR) spectroscopy has achieved an enormous importance and acceptance in chemical research for the elucidation of molecular structure. Experimental techniques underwent a revolution with the introduction of pulsed FOURIER transform spectroscopy [1.3] and highly sophisticated pulse sequences have been developed for the extraction of the desired information from one, two and even three-dimensional NMR spectra [1.4].

It was soon discovered that even 'simple' one-dimensional NMR spectra contained a wealth of information about coupled spin systems and because the extraction of NMR parameters was not always straightforward, methods for analyzing spectra were developed [1.5]–[1.8]. To understand the complexity of the measured spectra, computer programs evolved to perform the quantum mechanical calculation of NMR spectra. Within a few years a variety of iterative programs (operating on main frame computers) were written, optimizing parameters on the basis of experimental data to extract the true chemical shifts and coupling constants [1.9]–[1.11]. A review of the available programs is given in the appendix of reference [1.12]. Although numerous books and review articles have dealt with the analysis of high-resolution NMR spectra, the combination of analytical formulae, quantum mechanics and, for computer aided analysis, "user-unfriendly" software has meant that spin system analysis has not been very popular. Indeed, in many papers in the literature little or no attempt is made to analyze spin systems, signals often being reported as a "multiplet".

The introduction of new experimental techniques, particular two-dimensional experiments, has tended to push both the use and the teaching of one-dimensional spectral analysis further into the background. Consequently there is now a lack of understanding of NMR spin systems which can have serious repercussions on both the experimental and theoretical analysis of NMR data.

- In cases where the 'simple' single-pulse one-dimensional spectrum is not fully understood, the interpretation of multi-dimensional spectra can be erroneous.
- The vector diagrams used to illustrate the BLOCH equations refer, strictly speaking, to first-order spectra only.

- Second order effects are mostly interpreted as *artifacts*, but they are real and even contain important information about the spin system, that can be useful when correctly interpreted [1.13], [1.14].

In conclusion, the understanding of coupled spin systems is the precondition to be able to deal with the interpretation of multi-dimensional data and a lack of understanding cannot be remedied by simply performing more multi-dimensional experiments.

The rapid development in computer hardware and of powerful operating systems with simple, graphical user interfaces have laid the foundations for the adaptation of the main frame iterative programs to run on personal computers but with a “user-friendly” interface. It is now possible to separate the acquisition of NMR data done on the spectrometer from the processing, analysis and interpretation of the spectra which may be performed on personal computers (PC’s). This approach not only increases efficiency but also greatly simplifies the input into computer analysis programs.

Because the amount of NMR knowledge to be taught in universities and technical schools has increased enormously, the emphasis is usually placed on modern experimental techniques rather than on the detailed aspects of coupled spin systems. Students tend more to understand pulse sequences rather than to be able to analysis the spectrum obtained from a simple one-dimensional one pulse experiment and consequently the analysis of coupled spin systems is now a tool not frequently used in NMR laboratories. However, the NMR spectroscopist requires the help of all the tools at their disposal in solving structural and chemical problems and this also includes the analysis of coupled spin systems.

Modern Spectral Analysis is designed to fill the gap that has arisen in the understanding of spectrum analysis in an interactive way. The book contains the necessary theoretical background information to understand the links between NMR parameters and one-dimensional NMR spectra and also shows how to extract the various parameters from the experimental data. It has been assumed that you are familiar with the basics of NMR spectroscopy and with the processing of raw NMR data i.e. the FOURIER transformation of Free Induction Decays (FID). However, it is recommended that before starting the spectrum analysis you “brush-up”, if necessary, on your processing skills by practicing with some of the data supplied on CD ROM (see “Check its” in section 1.6.3). The spectra supplied on CD ROM will be used to generate the input data for the subsequent spectrum analysis that forms the major part of this book.

1.2 Organisation

Modern Spectral Analysis is composed of three main parts:

- The written book giving an introduction into the basic theory and presenting practical hints, examples and exercises – “Check its” – to enable you to apply directly what you have learnt in practice.
- Software tools including manuals (HELP routines) describing in detail the use of **1D WIN-NMR**, **WIN-DAISY**, **WIN-DR** and **WIN-DYNAMICS** supplied on CD-ROM.

- A large number of one-dimensional high-resolution NMR spectra and WIN-DAISY input files for a variety of compounds dealing with different spin systems plus T_1 and NOE data for glucose and an oligosaccharide taken from [1.15].



MODERN SPECTRAL ANALYSIS

Basic Theory,
Rules, Hints, Recommendations,
Examples, Exercises



WIN-NMR SOFTWARE

| | |
|---------------------|---|
| 1D WIN-NMR | Manual Analysis of 1D NMR Data, Help Routine. |
| WIN-DAISY | Simulation and iteration of coupled spin systems, Help Routine. |
| WIN-DR | Simulation of double resonance NMR spectra. |
| WIN-DYNAMICS | Simulation of exchange broadened NMR spectra. |



DATA

| | |
|--------------------|--|
| NMR data | 1D high-resolution NMR spectra and FIDs (DEPT, T_1 , NOE) are available on CD-ROM via the program setup. |
| Input Files | WIN-DAISY input documents are also available from the setup, installed with the program WIN-DAISY. |
| Solution* | The results for all example data are available on the CD ROM directory. |

Fig. 1.1: Components of Modern Spectral Analysis (volume 3).

* The spectra can be loaded from the CD-ROM (read only). In you want to work on these files, copy them onto your local hard disk.

These three parts are combined in such a way that you may use all these educational tools interactively with your PC. In this way as you learn about the basics in theory, you directly apply what you have learnt in practice following the instructions given in the numerous "Check its". You experience step by step the scope of the powerful software modules, their advantages and limitations and you acquire the necessary skills to become proficient in NMR spectral analysis. It is essential at this stage to exploit and make full use of the powerful help routines if necessary. The help text explains the functionality of the pull-down menu entries, dialog boxes, buttons and entry field in the programs as a manual, in contrast to the introductory text which discusses the effects and the purpose of the various analysis options.

In working through this book and analyzing the various one-dimensional high-resolution NMR spectra, you will learn how spin systems are derived from the spectrum. You will also start with the suspected structure and learn how to apply the predicted spectrum to the experimental data. The analysis always starts with a manual, first order analysis in WIN-NMR where the spin system is defined and the values of the various spectrum parameters estimated. This parameter data set is then exported to WIN-DAISY and the spectrum simulated to establish whether the spectrum is truly a first order spin system. If the spectrum is not first order and cannot be easily analyzed, the WIN-NMR analysis provides the input data for the iteration document used for the parameter optimization in WIN-DAISY. Emphasis is laid on the fact that spectra are connected with structure and that the abstraction of the spin system helps considerably in evaluation of the extracted NMR parameters, i.e. which scalar coupling constants are defined by the spectrum and whether the signs can be determined from the spectrum. You will also be shown how to look for distinct signals in the spectrum which will confirm the analysis. In cases where the appearance of the spectrum is independent of particular NMR parameters, methods to determine these "hidden" parameters will be illustrated.

Theory has been kept to a minimum and is only briefly mentioned where it is necessary to understand the current discussion. A more detailed theoretical description is given in the appendix and in the references at the end of each chapter.

Some experimental aspects such as spectrum resolution, phasing, baseline correction, spectrum calibration and integration are also briefly discussed. To help in the analysis of the experimental data in various "Check its", the values of some NMR parameters in particular environments are given in the text. This information is very specific and is nether intended to be or is comprehensive enough for use in solving all NMR problems. Similarly, this book does not claim to contain examples of, or to discuss all of the relevant parameters of every type of problem that may occur in high-resolution NMR spectroscopy.

1.3 Personal Qualifications

It is assumed that you are familiar with the WINDOWS operating system either WINDOWS 3.1x, WINDOWS 95 or WINDOWS NT and are acquainted with the basic handling of the operating system and the features of the graphical user interface.

You should also have a basic knowledge of NMR spectroscopy and be competent in processing one-dimensional NMR spectra. A precondition for any successful analysis is that the experimental data has been correctly processed and it is strongly recommended that you study the first volume in this series, *NMR Spectroscopy: Processing Strategies* [1.15].

1.4 Contents

The book is divided into six chapters:

1. Introduction
2. General Characteristics of Spin Systems
3. Structure and Spin System Parameters
4. NMR and the Periodic Table
5. Time Dependent Phenomena
6. Appendix

Chapter 2 introduces the mystery called the ‘spin system’. After a short introduction into the magnetic resonance effect the chapter is limited to the ^1H nucleus with spin quantum number $I = \frac{1}{2}$. Starting with a single spin in the magnetic field the NMR parameters chemical shift and half-height line width forming the line shape are introduced. In this way you become familiar with the parameter handling in WIN-DAISY and the data exchange with 1D WIN-NMR (section 2.1). As more spins become involved, the concepts of scalar coupling constants and first order spin systems containing magnetically non-equivalent spins are introduced (section 2.2). You will learn how to use the first order analysis tool of 1D WIN-NMR to construct the spin system directly from the spectrum and how to transfer and process this data in WIN-DAISY. The spectral parameter describing the relationship between scalar coupling constant and chemical shift is introduced and second order spin systems and the concept of non-isochronous spins discussed (section 2.3). Spectral analysis using WIN-DAISY is compared with traditional ‘by hand’ methods. In the last section 2.4, magnetic equivalence is introduced starting with simple first order spin systems which are expanded to include second order effects. The principal signal pattern composition and decomposition is illustrated using a number of examples. Because the principal aim of this chapter is to focus on the spin system *characteristics*, the examples are mainly of aromatic type compounds where the scalar coupling constants are well defined and the sign of the scalar coupling constants do not have to be considered. Only in the section on magnetic equivalence will the examples have a different structural skeleton.

Chapter 3 starts by discussing the effects of symmetry in NMR spectra. The resulting spectra are strongly second order and cannot be analyzed on a first order basis. In the “Check its” the focus is on the relationship between structure and NMR parameters and it is necessary to apply the knowledge about spin systems learnt in chapter 2 in analyzing

the spectra. Emphasis is laid on the definition of spin systems in order to determine which parameters can be identified in the spectrum and the recognition of spin systems which due to various parameter combinations may differ significantly in appearance. The sign of coupling constants and the methods used to determine sign are introduced. Double resonance techniques are discussed using the decoupling simulation program WIN-DR. Some advanced examples exhibiting special problems are included for you to analyze. The recognition of spin systems in overlapped spin systems and the occurrence of long-range coupling constants are also illustrated. Special emphasis is put upon the glucose and oligosaccharide spectra already discussed in volume 1 [1.15]. Finally the chapter closes with an analysis of the nicotine spin system.

Chapter 4 extends the concept of spin systems to other spin $\frac{1}{2}$ isotopes. Starting with the pure, 100% natural abundance elements ^{19}F , ^{31}P and ^{103}Rh , both homonuclear and heteronuclear spin systems involving ^1H are discussed and the analysis of heteronuclear coupling patterns in WIN-NMR is outlined. The application of double resonance techniques in heteronuclear spectra is introduced. Organic and inorganic examples are used and the isotope effect on chemical shift outlined. Spin $\frac{1}{2}$ isotopes with a natural abundance of less than 100% are then discussed and satellite spectra and the calculation of their intensities (probabilities) explained. Starting with ^{13}C spectra, (including the treatment of DEPT spectra starting from the FIDs) the determination of 'hidden' coupling constants is explained based on the analysis of satellite spectra. Only spin systems involving ^{15}N , ^{29}Si , ^{195}Pt and ^{77}Se are discussed in detail; some experimental spectra are provided for $^{115}\text{Sn}/^{117}\text{Sn}/^{119}\text{Sn}$. In the final section of this chapter quadrupolar nuclei and their basic features are introduced. The section starts with the most common quadrupolar nucleus in NMR spectroscopy, ^2H and discusses the isotope effect on coupling constants and the method of determination of 'hidden' proton-proton coupling constants by deuterium substitution. Other nuclei covered are ^{14}N , $^{11}\text{B}/^{10}\text{B}$, ^{17}O and finally one pure element ^9Be . Provided that you have worked consecutively through the text, these multi-nuclear spin systems will not present any problems.

Chapter 5 deals with the time relevant phenomena which have so far been ignored in the first chapters. Spin-lattice and (briefly) spin-spin relaxation are discussed using the glucose and oligosaccharide examples from reference [1.15]. NOE experiments are also discussed using the same examples. Because the data obtained from T_1 and NOE experiments is strongly influenced by the type of processing used, the data processing is regarded as an essential part of the analysis so that in these particular instances the FIDs are used as input data. Processing is performed in a semi- or fully automated way without any detailed discussion of the processing functionality's; detailed information regarding serial processing is given in volume 1 of this series [1.15]. The measured T_1 values and NOE enhancements are then related to the glucose and oligosaccharide structures. Finally a very brief introduction into dynamic NMR spectroscopy and the WIN-DYNAMICS program is given. Only the basic theory is discussed because to be treated properly dynamic processes would require its own volume. For a more detailed approach you are referred to the literature. The determination of the static parameters is outlined which directly picks up the thread of the analysis of spin systems discussed in

chapters 2, 3 and 4. Fast exchanging spin systems analyzed in the previous chapters are reference to. The emphasis is on covering a few topics comprehensively rather than many topics superficially. Consequently only two site exchanging systems of mutual and non-mutual type are outlined, no intermolecular examples with complicated reaction scheme constructions are considered.

Chapter 6 is the Appendix. Section 6.1 contains additional quantum mechanical explanations and is subdivided into various sections. The first section contains the description of the AB spin system with extension to the general case and the second part explains the composite particle theory starting with the A_2 system and then extending the theory to the A_2B spin system. The section 6.2 contains the probability calculation of satellite spin systems using the example given in section 4.2.5. Section 6.3 gives some background information about the optimization algorithms implemented in WIN-DAISY and the glossary is found in section 6.4.

1.5 Technical Requirements

In order to install and run the programs 1D WIN-NMR, WIN-DAISY, WIN-DR and WIN-DYNAMICS to perform the exercises described in this book, the PC used should have the following minimum hardware requirements:

- IBM compatible 386, 486 or Pentium processor.
- at least 8 MB RAM.
- Arithmetic coprocessor.
- Monitor and graphic card for at least standard VGA resolution.
- Pointing device compatible with a Microsoft two button mouse.
- CD-ROM drive.
- Hard-disk with at least 35 MBytes spare capacity for standard installation - to perform all the "Check its" in the book about 100 MBytes are required.
- Printer (not indispensable).

Software requirements are as follows:

- Operating system/graphical user interface WINDOWS 3.1x, WINDOWS 95 or WINDOWS-NT are supported.
- Standard WINDOWS accessories NOTEPAD and CALCULATOR.
- The printer device should be correctly installed.

Remark:

Although all MS-WINDOWS versions starting from 3.1x are supported, it is strongly recommended to use either WINDOWS 95 or WINDOWS-NT, the setup will then install the 32-bit version of WIN-DAISY which on *identical hardware* is almost twice as fast as the 16-bit WINDOWS 3.1x version.

1.6 Software

1.6.1 General Remarks

The programs available on CD-ROM are special Teaching Versions of the programs 1D WIN-NMR, WIN-DAISY, WIN-DR and WIN-DYNAMICS. To avoid any problems with the full version of any of these programs already installed on your PC, select different paths for the teaching program version! Do not give path names where the complete release version of the programs are located. It is possible to run full and teaching tool versions on one PC at the same time without any interference. If you have already installed the CD-ROM delivered with volume 1 of this series [1.15] you may safely overwrite the teaching version of 1D WIN-NMR, all “Check its” from volume 1 work with the new version included with this book.

Special fonts and paragraph styles are used in this book to outline different actions and will help you to identify the relationship between the written text and the commands to execute on your PC. Although a detailed description will be given in section 1.6.4, to enable the installation exercises to be started three basic points are mentioned here:

- **Bold** printed expressions belong to pull-down menu commands, buttons, check boxes, radio buttons, their group description and descriptions of edit fields.
- CAPITAL letters are used for file names.
- The contents of the following type of <brackets> requires key board input.

1.6.2 Installation

If you wish to install the software tools and the examples make sure that there is at least 35 MByte free space available on your hard disk. If the desired hard disk is a network drive it should be mounted properly, you should have read and write access and it should be available any time you wish to run the “Check its” in this book. Only very few hard disk space is required from the system directory.

Check it in WINDOWS:

Insert the green CD ROM (stored inside the inner back cover of this book) into your CD-ROM drive. The operating systems WINDOWS 95 and WINDOWS NT will start the setup automatically. For WINDOWS 3.1x use the standard procedure to start the setup in a MS-WINDOWS environment (from the **Program Manager** use the **Run** command and type <[CD-ROM drive letter]:SETUP> as shown on the CD-ROM label. Consult the WINDOWS manual or Help File if necessary. After a few seconds the setup window will appear on the screen showing the Welcome dialog (Fig. 1.2). Click the **Next** button to proceed with the installation process which will open a number of dialog boxes one after the other. If possible, confirm the default options and entries for the whole installation process by simply pressing the **Next** button.

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