

Challenges in Molecular Structure Determination

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Preface

The present book is the first English version of the successful book *Strukturanalytik organischer und anorganischer Verbindungen* that was published in 2007 by Vieweg-Teubner Publishing. The present English edition is intended for a broader group of readers and users.

Sound knowledge and experimental experience of the application of modern spectroscopic methods to unravel the structure of organic and inorganic compounds are part nowadays of the scientific background of synthesis chemists, physical chemists, as well as of analysts, biochemists, and pharmacists among other disciplines. For this reason many very good books about spectroscopic methods can be found on the market. Nevertheless, these books focus mainly on the theoretical background of spectroscopy and are limited to the structural analysis of organic compounds. Only seldom can method-based exercises be found in these books.

The use of spectroscopic methods to analyze molecule structures and to infer relations between the structure and features of molecules requires basic as well as extensive applied knowledge about spectroscopy. On the one hand, the right combination of spectroscopic methods has to be tailored as a function of the specific question at hand for one method seldom permits one to solve the analytical problem encountered. On the other hand, the sound interpretation of the collected data is challenging. Unfortunately, these data cannot be, in most cases, interpreted using only the theoretical background of spectroscopy. Rather the experience necessary to solve basic as well as more complex structure analysis problems can only be acquired by intensive training. The main focus of this book is thus not to provide theoretical background but applied exercises presented as *challenges*. Consequently, the theoretical section is kept quite short and refers to the main relevant literature on the subject. The appropriate literature for each spectroscopic method can be found at the end of the respective chapter. There are many good books written by specialists in the field, therefore, we apologize to colleagues whose work we could not cite because of space limitations.

It may surprise the reader that equally long chapters have been devoted to each of the four spectroscopic methods, whereas in other books UV–VIS spectroscopy is

hardly presented or even absent. In Sect. 3.5 the importance of this method is summarized and illustrated based on multiple examples coming from analytical practice. A prerequisite for the successful application of the spectroscopic methods in molecular structure determination is to have the necessary knowledge about the relations between chemical structure and spectrum. These relations will be presented in detail here, as the available books on the topic provide too general or no information on structure–spectrum relations. The reader may wonder why the four molecular spectroscopic methods are presented in approximately equally long sections, despite the fact that nuclear resonance and mass spectrometry play a more important role in the field of structure analysis than the two other methods. Indeed, their theoretical background is so large that we urge the reader to refer to the specific literature. The present book offers only the theoretical background necessary to be able to interpret the spectra.

Some considerations about methodological and didactical aspects have to be pointed out at this stage. This book begins with the chapter on mass spectrometry because it offers a good estimation of the general structure as well as to the number of double bonding equivalents which is necessary to obtain the correct structure of molecules. In the following chapters, vibration spectroscopy, electronic absorption spectroscopy, and NMR spectroscopy will be presented in this order. Some of the challenges related to each one of these methods will be presented based on spectral data of the preceding methods or the spectra will be complemented by synthetic or other types of information.

The theoretical materials will be illustrated in the whole book by challenges. Most of them originate from analytical practice. The solutions to these exercises are provided to the reader merely as an “indicator” to ascertain that the theory has been well understood.

Each of the most important exercises possesses a detailed solution/algorithm, which can then be used as a template to solve all the other exercises. Thus, this book constitutes a very good self-study reference. The reader will find the complete solutions on the website *extras.springer.com*, where the solutions are presented step-by-step as Power Point presentations.

The exercises consist of assignments to decode the molecular structure of inorganic compounds such as the geometry of small molecules or ions, classical complex bondings, the coordination of ligands, as well as the structure of organic molecules and biomolecules. Many assignments come from synthetic chemistry or analytical practice, such as for instance the analysis of HPLC/DAD products or products from the domain of environmental analytics. The reader is supposed to identify which method is the most appropriate to use to solve a particular analytical problem and the limitations of each method. Moreover, examples using exclusively UV–VIS spectroscopy are presented as this method is in some cases the only correct method to implement. Two additional examples will illustrate step-by-step how the whole range of methods from mass spectrometry to NMR correlation spectra gives the respective information; still open questions about the structure analysis of molecules remain. Finally, 22 sets of spectra are provided for the practice of molecular structure determination.

The issues surrounding structure analysis of inorganic molecules are clearly far less complicated than those for organic molecules. It is worth noting that the scope of the present book only includes *molecular* structure analysis using vibration and electron spectroscopy. It does not encompass the domains of nuclear resonance spectroscopy of solids, ESR, and other methods.

Our book was mainly conceived as a starting tool in the domain of structure analysis of molecules. The difficulty level of the exercises was adapted in consequence of this goal and the theory necessary to solve the exercises was synthesized in an understandable form. Since modern experimental NMR techniques belong nowadays to the basic knowledge of many disciplines, COSY, HSQC, NOESY, and TOCSY spectra were included in the 22 exercises presented in Chap. 5. The solution for the first challenges is given in detail and should be the algorithm for solving the following challenges.

Because of the broad array of methods and theories, it was impossible to include all molecular spectroscopic methods such as ESR or chiroptical methods in this book. In our opinion, however, the methods presented here provide students with all the basics needed to determine the structure of low-molecular weight compounds and ease the understanding of more complex methods of analysis to tackle more complex issues.

Thus, this exercise book on structure analysis is devoted to chemistry students as well as to students of many other disciplines (e.g., pharmacists, biologists, geologists, etc.), who face similar issues.

We are grateful to Dr. Wolfgang Günther and Dr. Manfred Friedrich (Faculty of Chemical and Earth Sciences, Friedrich-Schiller University, Jena) for the measurement of NMR spectra. We would also like to thank PD Dr. Thomas Mayerhöfer (Institute of Photonic Technology, Jena) for his corrections of earlier versions of this book. Finally, we thank Dr. Pauly (Springer) for the excellent cooperation.

Jena, Germany
January 2012

Manfred Reichenbächer
Jürgen Popp

Challenges

PowerPoint presentations for solving the challenges are available at <http://extras.springer.com>

Please note that solutions are presented in the book for challenges marked by an asterisk.

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List of Important Abbreviations

1°	Primary
2°	Secondary
3°	Tertiary
amu	Atomic mass unit
AO	Atomic orbital
b	Broad
CI	Chemical ionization
COSY	Correlation spectroscopy
CV	Combination vibration
DAD	Diode Array Detector
DBE	Double bond equivalent
DEPT	Distortionless enhancement by polarization transfer
dp	Depolarized Raman line
EE ⁺	Even number of electron ion
EI	Electron impact ionization
EN	Electronegativity
eV	Electron voltage
FID	Free induction decay
FIR	Far infrared
FM	Formula mass
gem	Geminal
HMBC	Heteronuclear multiple bond coherence
HMQC	Heteronuclear multiple quantum coherence
h-MS	High-resolution mass spectrometry
HSQC	Heteronuclear single quantum coherence
i. a.	Inactive
in	In-plane
IP	Ionization potential
IR	Infrared
LSR	Lanthanide shift reagents

M	Spin multiplicity
M ⁺	Molecular peak (ion)
m	Medium
MN	Mass number
MO	Molecular orbital
MS	Mass spectrum; mass spectroscopy
m/z	mass-to-charge ratio
NCI	Negative chemical ionization
NIR	Near infrared
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
NOESY	Nuclear Overhauser enhancement spectroscopy
OE ⁺	Odd number of electron ion
oop	Out-of-plane
OT	Overtone
P	Polarized Raman line
PCP	Polychlorinated biphenyls
R	Resolution
Ra	Raman
RDA	<i>Retro</i> -Diels-Alder
S	Total spin angular moment
sh	Shoulder
s	Electron spin
T	Triplet state
TAI	Trichloroacetyl isocyanate
TLC	Thin-layer chromatography
TMS	Tetramethylsilane
TOCSY	Total correlation spectroscopy
UV	Ultraviolet
vic	Vicinal
Vis	Visible
vs	Very strong
vw	Very weak
w	Weak

List of Important Symbols

Some important symbols and abbreviations are listed below. Further symbols and abbreviations the use of which is restricted to special sections are defined in those sections.

A	Absorbance (without unit)
B	Magnetic flux density (magnetic field strength)
c	Light velocity
E	Energy
f	Force constant
$h; \hbar$	Planck's constant; $\hbar = \frac{h}{2\pi}$
I	Intensity; nuclear spin quantum number
i	Charge-induced cleavage
J	Indirect nuclear spin coupling constant in Hz
\vec{J}	Nuclear spin
m	Atomic mass; magnetic quantum number
M	Relative atomic mass; multiplicity of a multiplet
n	Number of the atom; amount of substances
N	Number of the spins; number of atoms
r_H	McLafferty rearrangement
S	Singlet; incremental value
T_1	Spin–lattice relaxation time
T_2	Spin-spin relaxation time
ν	Vibrational quantum number
α	Molar absorptivity
γ	Out-of-plane vibration (oop, δ_{oop}); magnetogyric ratio
δ	Deformation vibration; chemical shift
Γ	Representation of a class
λ	Wavelength
μ	Reduced mass
$\vec{\mu}$	Nuclear magnetic moment
ν	Stretching vibration; wave number of the IR absorbance; frequency

$\tilde{\nu}, \nu$	Wave number in cm^{-1}
σ	Shielding constant
ρ	Polarization ratio
φ	Dihedral torsion angle

Superscript Indices

*	Excited state
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Subscript Indices

a	Axial
as	Asymmetrical
b	Broad
e	Equatorial
eff	Effective
i	Running index
max	Maximum
rel	Relative
s	Symmetrical
0	Ground state
1	First excited State
\perp	Parallel
\parallel	Perpendicular