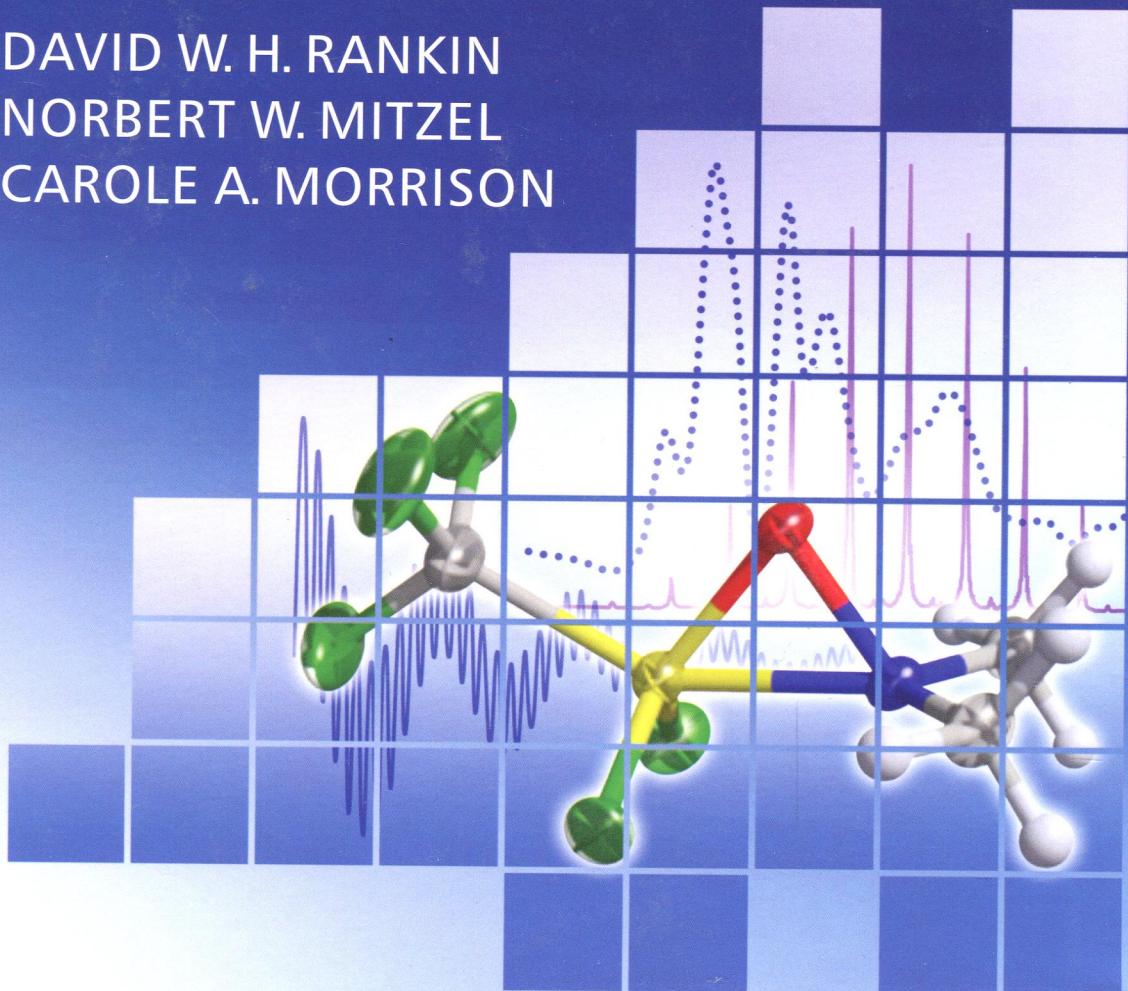


■ DAVID W. H. RANKIN
■ NORBERT W. MITZEL
■ CAROLE A. MORRISON



STRUCTURAL METHODS IN MOLECULAR INORGANIC CHEMISTRY

 WILEY

INORGANIC
CHEMISTRY
A WILEY
TEXTBOOK
SERIES

Structural Methods in Molecular Inorganic Chemistry

David W. H. Rankin

University of Edinburgh, UK

Norbert W. Mitzel

University of Bielefeld, Germany

Carole A. Morrison

University of Edinburgh, UK



A John Wiley & Sons, Ltd., Publication

This edition first published 2013
© 2013 John Wiley & Sons, Ltd

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book. This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The publisher and the author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may provide or recommendations it may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the publisher nor the author shall be liable for any damages arising herefrom.

Library of Congress Cataloging-in-Publication Data

Rankin, David W. H.

Structural methods in molecular inorganic chemistry / Professor David Rankin, Dr Carole Morrison, Professor Norbert Mitzel.
pages cm

Includes bibliographical references and index.

ISBN 978-0-470-97279-3 (hardback) – ISBN 978-0-470-97278-6 (paper)

1. Molecular structure. 2. Chemistry, Inorganic. I. Morrison, Carole A., 1972- II. Mitzel, Norbert W., 1966- III. Title.
QD461.R24 2013
541'.22–dc23

2012029024

A catalogue record for this book is available from the British Library.

Cloth ISBN: 9780470972793

Paper ISBN: 9780470972786

Set in 10/12pt Times by Thomson Digital, Noida, India

Printed and bound in Malaysia by Vivar Printing Sdn Bhd

Contents

Preface	xiii
Companion Website	xv
Acknowledgements	xvii
Biographies	xix
1. Determining Structures – How and Why	1
1.1 Structural chemistry – where did it come from?.....	1
1.2 Asking questions about structure.....	4
1.3 Answering questions about structure	5
1.4 Plan of the book	7
1.5 Supplementary information.....	8
2. Tools and Concepts	9
2.1 Introduction	9
2.2 How structural chemistry techniques work	10
2.3 Symmetry	11
2.3.1 Symmetry operations and elements	13
2.3.2 Point groups	15
2.3.3 Characters, character tables and symmetry species	17
2.4 Electron density	21
2.5 Potential-energy surfaces.....	21
2.6 Timescales	24
2.7 Structural definitions.....	26
2.8 Sample preparation	27
2.8.1 Unstable species.....	27
2.8.2 Solutions in supercritical fluids.....	28
2.8.3 Involatile species	28
2.8.4 Variable temperature and pressure measurements.....	29
2.9 Quantitative measurements.....	30
2.10 Instrumentation.....	32
2.10.1 Radiation sources	32
2.10.2 Detectors	35
2.11 Data analysis	36
2.11.1 Fourier transformation.....	36
2.11.2 Experimental errors and uncertainties	37
2.11.3 Least-squares refinement	39
2.11.4 Database mining	39
Review questions	41

Discussion problems	43
References	43
3. Theoretical Methods.....	45
3.1 Introduction	45
3.2 Approximating the multi-electron Schrödinger equation	46
3.2.1 The Hamiltonian operator, \hat{H}	46
3.2.2 The molecular wavefunction, Ψ	49
3.3 Exploring the potential-energy surface	52
3.4 Extending the computational model to the solid state.....	56
3.4.1 Modeling a delocalized wavefunction, Ψ ; periodic boundary conditions	58
3.4.2 Approximating \hat{H} for solid-state structures	60
3.4.3 Exploring the potential-energy surface for solid-state structures	60
3.5 Calculating thermodynamic properties	61
3.6 Calculating properties of chemical bonding	63
3.7 Comparing theory with experiment: geometry	65
3.8 Comparing theory with experiment: molecular properties	68
3.8.1 Vibrational spectra	69
3.8.2 NMR, EPR and Mössbauer spectra	69
3.8.3 Molecular orbitals	70
3.8.4 Electronic spectra	71
3.8.5 Modeling solvent effects	73
3.9 Combining theory and experiment	74
Review questions	75
Discussion problems.....	77
References	77
4. Nuclear Magnetic Resonance Spectroscopy.....	79
4.1 Introduction	79
4.2 The nuclear magnetic resonance phenomenon	79
4.3 Experimental set-up.....	83
4.3.1 NMR spectrometers	83
4.3.2 Sample preparation	85
4.3.3 Continuous wave and Fourier transform spectra	85
4.4 The pulse technique	86
4.4.1 Inducing magnetization by a pulse	86
4.4.2 Relaxation of magnetization after a pulse	87
4.4.3 Free induction decay and Fourier transformation	90
4.5 Information from chemical shifts	92
4.5.1 General principles	92
4.5.2 Proton chemical shifts	94
4.5.3 Chemical shifts of other elements	96
4.6 Information from NMR signal intensities.....	100
4.7 Simple splitting patterns due to coupling between nuclear spins	101
4.7.1 First-order spectra of spin-1/2 isotopes of 100% abundance	101
4.7.2 Nuclear spin systems	102
4.7.3 Coupling to spin-1/2 isotopes of low abundance	106

4.7.4	Spectra of spin-1/2 isotopes of low abundance	107
4.7.5	Coupling to quadrupolar nuclei.....	110
4.8	Information from coupling constants.....	112
4.8.1	General principles	112
4.8.2	One-bond coupling	112
4.8.3	Two-bond coupling	114
4.8.4	Coupling over three bonds	114
4.8.5	Coupling over more than three bonds.....	115
4.8.6	Coupling through space.....	116
4.9	Not-so-simple spectra	116
4.9.1	Second-order spectra	116
4.9.2	Chiral and prochiral non-equivalence.....	119
4.9.3	Coincidences.....	119
4.10	The multi-nuclear approach	120
4.11	Multiple resonance.....	121
4.11.1	Selective spin decoupling	122
4.11.2	Spin decoupling	123
4.11.3	Triple resonance.....	124
4.11.4	The Nuclear Overhauser Effect.....	125
4.11.5	Gated decoupling.....	126
4.12	Multi-pulse methods	126
4.12.1	Introduction.....	126
4.12.2	Sensitivity enhancement by polarization transfer	127
4.12.3	Spectrum editing	129
4.13	Two-dimensional NMR spectroscopy	129
4.13.1	General principles and homonuclear correlation experiments	129
4.13.2	Heteronuclear correlation experiments.....	134
4.13.3	Two-dimensional nuclear Overhauser effect spectra	136
4.13.4	Diffusion ordered spectroscopy (DOSY).....	138
4.14	Gases	140
4.15	Liquid crystals.....	140
4.16	Solids	141
4.17	Monitoring dynamic phenomena and reactions	147
4.17.1	Intramolecular dynamic phenomena.....	147
4.17.2	Exchange reactions and equilibria	149
4.17.3	Monitoring reactions: identification of intermediates	151
4.18	Paramagnetic compounds	154
	Review questions.....	159
	Discussion problems.....	161
	References	166
5.	Electron Paramagnetic Resonance Spectroscopy.....	169
5.1	The electron paramagnetic resonance experiment.....	169
5.2	Hyperfine coupling in isotropic systems.....	171
5.3	Anisotropic systems.....	175
5.3.1	Hyperfine splittings and <i>g</i> factors.....	175
5.3.2	Electron-electron interactions.....	176
5.4	Transition-metal complexes	179
5.5	Multiple resonance.....	182

Review questions	184
Discussion problems	186
References	187
6. Mössbauer Spectroscopy	189
6.1 Introduction	189
6.2 The Mössbauer effect	189
6.3 Experimental arrangements	192
6.4 Information from Mössbauer spectroscopy	194
6.4.1 The isomer shift	194
6.4.2 Quadrupole splitting	198
6.4.3 Magnetic splitting	202
6.5 Compound identification	204
6.5.1 The interhalogen compound $I_2Br_2Cl_4$	205
6.5.2 Iron in very high oxidation states – Fe(V) and Fe(VI) nitride complexes ..	206
6.6 Temperature- and time-dependent effects	208
6.6.1 Basic iron acetates	209
6.6.2 Spin crossover in the complex $[Fe(\text{phen})_2(\text{NCS})_2]$	210
6.6.3 Valence fluctuation	211
6.7 Common difficulties encountered in Mössbauer spectroscopy	212
6.8 Further possibilities in Mössbauer spectroscopy	213
Review questions	213
Discussion problems	214
References	217
7. Rotational Spectra and Rotational Structure	219
7.1 Introduction	219
7.2 The rotation of molecules	219
7.2.1 Classical rotation	219
7.2.2 Quantized rotation, moments of inertia and rotation constants	220
7.2.3 Centrifugal distortion; the semi-rigid rotor	223
7.3 Rotational selection rules	224
7.3.1 Pure rotation spectra	224
7.3.2 Vibration–rotation spectra	225
7.4 Instrumentation	228
7.5 Using the information in a spectrum	229
7.5.1 Fingerprinting	229
7.5.2 Determination of rotation constants	230
7.6 Using rotation constants to define molecular structures	232
Review questions	234
Discussion problems	235
References	236
8. Vibrational Spectroscopy	237
8.1 Introduction	237
8.2 The physical basis; molecular vibrations	237
8.2.1 Vibrational motions and energies	237
8.2.2 Non-ideal restoring forces; anharmonicity	238

8.3	Observing molecular vibrations	239
8.3.1	Absorption in the infrared	239
8.3.2	Raman scattering	242
8.3.3	Resonance Raman spectroscopy	242
8.3.4	Inelastic scattering of neutrons and electrons	244
8.4	Effects of phase on spectra	245
8.5	Vibrational spectra and symmetry	248
8.5.1	Fundamental vibrational selection rule	248
8.5.2	Symmetry selection rules	248
8.5.3	Symmetry of an entire set of normal vibrations	249
8.5.4	Symmetry of vibrational modes	251
8.6	Assignment of bands to vibrations	254
8.6.1	Raman polarization	255
8.6.2	Band contours in gases	256
8.6.3	Intensities of allowed fundamentals	259
8.6.4	Mode numbering	260
8.6.5	Non-fundamental transitions	260
8.7	Complete empirical assignment of vibrational spectra	262
8.8	Information from vibrational spectra	263
8.8.1	Quantitative information	263
8.8.2	Qualitative information	264
8.8.3	Transition-metal carbonyl complexes	267
8.8.4	Use of isotopes in interpreting and assigning vibrational spectra	269
8.9	Normal coordinate analysis	272
	Review questions	273
	Discussion problems	274
	References	276
9.	Electronic Characterization Techniques	277
9.1	Introduction	277
9.2	Electron energy levels in molecules	278
9.3	Symmetry and molecular orbitals	279
9.4	Photoelectron spectroscopy	281
9.4.1	Observing valence-shell electrons	281
9.4.2	Vibrational structure of PE bands	281
9.4.3	Structural information from valence-shell PE spectroscopy: making assignments	285
9.4.4	Observing core-shell electrons	286
9.5	Valence excitation spectroscopy	286
9.5.1	Experimental methods	286
9.5.2	The information in an electronic spectrum	288
9.6	Electronic energy levels and transitions in transition-metal complexes	289
9.6.1	Metal, ligand and metal–ligand bonding levels	289
9.6.2	Selection rules	290
9.6.3	Ligand–ligand and metal–metal transitions	292
9.6.4	Metal–ligand and ligand–metal (charge-transfer) bands	295
9.6.5	Inter-valence transitions	295
9.6.6	Assigning bands of transition-metal complexes	296

9.6.7	Spectra of compounds of elements with partly-filled f sub-shells (lanthanides and actinides).....	297
9.7	Circular dichroism	298
	Review questions	299
	Discussion problems.....	300
	References	302
10.	Diffraction Methods	303
10.1	Introduction	303
10.2	Diffraction of electrons, neutrons and X-rays	304
10.3	Diffraction by gases.....	308
10.3.1	Experimental set-up	308
10.3.2	Theoretical basis of gas-phase diffraction	309
10.3.3	Interpretation of results	314
10.3.4	Problems with underdetermined structures	315
10.3.5	Experimental limitations.....	320
10.4	Diffraction by liquids	321
10.5	Diffraction by single crystals; symmetry	323
10.5.1	The unit cell	324
10.5.2	Symmetry elements within the unit cell.....	324
10.5.3	The seven crystal systems.....	326
10.5.4	Three-dimensional periodic symmetry; space groups	329
10.6	Diffraction by single crystals; the theoretical basis	329
10.7	Diffraction by single crystals; the experiment.....	333
10.7.1	Crystal growth	333
10.7.2	Experimental set-up	334
10.7.3	Indexing and determining unit cell dimensions	336
10.7.4	Data collection	337
10.7.5	Experimental problems: X-ray absorption and extinction	338
10.7.6	Data analysis.....	338
10.8	Diffraction by single crystals; interpretation of results.....	341
10.8.1	How good is a structure?.....	341
10.8.2	Common problems: incorrect atom assignment.....	343
10.8.3	Common problems: disorder	344
10.8.4	Recognizing chemical bonds	347
10.8.5	Absolute structure determination	348
10.8.6	How big can we go?	348
10.9	Diffraction by single crystals; electron density determination.....	349
10.10	Topological features of the electron density.....	352
10.10.1	Displaying topological features of the electron density	353
10.10.2	Definition of a topological atom and its properties.....	354
10.10.3	Critical points	355
10.10.4	Bonding description	356
10.10.5	The Laplacian of the electron density	358
10.10.6	Some examples of electron topology studies	360
10.11	Phase dependence of molecular structures	363
10.12	Diffraction of neutrons by crystals	365

10.13	Diffraction by powders	368
10.14	High-pressure crystallography	368
10.15	Extended X-ray absorption fine structure	371
	Review questions	375
	Discussion problems	377
	References	381
11.	Mass Spectrometry	383
11.1	Introduction	383
11.2	Experimental arrangements.....	383
11.2.1	Ion sources.....	383
11.2.2	Mass analyzers and detectors.....	384
11.3	Data analysis	387
11.3.1	Molecular ions	387
11.3.2	Fragmentation.....	389
11.4	Combined mass spectrometry methods	392
11.4.1	Tandem mass spectrometry (MS/MS).....	392
11.4.2	Chromatography-coupled mass spectrometry	394
	Review questions	396
	Discussion problems	397
	References	397
12.	Case Histories	399
12.1	Introduction	399
12.2	Xenon compounds	400
12.2.1	Xenon hexafluoride	400
12.2.2	Xenon–xenon bonds – strange but true.....	404
12.3	The structure of N ₂ O ₃	407
12.4	Bismuthine	409
12.5	Tetrahydroborates.....	410
12.6	Is beryllocene a sandwich compound?	415
12.7	Silylum cations – free at last	418
12.8	True phosphinous acids	422
12.9	Dihydrogen and dihydride complexes	425
12.10	Agostic interactions: alkyl hydrogen atoms binding to metal atoms	428
12.11	Lower symmetry than expected in some phosphines and phosphoranes.....	430
12.12	Three-membered rings with dative bonds?.....	432
12.13	Stable radicals	436
12.13.1	Nitrogen radicals	436
12.13.2	Jack-in-the-box compounds.....	438
12.14	Induced proton transfer in an adduct of squaric acid and bipyridine	441
12.15	High-pressure studies of metal organic framework materials.....	443
12.16	Mistaken identity: mono-coordinate copper(I) and silver(I) complexes	446
12.17	Oxidation states in a palladium–tin complex.....	447
12.18	Structural and spectroscopic consequences of a chemical change in an iron complex	450

12.19	Some metalloproteins	454
12.19.1	Fixing N ₂ from air.....	455
12.19.2	Making oxygen from water	457
12.20	Atoms inside fullerene cages	459
12.21	Structural chemistry – where is it going?	463
	Discussion problem.....	464
	References	464
	Index.....	467