

Atomic and Molecular Spectroscopy

Advanced Texts in Physics

This program of advanced texts covers a broad spectrum of topics which are of current and emerging interest in physics. Each book provides a comprehensive and yet accessible introduction to a field at the forefront of modern research. As such, these texts are intended for senior undergraduate and graduate students at the MS and PhD level; however, research scientists seeking an introduction to particular areas of physics will also benefit from the titles in this collection.

**Springer-Verlag
Berlin Heidelberg
GmbH**

Physics and Astronomy

springeronline.com



Sune Svanberg

Atomic and Molecular Spectroscopy

Basic Aspects and Practical Applications

Fourth, Revised Edition
With 404 Figures and 14 Tables



Springer

Professor Sune Svanberg

Department of Physics
Lund Institute of Technology
P.O. Box 118
221 00 Lund
Sweden
E-mail: sune.svanberg@fysik.lth.se

ISSN 1439-2674

ISBN 978-3-540-20382-7

Library of Congress Cataloging-in-Publication Data

Svanberg, S. (Sune), 1943-

Atomic and molecular spectroscopy: basic aspects and practical applications/
Sune Svanberg. – 4th, rev. ed.

p. cm. – (Advanced texts in physics, ISSN 1439-2674)

Includes bibliographical references and index.

ISBN 978-3-540-20382-7 ISBN 978-3-642-18520-5 (eBook)

DOI 10.1007/978-642-18520-5

1. Atomic spectroscopy. 2. Molecular spectroscopy. I. Title. II. Series.

QC454.A8S85 2004 539'.6'0287 – dc22 2003063954

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable for prosecution under the German Copyright Law.

springeronline.com

© Springer-Verlag Berlin Heidelberg 1991, 1992, 2001, 2004

Originally published by Springer-Verlag Berlin Heidelberg New York in 2004

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Data conversion by LE- \TeX Jelonek, Schmidt & Vöckler GbR, Leipzig

Cover design: *design & production* GmbH, Heidelberg

Printed on acid-free paper SPIN 10963869 57/3141/di 5 4 3 2 1 0

To Katarina, Emilie, Kristina,
my Mother
and the memory of my Father

Preface

The present book – *Atomic and Molecular Spectroscopy – Basic Aspects and Practical Applications* – has been developed over a long time. The Third Edition, which appeared in 2001, was fully revised and updated to the state of the field at that time. The book appeared in hard cover well suited for individual and library use. However, the book is basically a text, also well suited as a base for a course on the topic. A lower-cost paper-back edition better serves such purposes, as did the Second (paper-back) Edition of the book. The Fourth Edition presented has now been corrected for misprints and contains some additional text. A number of important literature references up until mid-2003 have been added to provide a fully updated account of the dynamic field of Atomic and Molecular Spectroscopy.

Lund, October 2003

Sune Svanberg

Preface to the Third Edition

Atomic and molecular spectroscopy – both in its basic and in its applied aspects – is in a dynamic state of development. It continues to provide new fascinating possibilities for a deeper understanding of the fundamental properties of the building blocks of matter and their interaction with electromagnetic irradiation. It generates new possibilities for practical applications in industry, chemistry, astronomy, geosciences, biology, medicine and information technology.

Ten years after the appearance of the first edition there was a need for a thorough revision of the book, again bringing it up to the leading edge in the new millennium. This has led to a considerable extension of the material and thus of the size of the book. As previously, the focus has been on the physical understanding of the processes and phenomena, and on providing a broad overview of the possibilities of atomic and molecular spectroscopy. Thus, the mathematical description is frequently superficial – for the benefit of students and scientists in other natural sciences without a rigorous physics background. My belief is that the physical (and intuitive) understanding, when possible, is also the most important aspect for the hard-core physicist. The reader will find ample references to textbooks, review articles and research papers providing all the details on almost any topic in the field, and the reference list was, with considerable effort, updated till mid-2000 and in some cases till early 2001. This could still mean that important references are lacking, and I apologize to the authors for unfortunate omissions.

The reader who already knows the previous editions will notice that new material is added, particularly in the following fields: clusters, satellite remote sensing, astrophysical applications, the generation of ultrafast and ultraintense laser radiation, diode laser spectroscopy, ultrafast spectroscopy, femtochemistry, high-power laser–matter interaction, laser cooling and trapping, Bose–Einstein condensation, and lasers in environmental and medical research. Thus, it is felt that the book provides a rather extensive overview of the major spectroscopy fields.

In order to improve the usefulness of the book as a text for a course on the topic at the pre- or postgraduate level, a section of questions and exercises has been added. The material is presented following the chapters, and, in addition, material connecting wider areas is supplied. A detailed subject index

is also provided, helping the reader to easily find an entry to the introduction of a subfield and references to the relevant literature.

The author benefited a lot from the interaction with students and colleagues when developing this book. He is very grateful for comments and corrections.

Finally, I would like to thank Gertrud Dimler, Adelheid Duhm and Claus Ascheron at Springer-Verlag for their professional work, and Helmut Lotsch for his encouragement throughout this book project.

Lund, June 2001

Sune Svanberg

Preface to the First Edition

Atomic and molecular spectroscopy has provided basic information leading to the development of quantum mechanics and to the understanding of the building blocks of matter. It continues to provide further insight into the statics and dynamics of the microcosmos, and provides the means for testing new concepts and computational methods. The results of atomic and molecular spectroscopy are of great importance in astrophysics, plasma and laser physics. The rapidly growing field of spectroscopic applications has made considerable impact on many disciplines, including medicine, environmental protection, chemical processing and energy research. In particular, the techniques of electron and laser spectroscopy, the subjects of the 1981 Nobel prize in physics, have contributed much to the analytical potential of spectroscopy.

This textbook on *Atomic and Molecular Spectroscopy* has been prepared to provide an overview of modern spectroscopic methods. It is intended to serve as a text for a course on the subject for final-year undergraduate physics students or graduate students. It should also be useful for students of astrophysics and chemistry. The text has evolved from courses on atomic and molecular spectroscopy given by the author since 1975 at Chalmers University of Technology and at the Lund Institute of Technology. References are given to important books and review articles which allow more detailed studies of different aspects of atomic and molecular spectroscopy. No attempt has been made to cover all important references, nor have priority aspects been systematically considered.

It is assumed that the reader has a basic knowledge of quantum mechanics and atomic physics. However, the completion of a specialized course on atomic and molecular physics is not required. The present treatise (disregarding Chap. 4) is not particularly mathematical, but emphasizes the physical understanding of the different techniques of spectroscopy. In the course given by the author, the time for solving calculational problems has been reduced to allow a more complete overview of the field in the time available. Particular emphasis has been given to technical applications. However, by increasing the allotted problem-solving time or by omitting certain areas of spectroscopy, a more problem-oriented course can easily be taught based on this book. In his courses, the author has combined lectures with a number of 5-hour

laboratory experiments (performed on research equipment) and a number of 1-2 hour visits to local research groups in physics, chemistry and astronomy.

Part of the material is reworked from the Swedish textbook *Atomfysik* by I. Lindgren and S. Svanberg (Universitetsförlaget, Uppsala 1974). The author is very grateful to his teacher Prof. I. Lindgren for contributions and support through the years. He would also like to thank many colleagues, including Prof. D. Dravins, Dr. Å Hjalmarsson, Prof. I. Martinson, Prof. J. Nordgren, Prof. C. Nordling, Dr. W. Persson, Prof. A. Rósen, Prof. H. Siegbahn and Dr. C.-G. Wahlström for valuable suggestions and corrections.

Special thanks are due to Mrs. C. Holmqvist for typing numerous versions of the manuscript and Dr. H. Sheppard for correcting the English and assisting with the figures. Mr. Å. Bergqvist and Mr. G. Romerius helped by drawing some of the figures. Finally, the kind help and support of Dr. H. Lotsch of Springer-Verlag is gratefully acknowledged.

Lund, September 1990

Sune Svanberg

Contents

1. Introduction	1
2. Atomic Structure	5
2.1 One-Electron Systems	5
2.2 Alkali Atoms	7
2.3 Magnetic Effects	8
2.3.1 Precessional Motion	8
2.3.2 Spin-Orbit Interaction	9
2.4 General Many-Electron Systems	10
2.5 The Influence of External Fields	17
2.5.1 Magnetic Fields	18
2.5.2 Electric Fields	21
2.6 Hyperfine Structure	23
2.6.1 Magnetic Hyperfine Structure	23
2.6.2 Electric Hyperfine Structure	25
2.7 The Influence of External Fields (hfs)	26
2.8 Isotopic Shifts	29
3. Molecular Structure	31
3.1 Electronic Levels	32
3.2 Rotational Energy	35
3.3 Vibrational Energy	36
3.4 Polyatomic Molecules	37
3.5 Clusters	39
3.6 Other Molecular Structures	40
4. Radiation and Scattering Processes	41
4.1 Resonance Radiation	41
4.2 Spectra Generated by Dipole Transitions	51
4.2.1 Atoms	52
4.2.2 Molecules	55
4.3 Rayleigh and Raman Scattering	61
4.4 Raman Spectra	63
4.4.1 Vibrational Raman Spectra	63

4.4.2	Rotational Raman Spectra	64
4.4.3	Vibrational–Rotational Raman Spectra	64
4.5	Mie Scattering	65
4.6	Atmospheric Scattering Phenomena	66
4.7	Comparison Between Different Radiation and Scattering Processes	69
4.8	Collision-Induced Processes	70
5.	Spectroscopy of Inner Electrons	71
5.1	X-Ray Spectroscopy	71
5.1.1	X-Ray Emission Spectroscopy	73
5.1.2	X-Ray Absorption Spectroscopy	79
5.1.3	X-Ray Imaging Applications	82
5.2	Photoelectron Spectroscopy	85
5.2.1	XPS Techniques and Results	87
5.2.2	Chemical Shifts	90
5.3	Auger Electron Spectroscopy	95
6.	Optical Spectroscopy	97
6.1	Light Sources	97
6.1.1	Line Light Sources	98
6.1.2	Continuum Light Sources	106
6.1.3	Synchrotron Radiation	108
6.1.4	Natural Radiation Sources	113
6.2	Spectral Resolution Instruments	114
6.2.1	Prism Spectrometers	114
6.2.2	Grating Spectrometers	117
6.2.3	The Fabry–Pérot Interferometer	121
6.2.4	The Fourier Transform Spectrometer	126
6.3	Detectors	128
6.4	Optical Components and Materials	134
6.4.1	Interference Filters and Mirrors	134
6.4.2	Absorption Filters	138
6.4.3	Polarizers	141
6.4.4	Optical Materials	143
6.4.5	Influence of the Transmission Medium	144
6.5	Optical Methods of Chemical Analysis	148
6.5.1	The Beer–Lambert Law	149
6.5.2	Atomic Absorption/Emission Spectrophotometry	151
6.5.3	Burners, Flames, Sample Preparation and Measurements	155
6.5.4	Modified Methods of Atomization	156
6.5.5	Multi-Element Analysis	157
6.5.6	Molecular Spectrophotometry	158
6.5.7	Raman Spectroscopy	160

6.6	Optical Remote Sensing	162
6.6.1	Atmospheric Monitoring with Passive Techniques	164
6.6.2	Land and Water Measurements with Passive Techniques	171
6.7	Astrophysical Spectroscopy	176
7.	Radio-Frequency Spectroscopy	187
7.1	Resonance Methods	187
7.1.1	Magnetic Resonance	187
7.1.2	Atomic-Beam Magnetic Resonance	189
7.1.3	Optical Pumping	197
7.1.4	Optical Double Resonance	200
7.1.5	Level-Crossing Spectroscopy	203
7.1.6	Resonance Methods for Liquids and Solids	209
7.2	Microwave Radiometry	218
7.3	Radio Astronomy	222
8.	Lasers	227
8.1	Basic Principles	227
8.2	Coherence	230
8.3	Resonators and Mode Structure	231
8.4	Fixed-Frequency Lasers	236
8.4.1	The Ruby Laser	236
8.4.2	Four-Level Lasers	238
8.4.3	Pulsed Gas Lasers	241
8.4.4	The He–Ne Laser	243
8.4.5	Gaseous Ion Lasers	244
8.5	Tunable Lasers	246
8.5.1	Dye Lasers	246
8.5.2	Colour-Centre Lasers	255
8.5.3	Tunable Solid-State Lasers	256
8.5.4	Tunable CO ₂ Lasers	257
8.5.5	Semiconductor Lasers	259
8.6	Nonlinear Optical Phenomena	262
8.7	Ultra-short and Ultra-high-Power Laser Pulse Generation	276
8.7.1	Short-Pulse Generation by Mode-Locking	276
8.7.2	Generation of Ultra-high Power Pulses	282
9.	Laser Spectroscopy	287
9.1	Basic Principles	287
9.1.1	Comparison Between Conventional Light Sources and Lasers	287
9.1.2	Saturation	287
9.1.3	Excitation Methods	289

9.1.4	Detection Methods	290
9.1.5	Laser Wavelength Setting	292
9.2	Doppler-Limited Techniques	294
9.2.1	Absorption Measurements	294
9.2.2	Intracavity Absorption Measurements	296
9.2.3	Absorption Measurements on Excited States	297
9.2.4	Level Labelling	298
9.2.5	Two-Photon Absorption Measurements	299
9.2.6	Opto-Galvanic Spectroscopy	301
9.2.7	Single-Atom and Single-Molecule Detection	304
9.2.8	Opto-Acoustic Spectroscopy	304
9.3	Optical Double-Resonance and Level-Crossing Experiments with Laser Excitation	306
9.4	Time-Resolved Atomic and Molecular Spectroscopy	311
9.4.1	Generation of Short Optical Pulses	312
9.4.2	Measurement Techniques for Optical Transients	312
9.4.3	Background to Lifetime Measurements	318
9.4.4	Survey of Methods of Measurement for Radiative Properties	319
9.4.5	Quantum-Beat Spectroscopy	325
9.5	Ultrafast Spectroscopy	331
9.5.1	Ultrafast Measurement Techniques	332
9.5.2	Molecular Reaction Dynamics (Femtochemistry)	336
9.5.3	Coherent Control	338
9.6	High-Power Laser Experiments	339
9.6.1	Above Threshold Ionization (ATI)	340
9.6.2	High Harmonic Generation	342
9.6.3	X-Ray Laser Pumping	347
9.6.4	Broadband X-Ray Generation	348
9.6.5	Relativistic Effects and Laser Accelerators	351
9.6.6	Laser-Nuclear Interactions and Laser-Driven Fusion	351
9.7	High-Resolution Laser Spectroscopy	351
9.7.1	Spectroscopy on Collimated Atomic and Ionic Beams	352
9.7.2	Saturation Spectroscopy and Related Techniques	359
9.7.3	Doppler-Free Two-Photon Absorption	368
9.8	Cooling and Trapping of Ions and Atoms	374
9.8.1	Introduction	374
9.8.2	Ion Traps	376
9.8.3	Basic Laser Cooling in Traps	377
9.8.4	Trapped Ion Spectroscopy	379
9.8.5	Atom Cooling and Trapping	379
9.8.6	Sub-Recoil Cooling	382
9.8.7	Atom Optics	384
9.8.8	Bose-Einstein Condensation and “Atom Lasers”	384
9.8.9	Ultracold Fermionic Gases	387

10. Laser-Spectroscopic Applications	389
10.1 Diagnostics of Combustion Processes	389
10.1.1 Background	389
10.1.2 Laser-Induced Fluorescence and Related Techniques ..	392
10.1.3 Raman Spectroscopy	398
10.1.4 Coherent Anti-Stokes Raman Scattering	398
10.1.5 Velocity Measurements	403
10.2 Laser Remote Sensing of the Atmosphere	406
10.2.1 Optical Heterodyne Detection	407
10.2.2 Long-Path Absorption Techniques	408
10.2.3 Lidar Techniques	414
10.3 Laser-Induced Fluorescence and Raman Spectroscopy in Liquids and Solids	425
10.3.1 Hydrospheric Remote Sensing	426
10.3.2 Vegetation Monitoring	429
10.3.3 Monitoring of Surface Layers	430
10.4 Laser-Induced Chemical Processes	435
10.4.1 Laser-Induced Chemistry	435
10.4.2 Laser Isotope Separation	436
10.5 Spectroscopic Aspects of Lasers in Medicine	441
10.5.1 Thermal Interaction of Laser Light with Tissue	441
10.5.2 Photodynamic Tumour Therapy	443
10.5.3 Tissue Diagnostics with Laser-Induced Fluorescence ..	447
10.5.4 Scattering Spectroscopy and Tissue Transillumination.	454
 Questions and Exercises	 461
 References	 473
 Index	 575