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（影印版）

Atomic and Molecular Spectroscopy: Basic Aspects and Practical Applications (4th Edition)

原子和分子光谱学——基础及实际应用（第四版）

S. Svanberg

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国外物理名著系列序言

对于国内的物理学工作者和青年学生来讲，研读国外优秀的物理学著作是系统掌握物理学知识的一个重要手段。但是，在国内并不能及时、方便地买到国外的图书，且国外图书不菲的价格往往令国内的读者却步，因此，把国外的优秀物理原著引进到国内，让国内的读者能够方便地以较低的价格购买是一项意义深远的工作，将有助于国内物理学工作者和青年学生掌握国际物理学的前沿知识，进而推动我国物理学科研和教学的发展。

为了满足国内读者对国外优秀物理学著作的需求，科学出版社启动了引进国外优秀著作的工作，出版社的这一举措得到了国内物理学界的积极响应和支持，很快成立了专家委员会，开展了选题的推荐和筛选工作，在出版社初选的书单基础上确定了第一批引进的项目，这些图书几乎涉及了近代物理学的所有领域，既有阐述学科基本理论的经典名著，也有反映某一学科专题前沿的专著。在选择图书时，专家委员会遵循了以下原则：基础理论方面的图书强调“经典”，选择了那些经得起时间检验、对物理学的发展产生重要影响、现在还不“过时”的著作（如狄拉克的《量子力学原理》）。反映物理学某一领域进展的著作强调“前沿”和“热点”，根据国内物理学研究发展的实际情况，选择了能够体现相关学科最新进展，对有关方向的科研人员和研究生有重要参考价值的图书。这些图书都是最新版的，多数图书都是2000年以后出版的，还有相当一部分是当年出版的新书。因此，这套丛书具有权威性、前瞻性和应用性强的特点。由于国外出版社的要求，科学出版社对部分图书进行了少量的翻译和注释（主要是目录标题和练习题），但这并不会影响图书“原汁原味”的感觉，可能还会方便国内读者的阅读和理解。

“他山之石，可以攻玉”，希望这套丛书的出版能够为国内物理学工作者和青年学生的工作和学习提供参考，也希望国内更多专家参与到这一工作中来，推荐更多的好书。

中国科学院院士
中国物理学会理事长

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 untill 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 rigourous 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

1. Introduction

By *spectroscopy* we usually mean experimental charting of the energy-level structure of physical systems. For that purpose, the transition processes, spontaneous or induced, between different energy states are studied and spectroscopy therefore normally means analysis of various types of radiation – electromagnetic or particle emission. Spectroscopic investigations can be of a fundamental or an applied nature. In fundamental spectroscopy experimentally determined energy levels, transition probabilities, etc. are employed for obtaining an understanding of the studied systems using adequate theories or models. Usually, certain primary quantities (wavelengths, intensities, etc.) are measured in spectroscopic investigations. These quantities are then used to evaluate more fundamental quantities. This process is schematically illustrated in Fig. 1.1.

Fundamental quantities, such as wavelengths and transition probabilities, determined using spectroscopy, for atoms and molecules are of direct importance in several disciplines such as astrophysics, plasma and laser physics. Here, as in many fields of applied spectroscopy, the spectroscopic information can be used in various kinds of analysis. For instance, optical atomic absorption or emission spectroscopy is used for both qualitative and quantitative chemical analysis. Other types of spectroscopy, e.g. electron spectroscopy methods or nuclear magnetic resonance, also provide information on the chemical environment in which a studied atom is situated. Tunable lasers have had a major impact on both fundamental and applied spectroscopy. New fields of applied laser spectroscopy include remote sensing of the environment, medical applications, combustion diagnostics, laser-induced chemistry and isotope separation.

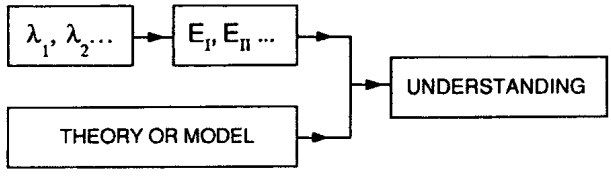

Fig. 1.1. The spectroscopic process

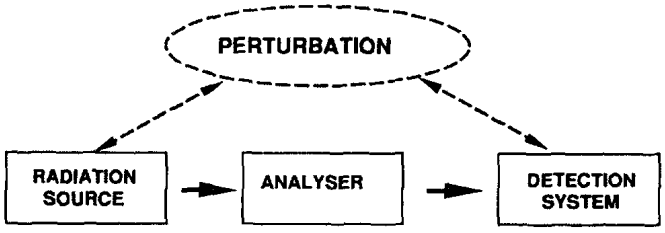

Fig. 1.2. Basic arrangement of a spectroscopic set-up

Dynamic properties of atomic and molecular systems can be studied by time-resolved spectroscopy. The recent availability of compact high-power lasers has allowed a quickly expanding research activity in ultra-intense laser–matter interaction, also offering many new challanges for theory.

In principle, a set-up for spectral studies consists of three components: a radiation source, an analyser and a detection system. In many modern techniques the system under investigation is subjected to different types of static or oscillatory fields and the influence of these fields on the system is studied in order to obtain a more complete picture of the system. Resonance methods are of special importance since they provide high accuracy in the determination of small energy splittings. The basic arrangement of a spectroscopic set-up is shown in Fig. 1.2.

The choice of spectroscopic method is primarily determined by the energy range of the phenomenon to be studied. In Fig. 1.3 the spectral ranges that

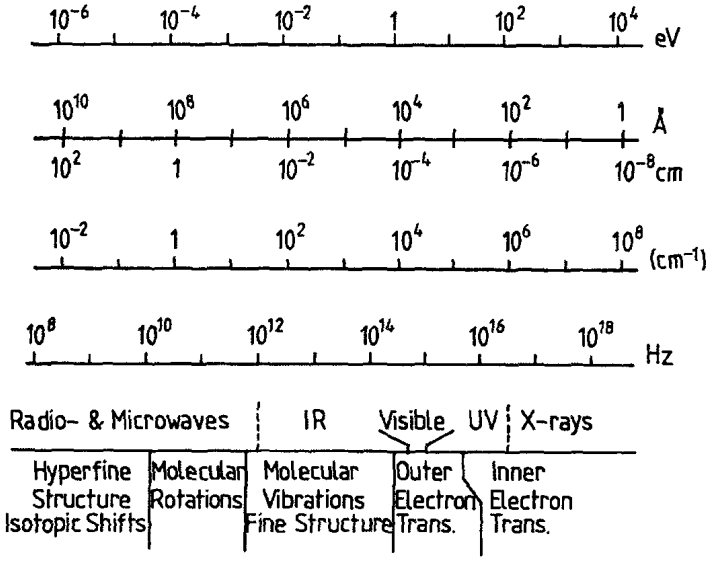

Fig. 1.3. Energy scales and spectroscopic phenomena

Table 1.1. Conversion factors between different energy units

Unit	Joule	cm^{-1}	Hz	eV
1 Joule (1 J)	1	5.03378×10^{22}	1.50919×10^{33}	6.24150×10^{18}
$1\,cm^{-1}$	1.98658×10^{-23}	1	2.99792×10^{10}	1.23992×10^{-4}
1 Hz	6.62608×10^{-34}	3.33565×10^{-11}	1	4.13567×10^{-15}
1 eV	1.60218×10^{-19}	8.06502×10^{3}	2.41799×10^{14}	1

are of interest in atomic and molecular spectroscopy are shown. The energy ranges for different types of structures and transitions are also indicated. Using the simple relations

$$\begin{array}{llll} \Delta E = h\nu, & \lambda = c/\nu, & 1/\lambda = \nu/c, & \nu = c(1/\lambda), \\ \text{Energy} & \text{Wavelength} & \text{Wavenumber} & \text{Frequency} \end{array} \tag{1.1}$$

(h: Planck constant, c: velocity of light) an energy interval ΔE can be uniquely expressed in eV (energy), nm (=10 Å) (wavelength), cm^{-1} (wavenumber) or Hz (frequency). $1\,cm^{-1}$ is sometimes called 1 Kayser. In Table 1.1 conversion factors between different units are given. The general field of scientific unit conversion is treated in [1.1]. The conversion factors are clearly connected to the values of the fundamental constants [1.2].

The choice of unit depends, to a great extent, on the energy region and on traditional factors:

X-ray region	keV ,
Visible and UV regions	nm , Å (in solid-state physics: eV) ,
Infrared region	μm , cm^{-1} ,
Radio-frequency region	MHz , cm^{-1} .

It is practical to memorize the following approximate relations

$$1\,eV \longleftrightarrow 8000\,cm^{-1} \longleftrightarrow 1200\,nm\,,$$
$$1\,cm^{-1} \longleftrightarrow 30\,GHz\,,$$

and kT at $T = 300\,K$ (room temperature)

$$kT_{300} \simeq 1/40\,eV\,.$$

(k is the Boltzmann constant, and T is the absolute temperature).

Transitions between inner electron orbitals normally occur in the keV range (X-rays) while the energies for transitions between outer orbitals are in the eV region (visible or near-UV and IR regions). The fine structure of atoms is of the order of $10^{-3}\,eV$ ($\sim 10\,cm^{-1}$) and hyperfine structures are typically about $10^{-6}\,eV$ ($\sim 300\,MHz$). Molecular vibrational energies splittings are of the order of $10^{-1}\,eV$, while rotational splittings are typically $10^{-3}\,eV$. Of course, these energies vary widely and the above values are given only to provide a first estimate of typical orders of magnitude.