Topics in Current Physics

Raman Spectroscopy
of Gases and Liquids

Editor: A. Weber

Springer-Verlag
Berlin Heidelberg New York

Raman Spectroscopy

of Gases and Liquids

Edited by A. Weber

With Contributions by
S. Brodersen J. M. Friedman H. W. Klöckner
G. V. Knighten J. W. Nibler D. L. Rousseau
H. W. Schrötter R. P. Srivastava A. Weber
P. F. Williams H. R. Zaidi

With 103 Figures

Springer-Verlag Berlin Heidelberg New York 1979

Professor Dr. Alfons Weber

Physics Department, Fordham University, Bronx, NY 10458, and

Molecular Spectroscopy Division, National Bureau of Standards,
Washington, DC, 20234, USA

ISBN 3-540-09036-3 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-09036-3 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Raman spectroscopy of gases and liquids. (Topics in current physics ; v. 11). Bibliography: p. Includes index. 1. Raman spectroscopy. 2. Gases—Spectra. 3. Liquids—Spectra. I. Weber, Alfons, 1927–. II. Series.
QC454.R36R35 535'.846 78-11693

Offset printing and bookbinding: Konrad Triltsch, Graphischer Betrieb, 8700 Würzburg.
2153/3130-543210

Topics in
Current Physics

11

Topics in Current Physics

Founded by Helmut K. V. Lotsch

Volume 1	**Beam-Foil Spectroscopy** Editor: S. Bashkin
Volume 2	**Modern Three-Hadron Physics** Editor: A. W. Thomas
Volume 3	**Dynamics of Solids and Liquids by Neutron Scattering** Editors: S. W. Lovesey and T. Springer
Volume 4	**Electron Spectroscopy for Surface Analysis** Editor: H. Ibach
Volume 5	**Structure and Collisions of Ions and Atoms** Editor: I. A. Sellin
Volume 6	**Neutron Diffraction** Editor: H. Dachs
Volume 7	**Monte Carlo Methods** in Statistical Physics Editor: K. Binder
Volume 8	**Ocean Acoustics** Editor: J. DeSanto
Volume 9	**Inverse Source Problems** in Optics Editor: H. P. Baltes
Volume 10	**Synchrotron Radiation** Techniques and Applications Editor: C. Kunz
Volume 11	**Raman Spectroscopy** of Gases and Liquids Editor: A. Weber
Volume 12	**Positrons in Solids** Editor: P. Hautojärvi
Volume 13	**Computer Processing of Electron Microscope Image** Editor: P. W. Hawkes
Volume 14	**Excitons** Editor: K. Cho
Volume 15	**Physics of Superionic Conductors** Editor: M. B. Salamon

Preface

The Raman effect is a most useful tool for the study of molecular vibrations and molecular structure. Information about the structure and symmetry of molecules, as well as about their vibrational energies can be obtained to a reasonable degree of satisfaction from their infrared and Raman vibrational spectra. The body of knowledge of the vibrational infrared and Raman spectra of molecules is immense and is now so well organized and understood that it is found to be represented in any standard upper level undergraduate curriculum in chemistry. The rotational energies of a molecule and quantitative details about its structure can only be obtained through the techniques of microwave, and high-resolution infrared and Raman spectroscopy of low pressure gases and vapors. The results of such investigations are of interest not only to the academic scientists, but also to scientists and engineers who are active in applied fields of chemistry and physics, as well as the atmospheric sciences.

This book deals with basic investigations of the Raman scattering of light by gases, with some attention also being given to liquid substances. After a brief introductory chapter that delineates the historical development of Raman spectroscopy of gases, high-resolution rotation-vibrational and pure rotational Raman spectroscopy is described in Chapters 2 and 3. The all-important intensity parameter, the Raman scattering cross section, is treated in Chapter 4, while the broadening of Raman lines due to the effects of intermolecular forces is taken up in Chapter 5. Resonance Raman scattering is presented in Chapter 6 while the new field of CARS, Coherent Anti-Stokes Raman Scattering, which owes its existence to the laser, is treated in the last chapter. The whole tone of the book reflects current research interests which are based on Raman spectra generated by laser sources.

The topics presented are arranged in such a manner that the reader is led from the study of the ideal, isolated molecule, to the effects of intermolecular forces, and finally to the considerations of the nonlinearities in the Raman scattering process. Each chapter contains an extensive list of references to the research literature whereby further details, and topics not taken up in this book, can be obtained. A supplementary list of references, compiled after the completion of the manuscripts, is added to the end of the book to insure a complete listing of the current litera-

ture. It was my intention to have this book carry the imprint date of 1978 so as to have its publication occur in the 50th anniversary year of the discovery of the Raman effect. Indeed the manuscript was well in hand but for technical reasons the publication date had to be set for 1979.

I am indebted to the authors of the various chapters for the careful preparation of their manuscripts and also for their good will and patience in seeing the results of their efforts reach the public domain. Finally I wish to thank Dr. H. Lotsch and the staff of Springer-Verlag for their cooperation and for bringing out this book in the minimum possible time.

Bronx, N.Y., and Washington, D.C. *Alfons Weber*
October, 1978

List of Contributors

BRODERSEN, SVEND

Kemisk Institut, Aarhus University, DK 8000 Aarhus C, Denmark

FRIEDMAN, JOEL

Bell Telephone Laboratories, Murray Hill, NJ 07974, USA

KLÖCKNER, HANS WOLFGANG

Sektion Physik, Universität München, Schellingstraße 4
D-8000 München 40, Fed. Rep. of Germany

KNIGHTEN, GARY

Chemistry Department, Oregon State University, Corvallis, OR 97331, USA

NIBLER, JOSEPH W.

Chemistry Department, Oregon State University, Corvallis, OR 97331, USA

ROUSSEAU, DENIS L.

Bell Telephone Laboratories, Murray Hill, NJ 07974, USA

SCHRÖTTER, HEINZ W.

Sektion Physik, Universität München, Schellingstraße 4
D-8000 München 40, Fed. Rep. of Germany

SRIVASTAVA, RAJENDRA P.

Physics Department, University of New Brunswick, Fredericton
New Brunswick, E3B 5A3, Canada

WEBER, ALFONS

Physics Department, Fordham University, Bronx, NY 10458, USA
and
Molecular Spectroscopy Division, National Bureau of Standards
Washington, DC, 20234, USA

WILLIAMS, FRAZER

Department of Electrical Engineering, Texas Tech University
Lubbock, TX 79413/USA

ZAIDI, HAIDER RAZA

Physics Department, University of New Brunswick, Fredericton
New Brunswick, E3B 5A3, Canada

Springer Series in Chemical Physics

Editors: V.I. Goldanskii, R. Gomer, F.P. Schäfer, J.P. Toennies

A Selection

Volume 1
I.I. Sobelman

Atomic Spectra and Radiative Transitions

1979. 21 figures, 58 tables. Approx. 330 pages
ISBN 3-540-09082-7

Contents:
Elementary Information on Atomic Spectra: The Hydrogen Spectrum. Systematics of the Spectra of Muli-Electron Atoms. Spectra of Multielectron Atoms. – Theory of Atomic Spectra: Angular Momenta. Systematics of the Level of Multielectron Atoms. Hyperfine Structure of Spectral Lines. The Atom in an External Electric Field. The Atom in an External Magnetic Field. Radiative Transitions. – References. – Subject Index.

Volume 3

Advances in Laser Chemistry

Proceedings of the Conference on Advances in Laser Chemistry, California Institute of Technology, Pasadena, USA, March 20–22, 1978
Editor: A. Zewail
Volume Editor: F.P. Schäfer
1978. 242 figures, 2 tables. X, 463 pages
ISBN 3-540-08997-7

Contents:
Laser-Induced Chemistry. – Picosecond Processes and Techniques. – Non-Linear Optical Spectroscopy and Dephasing Processes. – Multiphoton Excitation in Molecules. – Molecular Dynamics by Molecular Beams.

Springer-Verlag
Berlin
Heidelberg
New York

Topics in Applied Physics

Founded by H.K.V. Lotsch

A Selection

Volume 2

Laser Spectroscopy of Atoms and Molecules

Editor: H. Walther
1976. 137 figures, 22 tables. XVI, 383 pages
ISBN 3-540-07324-8

Contents:
H. Walther: Atomic and Molecular Spectroscopy with Lasers. – *E.D. Hinkley, K.W. Nill, F.A. Blum:* Infrared Spectroscopy with Tunable Lasers. – *K. Shimoda:* Double-Resonance Spectroscopy of Molecules by Means of Lasers. – *J.M. Cherlow, S.P.S. Porto:* Laser Raman Spectroscopy of Gases. – *B. Decomps, M. Dumont, M. Duclov:* Linear and Nonlinear Phenomena in Laser Optical Pumping. – *K.M. Evenson, F.R. Petersen:* Laser Frequency Measurements, the Speed of Light, and the Meter.

Volume 8

Light Scattering in Solids

Editor: M. Cardona
1975. 111 figures, 3 tables. XIII, 339 pages
ISBN 3-540-07354-X

Contents:
M. Cardona: Introduction. – *A. Pinczuk, E. Burstein:* Fundamentals of Inelastic Light Scattering in Semiconductors and Insulators. – *R.M. Martin, L.M. Falicov:* Resonant Raman Scattering. – *M.V. Klein:* Electronic Raman Scattering. – *M.H. Brodsky:* Raman Scattering in Amorphous Semiconductors. – *A.S. Pine:* Brillouin Scattering in Semiconductors. – *Y.-R. Shen:* Stimulated Raman Scattering.

Volume 14

Laser Monitoring of the Atmosphere

Editor: E.D. Hinkley
1976. 84 figures. XV, 380 pages
ISBN 3-540-07743-X

Contents:
E.D. Hinkley: Introduction. – *S.H. Melfi:* Remote Sensing for Air Quality Management. – *V.E. Zuev:* Laser-Light Transmission through the Atmosphere. – *R.T.H. Collis, P.B. Russell:* Lidar Measurement of Particles and Gases by Elastic Backscattering and Differential Absorption. – *H. Inaba:* Detection of Atoms and Molecules by Raman Scattering and Resonance Fluorescence. – *E.D. Hinkley, R.T. Ku, P.L. Kelley:* Techniques for Detection of Molecular Pollutants by Absorbing of Laser Radiation. – *R.T. Menzies:* Laser Heterodyne Detection Techniques.

Springer Series in Optical Sciences

Editor: D.L. MacAdam

A Selection

Volume 2
R. Beck, W. Englisch, K. Gürs

Table of Laser Lines in Gases and Vapors

2nd revised and enlarged edition 1978.
IX, 202 pages
ISBN 3-540-08603-X

Volume 3

Tunable Lasers and Applications

Proceedings of the Loen Conference, Norway, 1976
Editors: A. Mooradian, T. Jaeger, P. Stokseth

1976. 238 figures. VIII, 404 pages
ISBN 3-540-07968-8

Contents:
Tunable and High Energy UV-Visible Lasers. – Tunable IR Laser Systems. – Isotope Separation and Laser Driven Chemical Reactions. – Nonlinear Excitation of Molecules. – Laser Photokinetics. – Atmospheric Photochemistry and Diagnostics. – Photobiology. – Spectroscopic Applications of Tunable Lasers.

Volume 4
V.S. Letokhov, V.P. Chebotayev

Nonlinear Laser Spectroscopy

1977. 193 figures, 22 tables. XVI, 466 pages
ISBN 3-540-08044-9

Contents:
Introduction. – Elements of the Theory of Resonant Interaction of a Laser Field and Gas. – Narrow Saturation Resonances on Doppler-Broadened Transition. – Narrow Resonances of Two-Photon Transitions Without Doppler Broadening. – Nonlinear Resonances on Coupled Doppler-Broadened Transitions. – Narrow Nonlinear Resonances in Spectroscopy. – Nonlinear Atomic Laser Spectroscopy. – Nonlinear Molecular Lser Spectroscopy. – Nonlinear Narrow Resonances in Quantum Electronics. – Narrow Nonlinear Resonances in Experimental Physics.

Volume 7

Laser Spectroscopy III

Proceedings of the Third International Conference, Jackson Lake Lodge, Wyoming, USA, July 4–8, 1977
Editors: J.L. Hall, J.L. Carlsten

1977. 296 figures. XII, 468 pages
ISBN 3-540-08543-2

Contents:
Fundamental Physical Applications of Laser Spectroscopy. – Multiple Photon Dissociation. – New Sub-Doppler Interaction Techniques. – Highly Excited States, Ionization, and High Intensity Interactions. – Optical Transients. – High Resolution and Double Resonance. – Laser Spectroscopic Applications. – Laser Sources. – Laser Wavelength Measurements. – Postdeadline Papers.

Springer-Verlag
Berlin
Heidelberg
New York

Contents

1. Introduction

A. Weber

That the laser has revolutionized the field of molecular spectroscopy is a well known commonplace. This is indeed so emphatically true in the case of Raman spectroscopy, that a newcomer to this field is of the understandable impression that it was practically nonexistent prior to the invention of the laser in 1960. That such an impression is very much in error is, of course, well documented by the many research articles and books dealing with the Raman effect that have been published since its discovery just 50 years ago, in 1928. The impact made by the laser is, however, so strong that the appellation "Laser Raman Spectroscopy" is now often used to underline the break with the past.

There are now available many research monographs that deal with various specialized aspects or even whole research fields that are based on the Raman effect. To mention only a few of the more recently published ones we have the volumes edited by ANDERSON [1.1] which contain contributions that span nearly all aspects of the Raman effect, the books by KONINGSTEIN [1.2] and LONG [1.3], the series edited by CLARK and HESTER [1.4], and the books by CARDONA [1.5], and CLAUS et al. [1.6], which deal with light scattering by solids only. The proceedings of international Raman conferences are published in book form [1.7,8] and a specialized journal devoted to, among other light scattering phenomena, "all aspects of Raman spectroscopy" [1.9] began publication in 1973. The volumes on molecular spectroscopy issued by The Chemical Society [1.10] as part of their Specialist Periodical Reports contain annual reviews of the current literature on Raman spectroscopy.

The present volume grew out of a request to bring together in one book the results of contemporary research on Raman spectroscopy of gases as there have been numerous advances in this field since the appearance in 1973 of the last comprehensive review of this subject [1.11]. This restriction to gases would have been easily accomplished only a few years ago but is unwise now in view of the role played by liquid and solid substances in contributing to the understanding of resonance, nonlinear, and stimulated Raman processes. Nevertheless, the spotlight in this book is on the single molecule.

Although the Raman effect was experimentally discovered in 1928 in liquids and solids, Raman scattering by gases has played a fundamental role in the development of the basic theory of the phenomenon. The Raman spectra of gaseous hydrogen chloride

[1.12], hydrogen [1.13-15], oxygen [1.14,16,17], nitrogen [1.14,16], carbon monoxide [1.18,19], nitric oxide [1.14,19,20], carbon dioxide [1.21,22], nitrous oxide [1.22], ammonia [1.23-25], methane [1.23,26,27], ethane [1.25,27], ethylene [1.25, 27], and acetylene [1.25,27] were quickly studied under moderate resolution and using high pressures. These early investigations culminated in the PLACZEK and TELLER's [1.28] comprehensive theory of the rotational and rotation-vibrational Raman scattering by free molecules and also in the more inclusive general theory of the Raman effect of PLACZEK [1.29]. From then until the early 1950's Raman spectra of gases were studied only occasionally until new experimental techniques developed by H.L. Welsh at the University of Toronto and B.P. Stoicheff, then at the National Research Council of Canada, caused a revival of interest in this field. The new activity resulted in major contributions to our knowledge of molecular structures, Raman scattering cross sections, and intermolecular forces. These techniques, and the results that were obtained with them, have been described previously in several review articles [1.11,30-32,41].

The first laser excited Raman spectrum of a gas showing resolved rotational structure was reported in 1965 [1.33], and this was soon followed by several reports describing improvements in the experimental technique [1.34-37]. These advances were summarized in several reviews [1.11,38,40]. This early work in "Laser Raman Spectroscopy of Gases" addressed itself to the spontaneous Raman scattering and the quest for improvements in the efficiency and resolution capabilities of the method. Since that time there have been major advances in other aspects of gas-phase Raman spectroscopy, and the present book provides to the chemist and physicist a comprehensive review of this field of study.

Chapters 2 and 3 are on high-resolution studies of low pressure gases and vapors. Taken together they comprise a review of the current state of knowledge of the rotational and rotation-vibrational energies of diatomic and polyatomic molecules insofar as these have been studied by means of "Laser Raman Spectroscopy". Chapter 2 contains a modern version of the theory of rotational Raman scattering. This theory forms the basis of understanding of the results that are given in both chapters. The molecular-structure problems that are attacked by the method of high-resolution Raman spectroscopy are the same as those considered by infrared and microwave spectroscopy and an acquaintance with these topics will aid in the assimilation of the contents of these two chapters. The experimental techniques that are employed in high-resolution Raman spectroscopy of gases are still sufficiently novel and unique, and the apparatus is specially designed and built, that both chapters contain extensive and detailed descriptions of them. There is, therefore, some overlap between Chaps.2 and 3 but the duplication that does occur is believed to be more than made up by the complementary features to guide those interested in initiating their own research program in this field.

The determination of intensities and transition probabilities has been notoriously more difficult than that of finding accurate energy levels. This problem is particularly acute in Raman spectroscopy and, except for an occasional early result, reliable Raman scattering cross sections did not become available until the late 1950's (see [1.32] for a review of the pre-laser work). The availability of laser techniques has reopened this field of investigation and Chap.4 contains a treatment of the theory and experimental determination of Raman scattering cross sections from gases. The results that were obtained with pre-laser techniques only are also included in this chapter after having been reevaluated so as to place them on an equivalent basis with the newer, laser-derived results. This chapter also includes a discussion of the Raman scattering cross sections of molecules in the liquid state of aggregation.

Whereas Chaps.2 and 3, and most of Chap.4 deal with dilute gases in which molecules may be considered "free", the effects of intermolecular forces that become important with increasing gas density are taken up in Chap.5.

The Raman line widths, -shifts, and -shapes are functions of the gas pressure and density and also depend on the nature of the interaction partners. Quantitative studies of these dependencies were initiated in 1950 at the University of Toronto and the results of these investigations were summarized in a review by GRAY and WELSH [1.41] published in 1971. There have been many theoretical and experimental advances in this field since that time and Chap.5 addresses itself to these.

The phenomena described in Chaps.2-5 are those of the nonresonant Raman effect. Although strenuous efforts were made in the pre-laser era to experimentally study resonance Raman scattering it was only by means of narrow line, and also tunable lasers that sufficiently exact findings on simple molecules became available to allow quantitative evaluations of the various theoretical approaches. These questions are taken up in Chap.6.

The subject of the last chapter of this book, CARS (*C*oherent *A*nti-Stokes *R*aman *S*cattering) owes its existence to the laser. Although already observed in 1963 the CARS phenomenon could not be exploited in molecular spectroscopy until tunable lasers of sufficient power became available. This subject is currently the least settled and most actively investigated one of the various topics presented in this book.

An overview of the topics and their sequential appearance in the various chapters reveals an attempt to present a coherent coverage of Raman spectroscopy of molecules as a modern field of research. The topics covered in Chaps.2-6 were all studied prior to the invention of the laser, and indeed some of the molecules now under investigation with laser techniques were already studied as early as 1929. However, all of these topics have benefited from the laser, while that of the last chapter is a practical impossibility without laser sources. The "free" molecule is the center of attention in Chaps.2-4 while molecular interactions and Raman scattering by condensed phases are also considered in Chaps.5-7. Several subjects had to be excluded from this book due either to the desire to maintain a topical focus or because they are