

Topics in Current Physics

Raman Spectroscopy of Gases and Liquids

Editor: A. Weber

A. Weber	Introduction
S. Brodersen	High-Resolution Rotation-Vibrational Raman Spectroscopy
A. Weber	High-Resolution Rotational Raman Spectra of Gases
H. W. Schrötter	Raman Scattering Cross Sections in Gases and Liquids
H. W. Klöckner	
R. P. Srivastava	Intermolecular Forces Revealed by Raman Scattering
H. R. Zaidi	
D. L. Rousseau	The Resonance Raman Effect
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P. F. Williams	
J. W. Nibler	Coherent Anti-Stokes Raman Spectroscopy
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With Contributions by

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With 103 Figures

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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.

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Alfons Weber

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Contents

1. <i>Introduction</i> . By A. Weber	1
References	4
2. <i>High-Resolution Rotation-Vibrational Raman Spectroscopy</i> By S. Brodersen (With 19 Figures)	7
2.1 Theory	8
2.1.1 Intensity Expressions	8
2.1.2 Selection Rules	11
2.1.3 The Vibrational Matrix Element	13
2.1.4 Linear Molecules	14
2.1.5 Symmetric Top Molecules	17
2.1.6 Asymmetric Top Molecules	24
2.1.7 Spherical Top Molecules	27
2.1.8 Comparison with the Theory of Infrared Spectra	30
2.2 Experimental Technique	30
2.2.1 General Features of Instrumentation and Technique	31
2.2.2 Details of Present Instruments	34
2.2.3 Comparison to Infrared Experimental Techniques	39
2.3 Results	39
2.3.1 General Remarks	39
2.3.2 Linear Molecules	40
2.3.3 C _{3v} Molecules	47
2.3.4 Other Symmetric Top Molecules	54
2.3.5 Asymmetric Top Molecules	56
2.3.6 Spherical Top Molecules	62
2.3.7 Conclusion	66
References	67
3. <i>High-Resolution Rotational Raman Spectra of Gases</i> By A. Weber (With 19 Figures)	71
3.1 Instrumentation and Techniques	72

3.1.1	The Raman Source Unit	72
a)	The Laser System	72
b)	The Scattering Cell	73
c)	The Illuminating Optics	76
d)	The Transfer Optics	77
3.1.2	Filters	77
3.1.3	The Spectrograph	78
3.1.4	Recording Materials	80
3.1.5	Wavelength Standards	82
3.1.6	Determination of Raman Shifts	82
3.1.7	Photoelectric Spectrometers	84
3.1.8	Interferometric Techniques	84
3.2	Observed Rotational Spectra	85
3.2.1	Diatomic Molecules	85
3.2.2	Linear Polyatomic Molecules	92
3.2.3	Symmetric Top Molecules	96
3.2.4	Asymmetric Top Molecules	106
3.2.5	"Forbidden" Pure Rotational Spectra	114
a)	Spherical Top Molecules — T_d Symmetry	114
b)	Symmetric Top Molecules — C_{3v} Symmetry	115
3.3	Summary	115
	References	117
4.	<i>Raman Scattering Cross Sections in Gases and Liquids</i>	
	By H.W. Schrötter and H.W. Klöckner (With 14 Figures)	123
4.1	Raman Scattering Cross Sections in Gases	124
4.1.1	Theoretical Considerations	124
4.1.2	Determination of the Absolute Scattering Cross Section of Nitrogen	127
4.1.3	Measurement of Relative Scattering Cross Sections	130
a)	Experimental Procedure	132
b)	Results	135
c)	Influence of the Resonance Raman Effect	154
4.2	Raman Scattering Cross Sections in Liquids	156
4.2.1	Internal Field Effect and Intermolecular Interactions	156
4.2.2	Absolute Scattering Cross Sections	157
4.2.3	Relative Scattering Coefficients	159
4.3	Ratio of the Raman Scattering Cross Section in the Liquid and in the Gaseous State	160
4.4	Conclusion	163
	References	164

5. <i>Intermolecular Forces Revealed by Raman Scattering</i>	
By R.P. Srivastava and H.R. Zaidi (With 4 Figures)	167
5.1 Introductory Remarks	167
5.2 Spectral Function for Raman Scattering	169
5.3 Impact Theory	174
5.4 Isolated Lines	177
5.4.1 Calculation of Line Widths and Shifts	177
a) Non-Perturbative Approaches	178
b) Perturbative Approaches	179
c) Line Shift	184
5.4.2 Comparison of Theory with Experiment and Information Obtained about Intermolecular Potentials	185
5.5 Overlapping Lines and Band Shapes	189
5.6 Statistical Theories	192
5.7 Liquids	193
5.8 Conclusion	197
References	197
6. <i>The Resonance Raman Effect</i>	
By D.L. Rousseau, J.M. Friedman, and P.F. Williams (With 26 Figures)	203
6.1 Resonance Raman Scattering	204
6.2 Diatomic Molecules	210
6.2.1 Discrete Resonance Raman Scattering	212
6.2.2 Continuum Resonance Raman Scattering	218
6.2.3 Perturbed Diatomic Molecules	224
6.3 Polyatomic Molecules	230
6.4 Porphyrin Compounds	233
6.4.1 Porphyrin Absorption Spectrum	234
6.4.2 Helpful Diagrams	237
6.4.3 Scattering from Q_0 , Q_1 , and B	239
6.4.4 Anomalous Polarization	242
6.4.5 Interference Effects	244
6.4.6 Non-Adiabatic Effects	245
6.4.7 Influence of Jahn-Teller Distortion	249
6.5 Concluding Remarks	249
References	250
7. <i>Coherent Anti-Stokes Raman Spectroscopy</i>	
By J.W. Nibler and G.V. Knighten (With 21 Figures)	253
7.1 Theory	255
7.1.1 Maxwell's Equations for Macroscopic Samples	255

7.1.2	Symmetry Properties of $\chi^{(3)}$	258
7.1.3	CARS Amplitudes	260
7.1.4	Raman Amplitudes	263
7.1.5	Microscopic Third-Order Susceptibilities	265
7.2	Comparison of CARS and Raman Spectroscopy	268
7.2.1	Signal Strengths	268
7.2.2	Lineshapes and Maxima	269
7.2.3	Selection Rules	272
7.2.4	Orientation Averaging and Polarization Behavior	273
7.3	Experimental Aspects of CARS	276
7.4	Survey of CARS Experimental Results	281
7.4.1	Solids	281
7.4.2	Liquids	282
7.4.3	Gases	283
	a) Combustion and Gas Diagnostics	283
	b) Plasma Diagnostics	284
	c) Photochemical, Kinetic and Excited State Studies	286
	d) High-Resolution Spectroscopy	287
7.4.4	Solutions	289
7.4.5	Background Suppression in CARS	291
7.5	Summary	294
	References	295
	<i>Additional References with Titles</i>	301
	<i>Subject Index</i>	307

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 (*Coherent Anti-Stokes Raman Scattering*) 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