Laser Light Scattering

Benjamin Chu

Laser Light Scattering

Benjamin Chu

Chemistry Department
State University of New York
Stony Brook, New York

1974

ACADEMIC PRESS
New York San Francisco London

A Subsidiary of Harcourt Brace Jovanovich, Publishers

DSO3/28

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

Library of Congress Cataloging in Publication Data

Chu, Benjamin.
Laser light scattering.

(Quantum electronics–principles and applications)
Includes bibliographies
1. Laser beams–Scattering. I. Title.
QC446.2.C48 535.5'8 74-1630
ISBN 0-12-174550-3

PRINTED IN THE UNITED STATES OF AMERICA

Preface

This book is intended to serve as an introduction to the interdisciplinary area of laser light scattering. The treatment is not designed to review all the recent developments in this rapidly expanding field, for the subject matter is highly diversified. Rather it is based on a biased selection of topics which very much favor my own interests. The decision not to treat in detail the quantal approach was made in order to discuss theoretical concepts at a realistic level, readily understood by a (physical) chemistry graduate student. In this respect, pertinent references have been listed even in the first two review chapters (Chapters 2 and 3) for those who may need them. I have attempted to develop the topics following a sequence similar to my own experience and to smooth out the difficulties which I encountered when I first entered this field a few years ago.

The subject matter concentrates almost exclusively on quasielastic laser scattering. I assume as background some knowledge in the physical sciences equivalent to a chemistry graduate student whose training in physics is relatively limited, as he is likely to be unfamiliar with topics in electrodynamics, optics, electronics, hydrodynamics, and quantum mechanics. Therefore, Chapters 2 and 3, which constitute a brief review of classical electricity and magnetism and the general scattering theory, may appear to be a bit tedious to physicists and can certainly be omitted by a number of readers. However, normally experimentalists in fields other than physics are not familiar with *all* these physical theories.

Chapter 4 deals with basic theoretical concepts related to light mixing spectroscopy. The quantal approach has not been emphasized for the reason I have already stated, even though the equivalence of quantal and classical treatments in the present context has been discussed briefly. Chapter 5 on the Fabry–Perot interferometry may be skipped altogether. It is included with the anticipation that optical mixing spectroscopy and interferometry will become truly complimentary techniques. Eventually, stable single-frequency CW lasers and piezoelectric scanned Fabry–Perot etalons with servomechanisms that automatically compensate the laser frequency drift, and the tilt, nonlinearity, and cavity extension of the etalons, will become routine, so that the entire time domain ranging from seconds to 10^{-12} sec will be readily accessible. Photon counting fluctuations, discussed in Chapter 6, will become increasingly more important because digital photon counting and correlation are much more efficient than analog devices and are certain to play a prominent role in laser light scattering. Chapter 7 on experimental methods should be very useful to the novice experimentalist. I have intentionally skipped discussions on the standard conventional light scattering instrumentation and established precautionary procedures in solution clarification by ultrafiltration and ultracentrifugation. Instead, emphasis has been on considerations to set up a light scattering spectrometer using digital photon counting and correlation techniques.

The applications of laser light scattering to biology, chemistry, engineering, and physics will surely be expanded. I am certain that otherwise unavailable new information can be obtained for macromolecular systems (Chapter 8) using this technique. Anemometry (Chapter 10) is being revolutionized. However, its utility in reaction kinetics (Chapter 9) is less certain, even though specific successes have been realized (Section 9.4), and its potential capability is tempting indeed. Chapter 11 dealing with critical opalescence is more compact and is intended primarily for the expert. Research in critical phenomena should be particularly fruitful in asymmetry and tricritical point studies with both being difficult but challenging experiments.

Acknowledgments

I am grateful to the late Professor Peter J. W. Debye who introduced me to the study of light scattering, to the John Simon Guggenheim foundation which provided me an opportunity to have more free time to think and to learn, to Professors Bruno H. Zimm and George B. Benedek in whose departments at the University of California, San Diego, and the Massachusetts Institute of Technology, respectively, the project was launched. Professor S. H. Chen and Dr. W. Tscharnuter were helpful in making thoughtful criticisms and in pointing out a number of minor errors in the manuscript. I wish to express my appreciation to many of my professional colleagues who have supplied me with preprints, reprints, original tracings of figures, and occasional helpful comments during the preparation of this book. In particular, I have the pleasure of thanking Professors G. B. Benedek, S. H. Chen, H. Z. Cummins, and R. Pecora and Drs. P. Berge, S. Fujime, J. Lastovka, and E. R. Pike for sending me complete sets of their reprints and preprints. I also wish to gratefully acknowledge the support of my work by the National Science Foundation, the United States Army Research Office—Durham, the Petroleum Research Fund of the American Chemical Society, and the State University of New York. Finally, the most important support and encouragement throughout this endeavor has come from my wife Louisa, to whom this volume is dedicated.

Note added in proof†: We have so far emphasized the technique of optical heterodyning in laser Doppler velocimeters. For high-speed fluid flows, the shifted frequency is very large, and hence the use of scanning Fabry–Perot interferometry becomes a natural alternative. However, either approach is restricted to measuring mean flow and rms fluctuation velocities due to low duty cycle of the instruments. Laser Doppler velocimeters that permit direct measurements of instantaneous velocities have been reported (Paul and Jackson, 1971; Avidor, 1974). The technique uses a static slightly defocused spherical Fabry–Perot (DSFP) interferometer together with a cleverly designed mask that relates the Doppler shifted frequency to the photomultiplier tube output. Thus the PM tube displays the instantaneous flow velocity. A second PM tube can be introduced to monitor the total fringe intensity. By dividing the two signals, Avidor (1974) was able to retrieve the instantaneous velocity. The reader should consult the article by Avidor for the mask construction and the details of this ingenious LDV.

References

Avidor, J. M. (1974). *Appl. Opt.* **13**, 280.
Paul, D. M., and Jackson, D. A. (1971). *J. Phys. E.* **4**, 170.

† See p. 289.

Laser Light Scattering

Contents

Chapter I

INTRODUCTION

The study of electromagnetic scattering is a field tinted with considerable interdisciplinary complexion. Chemists have utilized light scattering and small-angle x-ray scattering to study the size and shape of macromolecules in solution as well as a whole range of materials including colloidal suspensions, glasses, and solid polymers. Meteorologists have used microwaves to observe the scattering by rain, snow, hail, and other objects in the atmosphere, while astrophysicists have been interested in the scattering of starlight by interplanetary and interstellar dust. The same basic scattering principles apparently govern all such different phenomena whenever the wavelength of the electromagnetic radiation is of the same magnitude as that of the scatterer. Before the onset of lasers, most light-scattering studies have been concerned with the integrated scattered intensity.

J. B. Richter reported observations of the phenomenon of light scattering by colloidal gold as far back as 1802. The scientific study of light scattering may be said to have commenced with the work of Tyndall on aerosols in 1869. It was in 1871 that Lord Rayleigh first explained the observed color and polarization of the sunlight scattered in the atmosphere even though he originally considered light as mechanical vibrations and based his treatment on the old elastic theory of light. Later, Rayleigh (1881, 1889) deduced the same results from Maxwell's electromagnetic wave theory and found that for noninteracting, nonabsorbing, and optically isotropic particles having sizes very small compared with the wavelength of the incident light the amount of scattering should be proportional to the reciprocal fourth power of the wavelength, now known as the Rayleigh law. Rayleigh's approach has since been elaborated to cover absorbing and anisotropic particles having sizes comparable to the wavelength of the incident radiation. Following the classical text by Van de Hulst (1957), Kerker (1969) has written a comprehensive book on "The Scattering of Light and Other Electromagnetic Radiation." There are also standard chapters in books (Flory, 1953; Tanford, 1961) and a monograph (Stacey, 1956) on applications of light scattering to macromolecules. Other specific topics have been presented by Kerker (1963) and Rowell and Stein (1967).

In condensed media or whenever the scatterers are close to one another, a detailed computation of the induced electromagnetic field surrounding a particle becomes very complex because intermolecular interactions have to be taken into account. Einstein (1910) was able to bypass the difficulties inherent in Rayleigh's analysis as applied to a collection of interacting particles. He assumed that local density fluctuations in neighboring volume elements could be independent of one another and carried out a quantitative calculation of the mean-square amplitude of those fluctuations from a statistical mechanics approach. Although Einstein's theory was able to explain the scattering from pure liquids and to predict the enormous increase in the scattering as the liquid–gas critical point was approached, the so-called *critical opalescence*, it failed to account for the angular dissymmetry of the strong scattered intensity in critically opalescent systems. Nevertheless, his theory remains valid for $K = 0$ [$K = ks = (2\pi/\lambda)(2 \sin \frac{1}{2}\theta)$] even in the critical region. Later Ornstein and Zernike (1914, 1915, 1916, 1926) tried to account for the scattering behavior at $K \neq 0$ by stressing the effects of correlation between fluctuations of neighboring volume elements. Again, there have been extensive reviews (Chu, 1967) on the fluctuation theory.

In laser light scattering (Chu, 1968), we study not only the changes in the number (intensity) and the direction (momentum) of each type of photon in the incident and the emerging light beams but also the corresponding frequency (energy) changes. Whereas angular dissymmetry and polarization of the scattered intensity can determine static properties such as the isothermal compressibility of a liquid and sizes and shapes of macromolecules in solution, polarized and depolarized optical spectra as well as their angular variations can be related to dynamical and structural properties of molecules. Brillouin (1914) realized that the local density fluctuations in a liquid could be considered as thermally excited sound waves (Debye, 1912). By retaining the time behavior of the thermal phonons, Brillouin (1922) reported the first consideration of the *spectrum* of light scattered from a condensed medium. In Russia, Mandel'shtam (1926) had independently deduced the spectrum of light scattered by thermal phonons and obtained the frequency shift. Gross (1930) made the first experimental observation of the Brillouin–Mandel'shtam components, and noticed the presence of an unshifted "central" component which was then explained by Landau and Placzek (1934) using nonpropagating local temperature fluctuations. Although the Landau–Placzek theory has been known for quite some time, accurate measurements on the frequency spectrum have been extremely difficult to obtain for the lack of intense monochromatic light sources and sufficiently high-resolution spectrometers. Thus, there are few noteworthy papers during the prelaser days (Fabelinskii, 1965).

In 1964, the first observations of the Brillouin–Mandel'shtam lines were reported using lasers coupled with ultrahigh-resolution Fabry–Perot etalons (Chiao *et al.*, 1964; Chiao and Stoicheff, 1964) and grating spectrometers (Benedek *et al.*, 1964). However, even the highest resolving power Fabry–Perot etalons fall short of providing sufficient resolution to measure the narrowing of the central component in critically opalescent systems. Thus, optical mixing spectrometers (Ford and Benedek, 1965; Cummins *et al.*, 1964) have been devised to measure very narrow linewidths. During the past few years, several types of laser-related spectroscopic techniques which permit high-resolution measurements of changes in photon energy have been improved. The time has come for us to utilize these new powerful tools as initial difficulties in both instrumentation and theory have been resolved.

The scattering process which will be discussed in this book can be described classically and will be based on selected topics covered in a review article on laser light scattering (Chu, 1970). Quantum-mechanical phenomena, such as the Raman effect, are excluded. There now exist many other review articles, all of which cover one or more aspects of topics related to laser light scattering, and several (those marked with *) include extensive references to the literature:

1.* Multiphoton Spectroscopy (Peticolas, 1967), Inelastic Light Scattering (Peticolas, 1972);
2. Optical Mixing Spectroscopy, with Applications to Problems in Physics, Chemistry, Biology, and Engineering (Benedek, 1969);
3.* Light Beating Spectroscopy (Cummins and Swinney, 1970);
4. A New Probe for Reaction Kinetics—The Spectrum of Scattered Light (Yeh and Keeler, 1969b);
5.* Quasi-Elastic Light Scattering from Macromolecules (Pecora, 1972).
6. Liquids: Dynamics of Liquid Structure (Mountain, 1970);
7.* Spectral Distribution of Scattered Light in a Simple Fluid (Mountain, 1966);
8.* Study of Fluids by Light Scattering (McIntyre and Sengers, 1968);
9. Brillouin Spectroscopy with Lasers (Stoicheff, 1968);
10.* Brillouin Light Scattering from Crystals in the Hydrodynamic Region (Griffin, 1968);
11. Correlation Functions for Molecular Motion (Gordon, 1968);
12. Light Scattering with Laser Sources (Porto, 1969);

Furthermore, the Physical Society of Japan (1969) has published a volume including thirty selected reprints and a list of references with titles consisting of ninety-five articles on Rayleigh and Brillouin scattering and one-hundred thirty-one articles on Raman scattering. Unfortunately, this volume is available for use mainly by domestic (Japanese) members. In view of the extensive number of review articles, we shall give only pertinent references which are intended as guides to the interested reader or are listed because of their historical significance.

In radiation-scattering studies, many types of radiation, each of which has different advantages, are available. However, in all such experiments there are usually two kinds of measurement that may be made. These are (a) the intensity as a function of the momentum and the energy transferred in the scattering process; and (b) the intensity as a function of the momentum transfer but integrated over all possible energy transfers. Figure 1.1 shows typical regions of momentum- and energy-transfer space covered by different types of radiation (Egelstaff, 1967). Using visible light, it clearly illustrates that optical scattering experiments follow the energy axis and involve only small momentum transfers. Extension of optical measurements to cover larger momentum transfers will be limited even if the incident radiation is extended to the ultraviolet wavelengths. On the other hand, optical mixing spectroscopy enables us to observe extremely small energy changes which are many orders of magnitude smaller than those detectable by other spectroscopic methods.

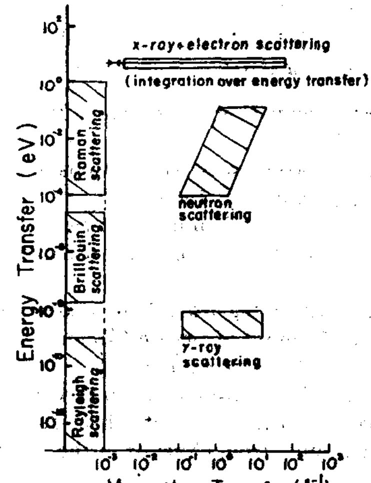

Fig. 1.1. Momentum- and energy-transfer space diagram showing regions covered by different types of radiation (Chu, 1970).

Table 1.1
Scattering phenomena[a]

Process	Detection[b] techniques	Principal application
Rayleigh	Spectrum analysis (Benedek, 1969, Cummins and Swinney, 1969) Signal correlation (Pusey and Goldburg, 1968; Chen and Polonsky-Ostrowsky, 1969) Interferometry (Chiao and Stoicheff, 1964)	Phase transitions (Swinney and Cummins, 1968; Chu *et al.*, 1968) Dynamics of macromolecules in solution (Pecora, 1972; Dubin *et al.*, 1967; Cummins *et al.*, 1969) Reaction kinetics (Yeh and Keeler, 1969a) Liquid crystals (Lister and Stinson, 1970)
Brillouin	Photobeating (Lastovka and Benedek, 1966) Interferometry (Chiao and Stoicheff, 1964) Spectrograph (Benedek *et al.*, 1964)	Fluid dynamics (Pike *et al.*, 1968) Phase transitions (Chen and Polonsky, 1968; Gammon *et al.*, 1967) Gases (Greytak and Benedek, 1966) Liquids (Eastman *et al.*, 1969). Solids (Benedek and Fritsch, 1966; Gammon and Cummins, 1966; Peticolas *et al.*, 1967) Solutions (Miller *et al.*, 1970)
Rayleigh wing (Raman anisotropy)	Interferometry	Orientational fluctuations, shear waves (Shapiro and Broida, 1967; Stegeman and Stoicheff, 1968; Ben-Reuven and Gershon, 1969)
Surface waves	Interferometry (Katyl and Ingard, 1967) Photobeating (Katyl and Ingard, 1968)	Ripplons

[a] Chu, 1970.
[b] Laser excitation: continuous-wave gas lasers.

The shaded area along the energy-transfer axis between Rayleigh and Brillouin scattering corresponds to energy changes which should be within reach by extending existing optical interferometric and beating techniques. Scattering of x rays and electrons usually involves the integration of intensity over all possible energy changes, as in (b). Then, by means of near-ultraviolet radiation for light scattering and extension of x-ray scattering to very small angles, the gap in the momentum transfer for integrated intensities can be filled (Chu, 1967) as shown by the two opposing arrows in Fig. 1.1. A striking feature of Fig. 1.1, as has been pointed out by Egelstaff (1967), is the extent of the blank spaces which are not accessible by present-day techniques, even though the shaded areas are being expanded rapidly, especially in neutron scattering. Thus, it becomes important to explore the complementary nature of various radiation-scattering processes.

A deeper understanding of the dynamical properties of systems often requires theoretical and experimental examinations of the scattering phenomena over wide ranges of momentum and energy changes and the combination of these results with measurements using other techniques such as ultrasonics, dielectric relaxation, and magnetic resonance. Brillouin scattering is often associated with optical interferometers. Studies of the spectral width of the central (Rayleigh) component have become very popular ever since the optical beat-frequency techniques were devised. Overlapping of detection techniques should become a logical extension of developments in the techniques of laser light scattering. Whenever the linewidth of the central (Rayleigh) component is very broad, optical interferometers become appropriate. Table 1.1 summarizes the common scattering phenomena related to laser light scattering (Chu, 1970) and should provide us with a broader perspective. Representative references of historical interest are listed to serve as convenient starting points for specific topics. Although the Raman effect definitely should be included as part of laser light scattering and is better developed when compared with Rayleigh and Brillouin scattering (Peticolas, 1972), we will discuss the scattering processes related mainly to light-beating spectroscopy and optical interferometry.

References

Benedek, G. B. (1969). "Polarization Matiere et Rayonnement, Livre de Jubile en l'honneur de Professeur A. Kastler," pp. 49–84. Presses Universitaires de France, Paris.

Benedek, G. B., and Fritsch, K. (1966). *Phys. Rev.* 149, 647.