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Volume 13

Spectroscopy

PART A

Edited by

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FOREWORD

Several aspects of spectroscopy have been treated in some of our earlier volumes (see Volumes 3A and 3B, Molecular Physics, second edition; Volume 10, Far Infrared; Volume 12A, Astrophysics). The rapid expansion of physics made it desirable to issue a separate treatise devoted to spectroscopy only, emphasizing such aspects which may not have been treated adequately in the volumes dealing essentially with other facets of physics. The present volumes contain a much more thoroughgoing treatment of the spectroscopy of photons of all energies. It is our intention to follow this with a volume devoted to particle spectroscopy.

Professor Dudley Williams, who is already well known to readers of "Methods of Experimental Physics" as editor of our Molecular Physics volumes, was kind enough to accept the editorship of the Spectroscopy volumes. His knowledge of the field and his excellent judgment will, no doubt, be appreciated by the users of "Spectroscopy" methods. We wish to express our profound gratitude to him and to all contributors to these volumes for their untiring efforts.

L. MARTON
C. MARTON

PREFACE

Spectroscopy has been a method of prime importance in adding to our knowledge of the structure of matter and in providing a basis for quantum physics, relativistic physics, and quantum electrodynamics. However, spectroscopy has evolved into a group of specialties; practitioners of spectroscopic arts in one region of the electromagnetic spectrum feel little in common with practitioners studying other regions; in fact, some practitioners do not even realize that they are engaged in spectroscopy at all!

In the present volumes we attempt to cover the entire subject of spectroscopy from pair production in the gamma-ray region to dielectric loss in the low radio-frequency region. Defining spectroscopy as the study of the emission and absorption of electromagnetic radiation by matter, we present a general theory that is applicable throughout the entire range of the electromagnetic spectrum and show how the theory can be applied in gaining knowledge of the structure of matter from experimental measurements in all spectral regions.

The books are intended for graduate students interested in acquiring a general knowledge of spectroscopy, for spectroscopists interested in acquiring knowledge of spectroscopy outside the range of their own specialties, and for other physicists and chemists who may be curious as to "what those spectroscopists have been up to" and as to what spectroscopists find so interesting about their own work! The general methods of spectroscopy as practiced in various spectral regions are remarkably similar; the details of the techniques employed in various regions are remarkably different.

Volume A begins with a brief history of spectroscopy and a discussion of the general experimental methods of spectroscopy. This is followed by a general theory of radiative transitions that provides a basis for an understanding of and an interpretation of much that follows. The major portion of the volumes is devoted to chapters dealing with the spectroscopic methods as applied in various spectral regions and with typical results. Each chapter includes extensive references not only to the original literature but also to earlier books dealing with spectroscopy in various regions; the references to earlier books provide a guide to readers who may wish to go more deeply into various branches of spectroscopy. The final chapters of Volume B are devoted to new branches of spectroscopy involving beam foils and lasers.

The list of contributors covers a broad selection of competent active research workers. Some exhibit the fire and enthusiasm of youth; others are at the peak of the productive activity of their middle years; and still others are battled-scarred veterans of spectroscopy who hopefully draw effectively on long experience! All contributors join me in the hope that the present volumes will serve a useful purpose and will provide valuable insights into the general subject of spectroscopy.

DUDLEY WILLIAMS

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CONTENTS

1. INTRODUCTION*

The success of spectroscopy has been so great that many of its terms have passed into common parlance; for example, the views expressed at a political meeting are sometimes described as representing a *broad spectrum* of opinion. In science, the term spectroscopy has come to mean the separation or classification of various items into groups; for example, the separation of the various isotopes of a chemical element is called *mass spectroscopy*. Similarly, the analysis of an acoustical wave train into sinusoidal components of different frequencies is called *acoustical spectroscopy*; a plot of the relative intensities of the components as a function of frequency is called the *acoustical spectrum* of the source. In nuclear physics, the study of resonances associated with bombarding particles of various energies has been termed *nuclear spectroscopy*. We even find the term spectroscopy being extended into high-energy physics, where the plots of energy-level diagrams for mesons and baryons have been termed a *new spectroscopy*!

In the present volumes, we shall restrict the term spectroscopy to the study of processes involving the emission and absorption of electromagnetic radiation. However, we shall attempt to cover the whole range of the electromagnetic spectrum, from the gamma-ray region to the low radio-frequency region. The general methods employed in the various spectral regions are remarkably similar; the details of the experimental techniques in the various regions are remarkably different!

Part 1 includes a brief chapter dealing with the history of spectroscopy from the Newtonian epoch to the present, and a second chapter dealing with the general methods of spectroscopy. Part 2 gives a general treatment of the theory of radiative transitions that is basic to an understanding of the phenomena treated in Parts 3 and 4, in which each chapter deals with special experimental methods employed in a particular spectral region; examples of the application of experimental methods to one or more problems of current interest and importance are presented. Part 5 covers the experimental methods being employed in two recently developed fields of spectroscopic investigation.

Since we shall be dealing with electromagnetic radiation, we can designate the various spectral regions in terms of frequency ν or vacuum wavelength λ,

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* Part 1 is by Dudley Williams.

where these quantities are connected by the familiar relation $\nu\lambda = c$. In Fig. 1 we give a plot of the electromagnetic spectrum with various spectral regions labeled. We should emphasize that the boundaries between the regions designated in Fig. 1 do not represent Dedekind cuts; for our purposes, the regions overlap in the sense that spectra in the ranges of overlap can be

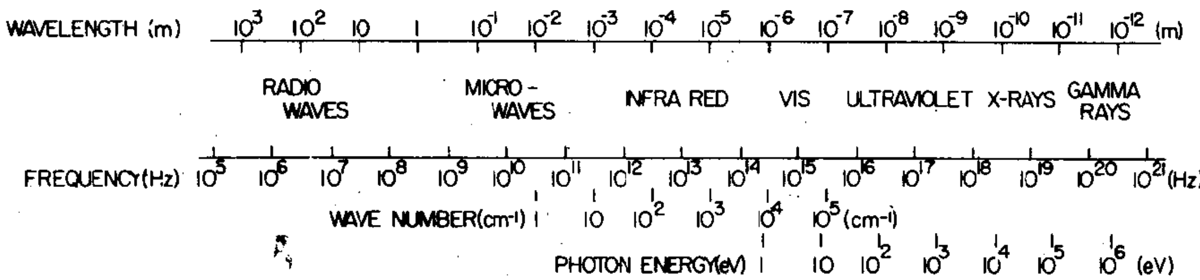

FIG. 1. The electromagnetic spectrum.

investigated by characteristic experimental methods used in either of the adjacent spectral regions; for example, spectra in the very near infrared can be mapped either by the photographic techniques used in the visible region or by means of the thermocouples frequently employed in the infrared. There is also overlap in the basic types of phenomena characteristic of the adjacent spectral regions, as labeled in Fig. 1; for example, the radiation produced in modern high-voltage x-ray machines can have frequencies that extend well into the gamma-ray region, as labeled in the figure.

We note that spectroscopists practicing their arts in various spectral regions have their own favorite special units for designation of frequency or wavelength. Those working in the radio frequency and microwave regions usually measure spectral frequencies in terms of standard radio frequencies broadcast by the National Bureau of Standards station WWV in the USA, the BBC in the UK, or other stations with similar missions; these spectroscopists prefer *frequency* units such as megahertz (MHz), gigahertz (GHz), or even terahertz (THz). In the infrared, visible, and near ultraviolet regions, spectroscopists measure *wavelengths* in terms of the spacing of the lines on gratings or in terms of distances in interferometers; these spectroscopists usually prefer designating *wavelengths* in terms of micrometers (μm) or nanometers (nm); although not recognized in modern SI units, the angstrom unit = 0.1 nm is still widely used in specifying wavelengths in the visible and near ultraviolet. Since there are no larger named SI multiples than tera = 10^{12}, there are no convenient frequency units for use in the infrared or in spectral regions of higher frequency; when frequencies are stated, they are usually specified indirectly in terms of wave number $\tilde{\nu}$ giving the number of waves per centimeter: $\tilde{\nu} = f/c = 1/\lambda_{\rm vac}$ with c in centimeters per second and $\lambda_{\rm vac}$ in centimeters. In the hard x-ray and γ-ray regions, it is usually desirable to characterize radiation in terms of its quantum energy $E = h\nu$; the quantum energy is nearly always expressed in electron volts (eV).

The spectroscopist working in any spectral region wishes to express his designation of a given spectral feature in terms of several significant digits and some unit that he regards as *convenient*. Similarly, in making actual measurements, he prefers to base his measurements on some *convenient* secondary standard of wavelength, frequency, or quantum energy rather than going back for every measurement to the primary international standards themselves; thus, in nearly every spectral region, secondary standards have been well established. Of course the primary standards of length and frequency themselves are at present based on indestructible spectral standards: 1 m $\equiv$ 1,650,763.73 times the wavelength of the orange light emitted by ^{86}Kr and 1 Hz = 1 cycle/sec, where 1 sec $\equiv$ the time for 9,192,631,770 cycles of the Cs atom in the molecular-beam device known popularly as the "atomic clock."

1.1. History of Spectroscopy

In this chapter, we trace the development of spectroscopy in the visible region and then return to the history of spectroscopy outside the visible region. We close the chapter with a brief discussion of the influence of spectroscopy on the development of twentieth-century physics.

1.1.1. Newton's Contributions

The first dispersed spectrum to be observed was, of course, the rainbow. Unable to explain this beautiful phenomenon, primitive man was disposed to attribute to it a supernatural significance sometimes related to legends such as the one included in the Biblical account of the flood. Its relationship to the laws of refraction was not understood even after these laws were firmly established by Willebrord Snell of Leyden (1591–1626). Although Snell was able to establish the fact that the ratio of the sines of the angles of incidence and refraction was a constant now known as the refractive index of the medium, he did not perform experiments on light of different colors. In fact, up to the time of Newton, even the best scientists had extremely vague ideas regarding the nature of color.

The first and possibly the most important step in the development of spectroscopy was taken by Newton in 1665 when, at the age of twenty three, he purchased a glass *prism* with the stated purpose "to try therewith the phenomena of colors"! His simple but fundamental experiments were reported first in the *Transactions of the Royal Society* in 1672; this paper led to his famous controversy with Robert Hooke. The experiments were described more fully in the first edition of "Opticks" in 1704. He placed red and blue strips of paper side by side; when he viewed them through the prism, he found that their apparent displacements were different. This first experiment showed that the refractive indices for red and blue light were different.[1]

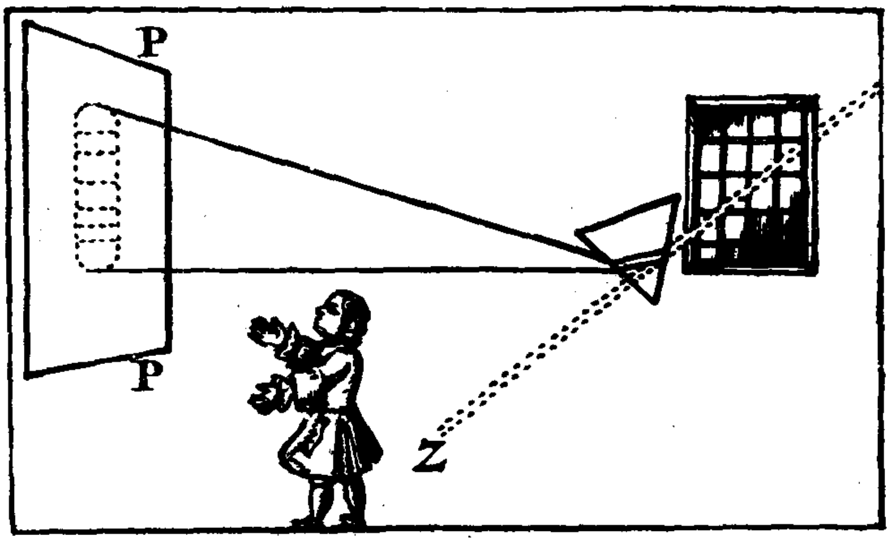

FIG. 2. "And so the true Cause of the Length of that Image was detected to be no other than that *Light* is not similar or Homogeneal, but consists of difform rays, some of which are more refrangible than others."—I. Newton. The cut in the figure is taken from Voltaire's "Elémens de la Philosophie de Neuton," published in Amsterdam in 1738.

Newton's second experiment involved a pencil of sunlight passing through a small hole in a shutter; after passing through the prism, the light reached a screen. Newton recognized that the resulting *spectrum* displayed on the screen was, in essentials, a series of colored images of the hole; the term spectrum was introduced by Newton. Subsequent experiments showed that light of a given color dispersed by his prism was further refracted but not further dispersed by a second prism. Such light, with all rays similarly *refrangible*, he termed as *homogeneal*, as distinguished from *heterogeneal* light with rays of differing *refrangibility*. He concluded that sunlight was "a heterogeneal mixture of difform rays, some of which are more refrangible than others." In the prism, the difform rays were "parted from one another."

Newton recognized that the separation of the rays and hence the purity of the spectrum could be improved by using a slit in the window shutter in combination with a lens to produce an image of the slit on the screen; when the light from the lens passed through the prism, a much purer spectrum was displayed on the screen. Although Newton was able to display a solar spectrum 25 cm long on the screen, he failed to observe the Fraunhofer

[1] I. Newton, "Opticks." London, 1703. Edition with commentary by E. T. Whitaker and I. B. Cohen is available from Dover Press, New York.

lines—presumably as a result of the poor quality of the glass in his prism and lens.

This work constituted Newton's contribution to spectroscopy. In his later treatment of the colors of various flames, he seems to have violated his credo, "*Hypotheses non fingo*!", and passed from experiment to speculation. His prestige was such that his unfortunate corpuscular theory of light served to stifle real progress in optics for nearly a century. His mistaken belief that dispersion was proportional to deviation for all types of glass delayed the development of achromatic lenses for many years.

1.1.2. Nineteenth-Century Developments

In the eighteenth century, the only noteworthy work in spectroscopy was Thomas Melvill's prism study of a sodium flame. In the "Physical and Literary Essays" (1752), Melvill gave the first description of a laboratory emission spectrum; this description was reprinted 162 years later.[2]

Early in the nineteenth century Thomas Young (1802) made the first wavelength determinations by applying his wave theory of light to the problem of interference colors in thin films; he showed with surprising accuracy that the range of wavelengths in the visible spectrum extends from 424 to 675 nm. In the same year, W. H. Wollaston[3] observed some of the dark lines that appear in the otherwise continuous spectrum of the sun but seems to have regarded them as natural boundaries between various pure colors. Wallaston also reported observations of flame spectra and the first investigations of spark spectra, but made no serious attempt to explain his observations, which were in fact hampered by crude apparatus and impure source samples.

The techniques of spectroscopy advanced rapidly as a result of the extraordinary work of Joseph Fraunhofer (1787–1826), a man with little formal education who was associated with a glass-making firm in Munich. By placing his flint-glass prism approximately 8 m from a slit in a window shutter, and by viewing the dispersed radiation with a theodolite telescope placed behind the prism, Fraunhofer was able to make highly precise angle measurements. He found that the solar spectrum was crossed by "an almost countless number of strong and weak dark lines"; experiments with different prisms demonstrated that those dark lines were actually characteristic of the solar spectrum. He mapped nearly 700 of those dark lines and assigned to the eight most prominent lines the letters A to H, by which they are still identified.[4] These lines provided standards that could be used for comparison

[2] T. Melvill, *J. Roy. Astron. Soc. Canada* **8**, 231 (1914).

[3] W. H. Wollaston, *Phil. Trans.* **92**, 365 (1802).

[4] J. Fraunhofer, *Ann. Phys.* **56**, 264 (1817).