PRACTICAL SPECTROSCOPY

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Preface

In operating the Spectroscopy Laboratory of the Massachusetts Institute of Technology, the authors have for some years felt the need of a text and reference book that would help the worker in any branch of science to evaluate the aid which the techniques of spectroscopy might lend to the solution of his own problems. In our attempt to fill this need, we, as a physicist, a chemist, and a biophysicist, respectively, have tried to synthesize our three viewpoints in a way that would be helpful to all who use or might use the techniques of experimental spectroscopy.

Since other texts are available which present effectively the history of spectroscopy, we have avoided the historical method of approach and have attempted rather to give a comprehensive view of the status and possibilities of experimental spectroscopy as it exists today. Because the subject matter to be covered is so extensive, we have had to choose between comprehensive and exhaustive coverage and have selected the former alternative.

In Chapter 1 we view the field as from a great altitude, to enable the reader who is unacquainted with the methods and accomplishments of spectroscopy to judge for himself which parts, if any, may be of importance to him. In the remainder of the book we reconsider the various topics in considerably greater detail. We have endeavoured to include a sufficient number of appropriate specific references to the literature to enable the reader to investigate still more closely subjects which may directly concern him.

References to specific points are given as footnotes; at the ends of most chapters appropriate general references are also given. While the bibliography is not intended to be exhaustive, we have attempted in specific references to cite both the original and the most up-to-date treatment of the topic involved, and in the general references to cover the subject broadly. Since we discuss many topics from several viewpoints, we have made liberal use of cross-references.

A book covering spectroscopy from several aspects is likely to contain a certain amount of inconsistency in terminology. Resolution of such inconsistencies is not made simpler by the fact that the symbology of spectroscopy is far from stabilized.

We gratefully acknowledge the courtesy of the Technology Press, John Wiley and Sons, the McGraw-Hill Book Co., Inc., Prentice-Hall, Inc., and others as specified later, for permission to reproduce figures and tables, and appreciate deeply the willing cooperation of the various manufacturers of spectroscopic equipment who have furnished illustrations of apparatus, as credited in each instance. We are especially grateful for the suggestions of Messrs. W. R. Brode, R. S. McDonald, W. F. Meggers, K. W. Meissner, R. A. Sawyer, A. L. Schoen, and Van Zandt Williams, each of whom has read and criticized one or more chapters dealing with his own specialty. We also thank Professor Donald H. Menzel, editor of the series of which the book forms a part, for his suggestions regarding the manuscript.

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Contents

CHAPTER 1

Spectroscopy as a Scientific Tool

THE ACCOMPLISHMENTS ACHIEVED BY SCIENTISTS through use of the spectroscope form a list so imposing as to leave no doubt that this instrument is one of the most powerful now available for investigating the natural universe. But spectroscopy is valuable not only to the research scientist; it finds everyday and increasing use in technological laboratories. Today directors of such varied enterprises as factories, assay offices, arsenals, mines, crime detection bureaus, public health departments, hospitals, museums, and technical research institutes consider access to spectroscopic equipment essential to the proper functioning of their laboratories.

THE SPECTRUM

A *spectrum* has been defined as the ordered arrangement of radiation according to wavelength. Electromagnetic radiations have been discovered that have wavelengths of every value in the range from thousands of kilometers to trillionths of a millimeter. A complete electromagnetic spectrum would comprise all these radiations arranged in order from the longest to the shortest wavelengths. Since no single instrument exists that will separate radiation containing all these wavelengths into a spectrum, the electromagnetic spectrum has been divided into various "regions" in accordance with the types of instruments available to produce and detect the waves of various lengths.

Long electromagnetic waves, upwards of a meter in length, can be separated from each other by means of ordinary tuned radio circuits. Shorter waves, down to a few millimeters long, can be analyzed by microwave equipment. When absorbed by matter, all electromagnetic waves produce heat. Since waves shorter than a few millimeters and longer than about 3×10^{-3} mm can be detected by this effect more readily than by any other, they are often called *heat waves.* The range of waves from a few millimeters to 2.5×10^{-2} mm in length is known as the *far infrared* region; that from 2.5×10^{-2} to 7.5×10^{-4} mm is known as the *near infrared.* Waves that can be seen by the eye range in length from 7.5×10^{-4} mm in the red to 4×10^{-4} mm in the violet; this range is called the *visible region.* Waves slightly too short to see, 4×10^{-4} to 3×10^{-4} mm, lie in the *near ultraviolet;* then come the *far ultraviolet* and the *extreme ultraviolet* regions, which extend from 3×10^{-4} to 2×10^{-4} mm and from there to 2×10^{-6} mm, respectively. Since air is opaque to these shorter waves, they are studied in vacuum, and the range from 2×10^{-4} to 2×10^{-6} mm is also known as the *vacuum ultraviolet.* We then come to the region of *soft Xrays,* and below 10^{-7} mm to the *hard Xray* and *gamma-ray* regions, to which air is again transparent. The names, ranges, and properties of these spectral regions are summarized in Table 1.1.

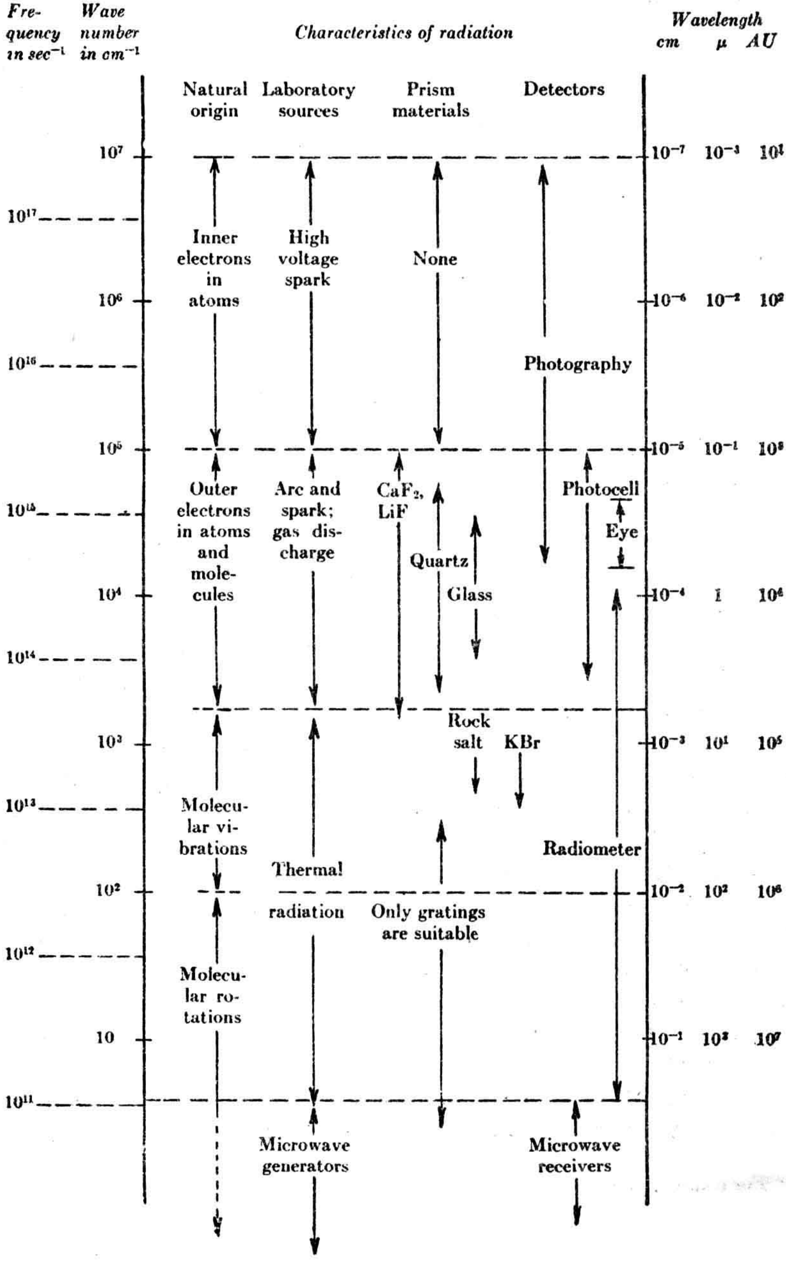
1.1. Spectroscopy. The term *spectroscopy* as used in this book is restricted to the study of those radiations which lie in the infrared, visible, ultraviolet, and vacuum ultraviolet regions. The techniques discussed are quite distinct from those used in such fields as microwave spectroscopy, X-ray spectroscopy, gamma-ray spectroscopy, and mass spectroscopy. We are concerned here only with those electromagnetic waves which can readily be separated into a spectrum by means of prisms, optical gratings, and optical interferometers.

1.2. Origins of Spectroscopy. The best-known early investigator of the spectrum was Sir Isaac Newton, who in 1666 inserted a prism in a beam of sunlight shining into a dark room and saw a band of colors on the wall. By using a lens in conjunction with the prism he was able to spread the colors out into a fairly pure spectrum 10 in. long. He fell short of producing a spectroscope of the modern type only because he let the light shine through a round hole instead of a narrow slit. It was not until 1802 that W. H. Wollaston, and in 1814 Joseph Fraunhofer, independently observed *spectrum lines,* that is, images of a narrow slit each containing only light of one color. The first practical spectroscope was developed by G. R. Kirchhoff and R. Bunsen in 1859.

Newton is responsible for the practical application of the prism and Fraunhofer for that of the diffraction grating; these are the basic components used in spectroscopes today to separate the wavelengths of light. Kirchhoff and Bunsen showed that the spectroscope could

TABLE 1.1

THE SPECTROSCOPIC PART OF THE ELECTROMAGNETIC SPECTRUM



be used as a new means of qualitative chemical analysis; with it they discovered several new elements and were able to demonstrate the presence of many known elements in the sun. They are in a very real sense the founders of modern spectroscopy.

1.3. Measurement of the Spectrum. The waves with which we are here concerned have lengths lying between 1 mm and 10^{-6} mm, which can be measured with a precision varying from one part in ten thousand to one part in sixty million, depending on the spectral region involved. Various systems of units have been developed in which to record wavelengths conveniently; of these the following are the most common:

$$1\ \mu\ \text{(micron)} = 10^{-4}\ \text{cm} = 10^{-3}\ \text{mm}$$
$$1\ \text{m}\mu\ \text{(millimicron)} = 10^{-7}\ \text{cm} = 10^{-6}\ \text{mm}$$
$$1\ \text{A (angstrom*)} = 10^{-8}\ \text{cm} = 10^{-7}\ \text{mm}$$
$$1\ \mu = 10{,}000\ \text{A} = 1000\ \text{m}\mu$$

In the infrared region wavelengths are commonly measured in microns, and in the range shorter than 1 μ in angstroms. Chemists and biologists frequently use the millimicron. The mean wavelength of the strong yellow light emitted by sodium atoms is, in the three systems, 0.5893 μ, 589.3 mμ, and 5893 A.

Spectroscopes analyze radiation in accordance with its wavelengths, but atoms and molecules emit radiation of characteristic frequencies. In a sense frequency is more fundamental than wavelength, for the frequency of monochromatic light remains constant no matter in what medium it may be traveling, whereas the wavelength varies inversely with the velocity of light in the medium. Therefore, in addition to the wavelength λ of a beam of light, it is often useful to specify the frequency of oscillation ν. This is related to λ by the formula $\lambda\nu = c_{(m)}$, where $c_{(m)}$ is the velocity of light in the medium. Frequencies in the optical range are, however, very large numbers (4 to 7.5×10^{14}), and it is more convenient to use a smaller number, the wave number σ, which is the number of waves per centimeter of path in vacuum. λ and σ are related by the formula $\lambda\sigma = 10^8$ when λ is expressed in angstroms. σ is then expressed in reciprocal centimeters, written cm^{-1}.

1.4. The Infrared Spectrum. Sir William Herschel in 1800 used a simple thermometer to measure the heating power of the various

* For a more exact definition of the angstrom see § 9.8.