

PRACTICAL SPECTROSCOPY

By

GEORGE R. HARRISON, PH.D., SC.D.

Professor of Physics

RICHARD C. LORD, PH.D.

Associate Professor of Chemistry

JOHN R. LOOFBOUROW, SC.D.

Professor of Biophysics

OF THE

SPECTROSCOPY LABORATORY

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

PRENTICE-HALL, INC.

Englewood Cliffs, N. J.

COPYRIGHT, 1948, BY
PRENTICE-HALL, INC.
Englewood Cliffs, N. J.

ALL RIGHTS RESERVED. NO PART OF THIS BOOK
MAY BE REPRODUCED IN ANY FORM, BY MIMEO-
GRAPH OR ANY OTHER MEANS, WITHOUT PERMIS-
SION IN WRITING FROM THE PUBLISHERS.

First Printing.....October, 1948
Second Printing.....October, 1949
Third Printing.....June, 1954
Fourth Printing.....October, 1955

PRINTED IN THE UNITED STATES OF AMERICA

69425

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.

George R. Harrison
Richard C. Lord
John R. Loofbourow

Cambridge, Massachusetts

Contents

| CHAPTER | PAGE |
|---|-----------|
| 1. SPECTROSCOPY AS A SCIENTIFIC TOOL | 1 |
| THE SPECTRUM | 1 |
| 1.1 Spectroscopy. 1.2 Origins of Spectroscopy. 1.3 Measurement of the Spectrum. 1.4 The Infrared Spectrum. 1.5 The Visible Spectrum. 1.6 The Ultraviolet. 1.7 Spectroscopes and Spectrographs. | |
| TECHNIQUES OF SPECTROSCOPY | 10 |
| 1.8 Emission Spectroscopy. 1.9 Qualitative Spectroscopic Analysis of Materials. 1.10 Quantitative Spectroscopic Analysis. 1.11 Absorption Spectroscopy. 1.12 Absorption Spectrophotometry. 1.13 Fluorescence Spectroscopy. | |
| USES OF SPECTROSCOPY | 15 |
| 1.14 The Spectroscope in Chemistry. 1.15 Spectroscopy in Astronomy. 1.16 Spectroscopy in Physics. 1.17 Spectroscopy in Biology and Medicine. 1.18 Spectroscopy in Food Research. 1.19 Spectroscopy in Metallurgy and Mineralogy. 1.20 Forensic Spectroscopy. | |
| 2. SELECTION OF SPECTROSCOPIC INSTRUMENTS . . . | 27 |
| 2.1 Dispersion. 2.2 Resolving Power. 2.3 The Dispersing Element. 2.4 Dispersing Prisms. 2.5 Diffraction Gratings. 2.6 The Slit. 2.7 The Collimating and Focusing Systems. 2.8 Observing and Recording Systems. 2.9 Comparison of Prism and Grating Spectrographs. 2.10 Speed and Efficiency. 2.11 Scattered Light and False Lines. 2.12 Shapes of Spectrum Lines. 2.13 Astigmatism. 2.14 Space Requirements. 2.15 Summary of Comparison. 2.16 Monochromatic Illuminators. | |
| 3. PRISM SPECTROSCOPES AND SPECTROGRAPHS . . . | 51 |
| 3.1 Materials for Dispersive Prisms. 3.2 The Simple Spectrometer. 3.3 Modern Wavelength Spectrometers. 3.4 Direct-Vision Spectroscopes. 3.5 Portable Spectrographs. 3.6 Special Glass-Prism Spectrographs. 3.7 Quartz-Prism | |

| CHAPTER | PAGE |
|--|------|
| Spectrographs. 3.8 The Littrow Mounting. 3.9 The Féry Spectrograph. 3.10 The Gaertner Large Quartz Spectrograph. 3.11 Spectrographs with Interchangeable Optical Systems. 3.12 Prism Monochromators. | |
| 4. DIFFRACTION-GRATING SPECTROGRAPHS | 71 |
| 4.1 Plane-Grating Spectrographs. 4.2 The Rowland Concave Grating. 4.3 The Rowland Mounting. 4.4 The Abney Mounting. 4.5 The Paschen-Runge Mounting. 4.6 The Eagle Mounting. 4.7 The Wadsworth Stigmatic Mounting. 4.8 The Choice of a Grating Mounting. 4.9 Astigmatism of the Concave Grating and Its Reduction. 4.10 The Testing of Diffraction Gratings. 4.11 Grating Monochromators. | |
| 5. THE TESTING, ADJUSTMENT, AND CARE OF SPECTROSCOPIC EQUIPMENT | 96 |
| THE TESTING OF SPECTROSCOPIC COMPONENTS | 96 |
| 5.1 The Testing of Slits. 5.2 The Testing of Prisms and Lenses. 5.3 The Testing of Gratings. 5.4 The Testing of Prism Spectrographs. 5.5 The Hartmann Test. | |
| ADJUSTMENT OF PRISM AND GRATING SPECTROGRAPHS | 103 |
| 5.6 Adjustments Required for Various Types of Instruments. 5.7 Adjustment of Slit Width and Length. 5.8 Adjustment of Slit Perpendicular to the Direction of Dispersion. 5.9 Focusing the Spectrum: Commercial Prism Spectrographs. 5.10 Focusing the Spectrum: Commercial Littrow and Eagle-Mounting Spectrographs. 5.11 Adjustment of Spectrometers. 5.12 Adjustment of Concave Gratings. 5.13 Adjustment of Wadsworth Grating Mountings. 5.14 Adjustment of Plane Gratings. | |
| THE CARE OF SPECTROSCOPIC EQUIPMENT | 115 |
| 5.15 General. 5.16 Care of Mirrors, Prisms, and Lenses. 5.17 Cleaning and Care of Gratings. | |
| 6. ILLUMINATION OF THE SPECTROSCOPE | 118 |
| 6.1 Coherent and Noncoherent Radiation. 6.2 Spectral Line Shape and the Rayleigh Criterion for Resolution. 6.3 Selection of Optimum Slit Width. 6.4 Filling the Aperture of the Spectroscope with Light. 6.5 Use of a Condensing Lens or Mirror. 6.6 Uniform Illumination of the Slit. 6.7 Illumination of the Slit by a Source Extended in Depth. 6.8 Illumination to Obtain Maximum Radiant Intensity or Total Radiant Power in the Spectral Image. 6.9 Factors Governing the Radiant Power Transmission of a Spectroscopic System. 6.10 Effect of Entrance Slit Width on Spectral Purity. 6.11 Effect | |

of Exit Slit. 6.12 Expression for Radiant Power Transmission of a Spectroscopic System.

7. PHOTOGRAPHY OF THE SPECTRUM 141

7.1 Photographic Plates and Films. 7.2 Response of the Emulsion to Light. 7.3 Contrast. 7.4 Speed, Inertia, and Latitude. 7.5 Resolving Power and Graininess. 7.6 Types of Plates and Films. 7.7 Variation of Emulsion Characteristics with Wavelength. 7.8 Storage and Handling of Photographic Materials. 7.9 The Photographic Darkroom. 7.10 Development and Processing. 7.11 Developers. 7.12 Common Defects in Spectrum Photographs. 7.13 The Eberhard Effect. 7.14 Halation and Spreading. 7.15 Photography of Various Regions of the Spectrum. 7.16 Selection of Spectrally Sensitive Emulsions.

8. LIGHT SOURCES FOR SPECTROSCOPY 166

GENERAL CHARACTERISTICS OF SOURCES 167

8.1 Spectral Energy Distribution. 8.2 The Power Output of Sources. 8.3 Practical Considerations.

THERMAL EMISSION SOURCES 170

8.4 Spectral Characteristics of Blackbody Radiation. 8.5 Blackbody Radiators. 8.6 Incandescent Electric Lamps. 8.7 Enclosed Metallic Arcs with Incandescent Electrodes. 8.8 Low-Temperature Thermal Radiators. 8.9 Other Thermal Radiators.

OPEN ARCS 179

8.10 Electrical Characteristics. 8.11 Carbon Arcs. 8.12 Metallic Arcs.

ENCLOSED ARCS 184

8.13 Electrical Characteristics. 8.14 Low-Pressure Mercury Arcs. 8.15 High-Pressure Mercury Arcs. 8.16 Other Enclosed Metallic-Vapor Arcs. 8.17 Enclosed Carbon Arcs.

DISCHARGE TUBES 188

8.18 General Characteristics. 8.19 Glow-Discharge Tubes.

ELECTRIC SPARKS 192

8.20 General Characteristics. 8.21 The Spark in Air and Other Gases. 8.22 The Hot Spark in Vacuum. 8.23 The Underwater Spark. 8.24 The Spark as a Source in Qualitative and Quantitative Analysis.

MISCELLANEOUS SOURCES 196

8.25 Cathodoluminescence Devices. 8.26 Fluorescence, Phosphorescence, Resonance Radiation, and Chemilumines-

| CHAPTER | PAGE |
|--|------|
| cence. 8.27 Pulsed Discharge Tubes. 8.28 The Sun as a Source of Radiation. | |
| 9. IDENTIFICATION OF SPECTRUM LINES | 199 |
| 9.1 Identification of Lines and Bands by Appearance. 9.2 Identification by Comparison Spectra. 9.3 Spectrum Charts for Comparison. 9.4 Identification of Lines by Wavelength Determination. 9.5 Measurement of Spectrograms. 9.6 Use of the Comparator. 9.7 Calculation of Wavelengths. 9.8 Standards of Wavelength. 9.9 Intensity Estimates. 9.10 Catalogues of Wavelengths. 9.11 The Harrison Automatic Comparator. 9.12 Limitations of Wavelength Measurement with Diffraction Gratings. | |
| 10. THE ORIGINS OF ATOMIC SPECTRA | 228 |
| SPECTRAL SERIES AND ATOMIC ENERGY STATES | 228 |
| 10.1 The Hydrogen Atom. 10.2 Quantum Numbers in Atomic Spectra. 10.3 Series in Atoms with Many Electrons. 10.4 Multiplicity in Atomic Spectra. | |
| LINE INTENSITIES IN ATOMIC SPECTRA | 243 |
| 10.5 Some Basic Results of Quantum Mechanics. 10.6 Selection Rules and Intensities of Spectral Lines. 10.7 The Effect of External Influences on Atomic Spectra. 10.8 The Stark and Zeeman Effects. | |
| ATOMIC SPECTRA AND ATOMIC STRUCTURE | 252 |
| 10.9 The Pauli Exclusion Principle and the Periodic Table. | |
| 11. MOLECULAR SPECTRA AND MOLECULAR STRUCTURE | 261 |
| ENERGY LEVELS IN MOLECULES | 261 |
| 11.1 Rotational Energy Levels in Molecules. 11.2 Vibrational Energy Levels. 11.3 Electronic Energy Levels. | |
| MOLECULAR SELECTION RULES AND THE APPEARANCE OF MOLECULAR SPECTRA | 276 |
| 11.4 Pure Rotational Spectra. 11.5 Vibrational Spectra. 11.6 Rotational Fine Structure in Vibrational Spectra. 11.7 Electronic Spectra of Diatomic Molecules. 11.8 Vibrational Structure of Diatomic Spectra. 11.9 Rotational Fine Structure of an Electronic-Vibrational Band. 11.10 Electronic Spectra of Polyatomic Molecules. 11.11 Vibrational Structure of Electronic Spectra in Polyatomic Molecules. 11.12 Rotational Fine Structure in Electronic Spectra. 11.13 The Effects of External Influences on Molecular Spectra. 11.14 Summary of Molecular Spectra. | |

| CHAPTER | PAGE |
|---|------|
| 12. THE MEASUREMENT OF SPECTRAL INTENSITIES | 300 |
| RADIOMETRY | 302 |
| 12.1 Bolometers. 12.2 Metal Bolometers. 12.3 Semiconductor Bolometers. 12.4 A Superconductor Bolometer. 12.5 Thermocouples and Thermopiles. 12.6 Other Thermal Detectors. 12.7 Amplification and Recording Methods in Radiometry. 12.8 Photorelays. 12.9 Alternating-Current Amplifiers. 12.10 A Direct-Current Amplifier. 12.11 Recorders. | |
| PHOTOELECTRIC MEASUREMENT OF INTENSITY | 314 |
| 12.12 Photoemissive Cells and Electron-Multiplier Tubes. 12.13 Photoconductive Cells. 12.14 Photovoltaic Cells. 12.15 The Incorporation of the Photocell in the Spectrograph. 12.16 Amplification and Recording of Photocurrents. 12.17 Photoelectric Spectrometers. | |
| 13. PHOTOGRAPHIC PHOTOMETRY | 326 |
| 13.1 Photometric Characteristics of the Emulsion. | |
| HOMOCHROMATIC PHOTOMETRY | 330 |
| 13.2 Calibrating the Emulsion. 13.3 Methods of Varying Light Intensity. | |
| HETEROCHROMATIC PHOTOMETRY | 342 |
| 13.4 Uses of Heterochromatic Photometry. 13.5 Light Sources for Standardization. | |
| APPARATUS AND METHODS FOR PHOTOGRAPHIC PHOTOMETRY | 346 |
| 13.6 Selection of the Spectrograph. 13.7 Selection of the Emulsion. 13.8 Timing the Exposure. 13.9 The Brush Effect. 13.10 Processing the Spectrogram. 13.11 Short-Cut Methods of Photographic Photometry. | |
| DENSITOMETRY | 350 |
| 13.12 Densitometers. 13.13 Photoelectric Densitometers. 13.14 Thermoelectric Densitometers. 13.15 Operation of the Densitometer. 13.16 Recording Densitometers. 13.17 Precision of Densitometers. 13.18 Special Computing Densitometers. | |
| 14. ABSORPTION SPECTROPHOTOMETRY | 362 |
| LAWS OF ABSORPTION AND THEIR APPLICATION TO ABSORPTION SPECTROPHOTOMETRY | 362 |
| 14.1 Lambert's Law. 14.2 Beer's Law. 14.3 Variables Measured in Absorption Spectrophotometry. 14.4 Elimination of Effects Due to Reflections and Absorption by Cell Windows and by Solvents. 14.5 Presentation of Data. | |

| CHAPTER | PAGE |
|--|------|
| SELECTION OF APPARATUS FOR ABSORPTION SPECTROPHOTOMETRY | 368 |
| 14.6 Choice of Source of Radiation. 14.7 Choice of Absorption Cells. 14.8 Choice of Spectrophotometric Method. | |
| VISUAL ABSORPTION SPECTROPHOTOMETRY | 374 |
| 14.9 General Considerations. 14.10 Advantages and Limitations of the Visual Method. 14.11 Instruments Using the Martens Type of Polarizing Photometer. 14.12 Hilger-Nutting Polarizing Spectrophotometer. 14.13 Manipulation of Polarizing Spectrophotometers. 14.14 Other Visual Spectrophotometers and Their Manipulation. | |
| PHOTOGRAPHIC ABSORPTION SPECTROPHOTOMETRY | 384 |
| 14.15 General Considerations. 14.16 Advantages and Limitations of the Photographic Method. 14.17 Spectrographs for Photographic Absorption Spectrophotometry. 14.18 Photographic Materials and Processing. 14.19 Semiquantitative and Plate-Calibration Methods. 14.20 Split-Beam Photometers. 14.21 Multiple-Beam Photometers. 14.22 Considerations Governing Alignment and Illumination. 14.23 Choice of Density in Specimens: Determination of Match Points. 14.24 Precision of Determination of Wavelengths and Densities. | |
| PHOTOELECTRIC ABSORPTION SPECTROPHOTOMETRY | 399 |
| 14.25 General Considerations. 14.26 Point-by-Point Instruments for Relative Intensity Measurements. 14.27 Photoelectric Null Methods: Nonrecording. 14.28 Automatic Recording Photoelectric Spectrophotometers. 14.29 Abbreviated Absorption Spectrophotometry and Fluorimetry. 14.30 Optical Filters. | |
| ABSORPTION OF SUBSTANCES IN SOLUTION | 417 |
| 14.31 General Remarks Regarding Solvents. 14.32 Absorption by Solvents: Purification. 14.33 Relation of Absorption to Chemical Constitution. 14.34 Photochemical Effects. Fluorescence. | |
| 15. QUALITATIVE SPECTROGRAPHIC ANALYSIS OF MATERIALS | 424 |
| 15.1 Sensitivity of Detection of Various Elements. 15.2 Sensitive Lines and Ultimate Lines. 15.3 Improvement of Sensitivity Limits. 15.4 Identification of Elements. 15.5 Light Sources and Handling of Material. 15.6 Moving-Plate and Fractional Distillation Methods. 15.7 Analysis for Elements Difficult to Detect. 15.8 The Qualitative Analysis. | |

| CHAPTER | PAGE |
|--|------|
| 16. QUANTITATIVE SPECTROCHEMICAL ANALYSIS . . . | 450 |
| THE BASIC METHOD OF QUANTITATIVE ANALYSIS | 451 |
| 16.1 Basic Procedure. 16.2 Sources of Excitation. 16.3 Form and Preparation of the Sample. 16.4 Standards for Comparison. 16.5 Burning of the Sample. 16.6 Selection and Use of the Spectrograph. 16.7 Selection of Lines for Quantitative Analysis—The Working Curve. 16.8 The Calibration Curve. 16.9 A Typical Analysis. | |
| SPECIAL METHODS | 461 |
| 16.10 The Method of Internal Standards. 16.11 Methods for High Concentrations. 16.12 Methods for Extremely Low Concentrations. 16.13 High-Precision, Rapid, and Short-Cut Methods. 16.14 Methods for Special Elements. 16.15 Photoelectric Methods of Analysis. | |
| 17. SPECTROSCOPY OF THE INFRARED REGION | 472 |
| 17.1 Radiation Sources and Filters for Infrared Spectroscopy. 17.2 Prism Spectrometers for the Infrared. 17.3 Grating Spectrometers. 17.4 The Measurement of Infrared Absorption. | |
| APPLICATIONS OF INFRARED SPECTROSCOPY | 494 |
| 17.5 Qualitative Chemical Analysis by Infrared Absorption Spectra. 17.6 Quantitative Chemical Analysis by Infrared Absorption Spectra. 17.7 The Determination of Molecular Structure from Infrared Spectra. 17.8 Astrophysical and Biological Applications of Infrared Spectroscopy. | |
| 18. RAMAN SPECTROSCOPY | 506 |
| 18.1 The Raman Effect. 18.2 Technique of the Raman Effect. 18.3 Sources for Excitation of the Raman Effect. 18.4 Filters for the Raman Effect. 18.5 Arrangement of the Excitation Unit. 18.6 The Scattering Tube. 18.7 Spectrographs for the Raman Effect. 18.8 Measurement of Intensity and Polarization of Raman Lines. 18.9 Applications of the Raman Effect. 18.10 Determination of Molecular Structure. 18.11 Qualitative and Quantitative Chemical Analysis. | |
| 19. SPECTROSCOPY OF THE VACUUM ULTRAVIOLET . . . | 530 |
| SPECTROGRAPHS FOR THE VACUUM ULTRAVIOLET | 531 |
| 19.1 General Considerations. 19.2 Prism Spectrographs. 19.3 Normal-Incidence Grating Spectrographs. 19.4 Grazing-Incidence Grating Spectrographs. 19.5 Housings and Vacuum Equipment. | |

| CHAPTER | PAGE |
|--|------|
| ACCESSORY APPARATUS | 540 |
| 19.6 Light Sources. 19.7 Photographic Materials. 19.8 Nonphotographic Radiation Detectors. 19.9 Accessories for Absorption Measurements. | |
| APPLICATIONS | 543 |
| 19.10 Atomic Spectra. 19.11 Wavelength Standards. 19.12 Molecular Spectra. 19.13. Miscellaneous Applications. | |
| 20. INTERFEROMETRIC SPECTROSCOPY | 547 |
| 20.1 Line Broadening and Its Causes. 20.2 Line Sources for High-Resolution Spectroscopy. 20.3 Selection of a Spectroscope of High Resolving Power. 20.4 Limitations of Diffraction Gratings at High Resolutions. 20.5 The Lummer-Gehrcke Plate. 20.6 The Fabry-Perot Etalon. 20.7 Operation and Design of the Etalon. 20.8 Plate Coatings for the Etalon. 20.9 Adjustment of the Etalon. 20.10 Crossing of Etalon Dispersion with that of a Spectroscope. 20.11 Reduction of Etalon Patterns. 20.12 Direct Determination of Wavelengths from Fabry-Perot Patterns. 20.13 The Michelson-Williams Echelon. 20.14 Optical Systems Using the Reflection Echelon. | |
| APPENDIX 1. Sensitive Lines of the Elements Arranged According to Elements | 574 |
| APPENDIX 2. Sensitive Lines of the Elements Arranged According to Wavelengths | 582 |
| INDEX | 587 |

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 X-rays*, and below 10^{-7} mm to the *hard X-ray* 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.

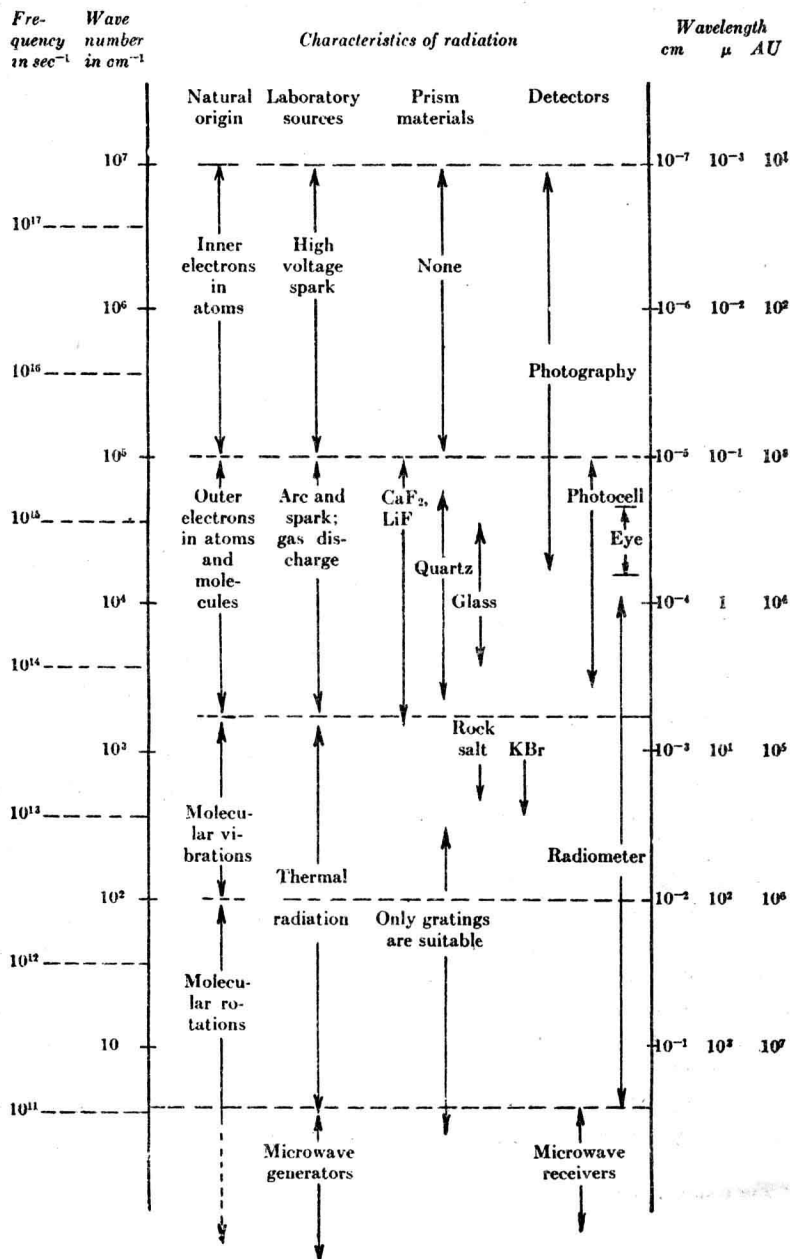
1.1. Spectroscopy. The term *spectroscopy* as used in this book is restricted to the study of those radiations which lie in the infrared, visible, ultraviolet, and vacuum ultraviolet regions. The techniques discussed are quite distinct from those used in such fields as microwave spectroscopy, X-ray spectroscopy, 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:

$$1 \mu (\text{micron}) = 10^{-4} \text{ cm} = 10^{-3} \text{ mm}$$

$$1 \text{ m}\mu (\text{millimicron}) = 10^{-7} \text{ cm} = 10^{-6} \text{ mm}$$

$$1 \text{ \AA} (\text{angstrom}^*) = 10^{-8} \text{ cm} = 10^{-7} \text{ mm}$$

$$1 \mu = 10,000 \text{ \AA} = 1000 \text{ m}\mu$$

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 m μ , and 5893 \AA .

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.