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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
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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 13 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 battle-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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4. MOLECULAR SPECTROSCOPY

4.1. Infrared Region*

During the closing decades of the 19th century and the early decades of the present century infrared spectroscopy began to take form; developments during this period have been summarized in several books.[1-4] The volume by Schaefer and Matossi is especially valuable in giving an excellent history of the subject along with a wealth of detail regarding the experimental methods employed in the era prior to 1930. In the period immediately following 1940, infrared spectroscopy advanced from a series of beautiful experiments conducted by painstaking individuals having an abundant supply of patience to an established branch of spectroscopy practiced in industrial laboratories as well as in laboratories devoted to pure research. Much of this rapid expansion came about as a result of a wider appreciation of the importance of infrared methods to molecular physics and chemistry.[5, 6] This was also the period when recording spectrographs or spectrophotometers were developed to replace earlier instruments which had relied on galvanometers to provide data on a point-by-point basis; commercial manufacture of recording spectrographs made infrared spectroscopy a tool of industry. Williams[7] and Sutherland and Lee[8] have provided excellent surveys of the rapid developments of experimental techniques during this period and have included extensive references to the pertinent literature.

Great impetus was given to the development of infrared techniques by the recognition during World War II of the military importance of infrared

[1] J. Lecomte, "Le Spectre Infrarouge." Presses Univ. de France, Paris, 1928.

[2] C. Schaefer and F. Matossi, "Das Ultrarote Spektrum." Springer-Verlag, Berlin and New York, 1930.

[3] F. I. G. Rawlins and A. M. Taylor, "Infrared Analysis of Molecular Structure." Cambridge Univ. Press, London and New York, 1929.

[4] G. B. B. M. Sutherland, "Infrared and Raman Spectra." Methuen, London, 1935.

[5] G. Herzberg, "Spectra of Diatomic Molecules." 2nd ed. Van Nostrand-Reinhold, Princeton, New Jersey, 1950.

[6] G. Herzberg, "Infrared and Raman Spectroscopy." Van Nostrand-Reinhold, Princeton, New Jersey, 1945.

[7] V. Z. Williams, *Rev. Sci. Instrum.* **19**, 135 (1948).

[8] G. B. B. M. Sutherland and E. Lee, *Rep. Progr. Phys.* **11**, 144 (1948).

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*Chapter 4.1 is by Dudley Williams.

radiation as a means of detection and signal transmission. The new methods of detecting and measuring infrared radiation that were developed during this period have been described in considerable detail in the excellent book by Smith and his colleagues.[9] Since 1960 numerous books on infrared spectroscopy have appeared and provide extensive references to the more recent literature.[10-15] There are other recent useful books dealing primarily with surveys of experimental results and theoretical interpretations of the results.[16-20]

In this chapter we shall discuss the various types of sources, detectors, resolving instruments, and optical materials used in the infrared and shall attempt to present typical experimental results along with their interpretation in terms of the theory presented in Chapter 2, Part A. We make no attempt to be encyclopedic; the range of topics treated, which reflects to some extent the present author's personal interests, is also limited to subjects not previously covered in detail in other recent books.

4.1.1. Infrared Sources

The range of quantum energies encompassed by the infrared region represents energies well below those separating the lowest energy levels of most atoms. Therefore, the atomic lines appearing in this region are associated with transitions between highly excited states of atoms and can usually be studied only in emission. For example, in the hydrogen spectrum the Paschen, Brackett, Pfund, and Humphreys[21] series with lower quantum

[9] R. A. Smith, F. E. Jones, and R. P. Chasmar, "The Detection and Measurement of Infrared Radiation." Oxford Univ. Press, London and New York, 1957. (Revision, 1968.)

[10] P. W. Kruse, E. D. McGlauchlin, and R. B. McQuistan, "Elements of Infrared Technology." Wiley, New York, 1962.

[11] J. A. Jamieson, R. H. McFee, G. N. Plass, and R. G. Richards, "Infrared Physics and Engineering." McGraw-Hill, New York, 1963.

[12] H. A. Szymanski, "Theory and Practice of Infrared Spectroscopy." Plenum Press, New York, 1964.

[13] J. E. Stewart, "Infrared Spectroscopy." Dekker, New York, 1970.

[14] K. D. Möller and W. D. Rothschild, "Far-Infrared Spectroscopy." Wiley (Interscience), New York, 1971.

[15] L. C. Robinson, "Physical Principles of Far-Infrared Radiation." Academic Press, New York, 1973.

[16] H. H. Nielsen, "Handbuch der Physik" (S. Flugge, ed.), Vol. 37/1, p. 153. Springer-Verlag, Berlin and New York, 1959.

[17] H. C. Allen and P. C. Cross, "Molecular Vib-Rotors." Wiley, New York, 1966.

[18] J. E. Wollrab, "Rotational Spectra and Molecular Structure." Academic Press, New York, 1967.

[19] R. T. Conley, "Infrared Spectroscopy." Allyn & Bacon, Boston, Massachusetts, 1966.

[20] G. Amat, H. H. Nielsen, and G. Tarrago, "Higher-Order Rotation-Vibration Energies of Polyatomic Molecules." Dekker, New York, 1971.

[21] C. J. Humphreys, J. Opt. Soc. Amer. 42, 432 (1952).

numbers $n = 3, 4, 5$, and 6, respectively, appear in the infrared. Since more interesting phenomena are usually encountered in the transitions between lower atomic states, the infrared portions of atomic emission spectra have been somewhat neglected as compared with the visible and ultraviolet portions. In general, however, the sources employed for studies of atomic spectra in the infrared represent only modifications of those used in other regions.

The quantum energy range in the infrared does encompass the energies associated with transitions between vibrational and rotational energy states of molecules in their electronic ground states. Many of these transitions can be studied in emission from flames. In the emission spectrum of nearly every hydrocarbon–oxygen flame, H_2O vapor and CO_2 emission spectra can be observed; these spectra are most useful in providing information regarding these two molecules in highly excited vibrational and rotational states. By proper adjustment of the flames, emission from CO and the free radicals OH and CH can be observed.[22, 23] By injection of other molecules into the flame from a burner it is possible to observe the emission spectra of these molecules. Various types of nonhydrocarbon flames can also be employed for other molecules. Since many of the lower vibrational states of molecules are excited at ambient temperatures, transitions between these lowest states and the ground states can be studied by comparing the emitted radiation with that emitted by a blackbody at low temperature.[24]

Infrared spectroscopy as generally practiced, however, has been concerned chiefly with absorption. In the remainder of this section we shall discuss the sources commonly employed in laboratory investigations. In later sections, we shall return briefly to some of the problems encountered in studies of the emission spectra of astronomical and atmospheric sources.

In investigations of absorption spectra it is usually desirable to have a source that provides intense continuous spectral emission $I(v)$ throughout the region to be investigated.[†] In view of Kirchhoff's law, it would thus appear that a blackbody would be not only the perfect radiator but also the ideal source for use in infrared spectroscopy. In many respects, this is true, and blackbody radiators furnish excellent references with which other radiators can be compared. It is not necessary, however, to employ a blackbody cavity radiator to obtain a satisfactorily continuous spectral source. Any sufficiently hot opaque solid will serve satisfactorily; the radiation from a narrow V-shaped slot cut into the wall of such a solid gives an extremely

[22] R. C. Herman and G. Hornbeck, *Astrophys. J.* **118**, 214 (1953).

[23] G. Herzberg, "The Spectra and Structures of Simple Free Radicals," p. 3. Cornell Univ. Press, Ithaca, New York, 1971.

[24] R. Sloan, J. H. Shaw, and D. Williams, *J. Opt. Soc. Amer.* **45**, 455 (1955).

[†] Noncontinuous sources are discussed in Chapter 5.2.

close approximation of a blackbody. Similarly, if a metal ribbon is folded to form a narrow V, the emission from the V-shaped opening closely resembles the emission from a blackbody at the temperature of the ribbon. No thermal source can have a greater emissive power than that of a blackbody at the same temperature; therefore knowledge of Planck's radiation law can serve as a guide to the design of sources.

The experimental methods of studying blackbody radiation have been described by Schaefer and Matossi[2] and the derivation of the radiation laws have been briefly summarized by Smith et al.[9] It will be recalled that the total radiant power from a blackbody is proportional to the fourth power of its absolute temperature. The peak of the radiation curve[†] giving $I(\lambda)$ versus λ shifts toward shorter wavelengths as the temperature increases; the product $\lambda_{max}T$ = const, where λ_{max} is the wavelength at which the peak occurs. It is useful to remember that $\lambda_{max} = 1$ μm for $T = 2897$ K $\simeq$ 3000 K; the location of the peak at any other temperature can thus be conveniently computed. Blackbody radiation curves never cross; the blackbody radiation curve for a given temperature is at every wavelength above that for a lower temperature. Thus it is usually desirable to use a source with as high a temperature as possible. The spectral flux intensity $I(\lambda)$ at wavelengths long as compared with the wavelength at the peak is directly proportional to the source temperature in accordance with the Rayleigh–Jeans law, which applies in good approximation at long wavelengths. In the vicinity of the peak, $I(\lambda)$ increases rapidly with increasing temperature.

Of the commercially available sources, the one most widely used is probably the *globar*, which consists of a rod of silicon carbide several centimeters in length and approximately 6 mm in diameter. Heated electrically by a current of about 5 A, the globar operates satisfactorily at a maximum temperature of 1400 K; above this temperature oxidation becomes a serious problem and the binding material boils out. The globar mount must usually be water cooled in order to maintain good electrical contact between the rod and the external circuit. Since the diameter of the globar is larger than necessary for use with most spectrometers, it is wasteful of electrical power; however, its large thermal capacity minimizes the effect of short-term variations in line voltage; for long-term stability it is desirable to operate the globar from a voltage-regulated power supply or constant-voltage transformer. Silverman[25] has shown that the emissivity of a globar is approximately 80% of that of a blackbody over most of the range between 2

[25] S. Silverman, *J. Opt. Soc. Amer.* **38**, 989 (1948).

[†] In keeping with modern spectroscopic practice it would be preferable to present a plot of $I(\nu)$ versus ν for the blackbody, but the $I(\lambda)$ versus λ plot is in such wide use that there is no move toward change. In fact, the $I(\nu)$ versus ν plot would not be immediately recognized by the uninitiated.

and 16 μm (5000–600 cm^{-1}). The globar is useful to 100 cm^{-1} in the far infrared.

Another commonly used infrared source is the *Nernst glower*, which was initially developed by Nernst and Bose[26]; it consists of a rod approximately 3 cm long and 1 mm in diameter and is composed of a mixture of zirconium and yttrium oxides. Platinum wires are attached to the ends of the rod,[27] which is heated electrically. With properly attached platinum wires, the Nernst glower can operate satisfactorily at 2000 K for prolonged periods without water cooling. At room temperature the Nernst glower is non-conducting and must be preheated by a flame or by a nearby electrical heater in order to make it a conductor. In view of its large negative temperature coefficient of resistance, it is usually necessary to operate it in series with a current-limiting device; in commercial devices operated from ac lines or regulated power supplies, this is usually accomplished by means of barretters or by more elaborate control devices. We find, however, that it gives completely satisfactory performance when operated from the laboratory power line in series with a tungsten filament lamp. In view of its small thermal capacity, the Nernst glower should be shielded from air currents in the laboratory, which change its temperature and thus its resistance. Although Nernst glowers allegedly give off a fine powder when operated in vacuum, we have used these devices for prolonged periods in vacuum without encountering serious difficulties. The Nernst glower has an emission spectrum closely approximating that of a blackbody in the spectral range between the visible and 15 μm (665 cm^{-1}); in the far infrared it is inferior to the globar. It is a convenient and electrically efficient source with a size and shape admirably suited for use with most spectrometers.

Another commercially available source is the *carbon arc*, which can be operated with the positive crater of the arc at 4100 K. This source has been extensively investigated by Strong and his associates.[28] Although the carbon arc provides high spectral emission $I(v)$ throughout the near infrared (4000–600 cm^{-1}), it is rather bulky for many applications in spectroscopy and tends to be somewhat unstable as compared with other sources. Automatic feeding of the carbon rods employed in some commercial models provides fairly satisfactory short-term stability.

In the near infrared (10,000–3000 cm^{-1}) *tungsten filament* lamps are available commercially; in one form a tungsten ribbon filament requiring a current of 20 to 30 A is operated in a glass envelope equipped with a quartz window. Quartz-enclosed *iodine lamps with a tungsten filament* sold commercially for photographic purposes are excellent sources for the near infrared; selected lamps have stable radiant output and long life.

[26] W. Nernst and E. Bose, *Phys. Z.* 1, 289 (1900).

[27] E. S. Ebers and H. H. Nielsen, *Rev. Sci Instrum.* 11, 429 (1940).

[28] C. S. Rupert and J. Strong, *J. Opt. Soc. Amer.* 39, 1061 (1949).

For use in the far infrared (250–10 cm^{-1}) the quartz-enclosed *mercury arc* is the best available source.[29] Most of the emission originates in the discharge plasma but emission from the quartz walls apparently makes some contribution. Although the quartz walls darken as the arc is used, the output of the arc in the far infrared remains nearly constant. Water cooling of the housing must be provided.

The so-called *carbon-rod furnace* is now widely used in high-resolution spectroscopy in the intermediate infrared. The use of carbon-rod sources was first discussed by Smith,[30] but considerable improvements have been made more recently by Rao and his associates,[31] who have used resistively heated rods at 3000 K; water-cooled mountings are required. By cutting a V-shaped slot in the wall of the carbon rod, blackbody emission at 3000 K can be closely approximated.

Another source, the Welsbach gas mantle, widely used in the early days of infrared spectroscopy, offers advantages in certain spectral regions,[32, 33] but has fallen into disuse with the advent of more convenient electrically powered sources.

4.1.2. Detection and Measurement of Infrared Radiation

The devices employed for the detection of infrared radiation can be classified as (a) *thermal detectors*, which depend for their operation on the increase in the temperature of the sensing element, and (b) *quantum detectors*, which usually depend for their operation on internal photoelectric processes producing changes in the resistance of the sensing element or producing photovoltaic effects in the sensing element. Thermal detectors were developed first and have survived with various refinements to the present. The quantum detectors are essentially products of modern solid-state physics and have come into wide use since World War II.

Detectors usually supply a dc voltage change that is proportional to the radiant flux reaching the sensing element; in the early work this voltage change was usually measured by the deflection of a sensitive galvanometer. Various cleverly designed dc amplification systems were developed and used to advantage; all of these were subject to the chronic drifts that usually plague dc amplifiers. Later it was recognized that periodically varying voltages could be produced by periodic interruption of the radiant flux reaching the detector and that these varying voltages could be amplified by conventional electronic amplifiers. The process of periodic interruption

[29] E. K. Plyler, D. J. C. Yates, and H. A. Gebbie, *J. Opt. Soc. Amer.* **52,** 859 (1962).

[30] L. G. Smith, *Rev. Sci. Instrum.* **13,** 63 (1942).

[31] R. Spanbauer, P. E. Fraley, and K. N. Rao, *Appl. Opt.* **2,** 340 (1963).

[32] R. B. Barnes, *Rev. Sci. Instrum.* **5,** 237 (1934).

[33] T. K. McCubbin and W. M. Sinton, *J. Opt. Soc. Amer.* **42,** 113 (1952).