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Nineteenth-Century SPECTROSCOPY

Development of the Understanding of Spectra

1802-1897

The Johns Hopkins Press
Baltimore and London

Manufactured in the United States of America

The Johns Hopkins Press, Baltimore, Maryland 21218
The Johns Hopkins Press Ltd., London

Library of Congress Catalog Card Number 74-94886
Standard Book Number 8018-1059-0

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To Walter F. Cannon

Acknowledgments

This volume is, with a few minor emendations, my doctoral dissertation, written at the University of Pennsylvania, which I attended as a Thouron Scholar. For that privilege I am deeply thankful to Mr. and Mrs. John R. Thouron, C.B.E.

My interest in the history of spectroscopy was first aroused during a graduate seminar on physics from Thomas Young to Bohr. This was given by Dr. Walter F. Cannon of the Smithsonian Institution, to whom I am most grateful for his supervision of this book from its conception as a dissertation to its publication. All shortcomings, needless to say, are mine alone.

I am also indebted to Dr. Philip George and the Graduate School of Arts and Sciences, both of the University of Pennsylvania, for the award of a Dissertation Year Fellowship. This enabled me to complete much of the research and writing of the book.

Introduction

My story tells of the efforts made, and the success achieved, in understanding spectra during most of the nineteenth century—that is, from William Hyde Wollaston's observation of dark solar lines in 1802 to J. J. Thomson's discovery of the electron in 1897.

I begin by examining the origins of spectrum analysis as established in 1860 by Robert Bunsen and Gustav Kirchhoff. The central theme here is the early development of the principle of spectrum analysis, which states that each 'substance' has a characteristic spectrum. The further development of this principle in the 1860s and 1870s is discussed in sections 2, 3, and 4 of chapter II; and as this involves a significant change in physical notions of atoms and molecules, and consequently in spectral theory, an account of the original (molecular) theory of spectra is given in section 1. Indeed, the understanding of spectra at an atomic/molecular level forms the major theme of the remainder of the story. The final section of chapter II deals with Norman Lockyer's hypothesis of the dissociation of the elements, which was prompted by spectral considerations. This is a subject closely related to those of the previous sections of the chapter.

Spectroscopy, meanwhile, had led in a second way to an interest in atoms and molecules. It was thought that if the law or laws governing the distribution of lines in spectra were found, then something might therefore be known of the physical nature of atoms and molecules. The search for such a law or laws forms the subject of chapter III. Once such laws were found, and even before, the need for a mathematical theory of spectra was felt. Several attempts were made to give such a theory, but before considering these in chapter V, account has first to be taken of other developments in physical science which, either independently or in conjunction with spectral considerations, were also changing the physicist's conceptions of atoms and molecules. Accordingly, chapter IV considers the evolution of qualitative theories of spectra during the last quarter of the century. An interesting difference is found between the British and the Germans in their choice of an atomic model, and a link is established between the British model and Zeeman's discovery of the magnetic splitting of spectral lines.

In the epilogue, the discovery of the electron is seen as bringing to a close one era, while simultaneously ushering in another, in the continuing attempt to understand spectra.

I have not attempted to write a history of spectroscopy during the nineteenth century. No accounts will be found of such subjects as spectroscopy's role in discovering further elements, the rise of astrophysics, infra-red spectroscopy, radiation studies, spectroscopic apparatus, and many others. But where any subject becomes important for a full understanding of my story, I have made appropriate mention of it. Thus, for example, there is no discussion of the development of diffraction gratings, but when Henry Rowland's concave grating leads in the 1880s to a considerably higher degree of accuracy in wavelength determinations its importance is mentioned.

Throughout the work I have endeavored to get to the root or roots of each development, to know exactly how it occurred, and to be aware of its various connections.

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I

Origins of Spectrum Analysis

WHILE THE OCCURRENCE of dark, or Fraunhofer, lines in the solar spectrum was generally known in Europe from about 1820, their origin was not successfully explained until some forty years later. The successful explanation was given in 1859 by the Professor of Physics at Heidelberg, Robert Gustav Kirchhoff, who, about the same time and in collaboration with his counterpart in chemistry, Robert Bunsen, placed in order the many and complex spectra of incandescent salts. These splendid achievements formed the basis of spectrum analysis, whose origins in the progressive scientific climate of the nineteenth century are here considered.

The first section of this chapter tells how the Fraunhofer lines were discovered, and mentions some related observations of flame spectra. The next three sections treat main divisions of the story from the time of Fraunhofer down to the years immediately before Bunsen and Kirchhoff's collaboration—section 2 dealing with colored flame spectra in relation to chemical analysis, section 3 with the so-called electric spectra of metals, and section 4 with attempted explanations of the Fraunhofer lines. Section 5 considers the work of Bunsen and Kirchhoff and the immediate events leading up to it. The final section deals with Kirchhoff's explanation of the Fraunhofer lines.

1. Discovery of the Fraunhofer Lines and Early Observations of Flame Spectra

Fraunhofer lines and emission spectra later came to be associated with chemistry and physics, but in the beginning the former were discovered and studied together with the latter in relation to certain optical questions. Thus, the English physician, William Hyde Wollaston, who first discovered dark solar lines in 1802, made the discovery while investigating the contemporary question of the number of primary colors to be found in the solar spectrum. Some observers claimed three, while from the appearance of the rainbow others argued for seven. But Wollaston found that if daylight, admitted into a darkened room through a narrow slit, was viewed through a glass prism held close to the eye, only four colors were visible: red, yellowish green, blue, and violet. And the boundaries of these colors were marked by certain dark lines—

> The line A that bounds the red side of the spectrum is somewhat confused. . . . The line B, between the red and green, in a certain position of the prism, is perfectly distinct; so also are D and E, two limits of the violet. But C, the limit of the green and blue, is not so clearly marked as the rest; and there are also, on each side of this limit, other distinct dark lines, f and g, either of which, in an imperfect experiment, might be mistaken for the boundaries of these colours.[1]

Wollaston's interest, however, as that of his contemporaries, was in the spectral colors and not in the dark lines, and so the latter were ignored and subsequently forgotten.

Wollaston repeated his experiment using both candlelight and "electric light," and so also became one of the first to observe emission spectra.[2] The blue light of the lower part of a candle flame gave five "images." The first was broad and red and terminated by a bright yellow line, the second and third were green, and the fourth and fifth blue. As for the blue electric light, it also gave several, though somewhat different, images. There Wollaston stopped, thinking it needless minutely to describe appearances which seemed to vary according to the intensity of the light and which he could not anyhow explain. His contemporaries seem to have concurred in this, and we need only note again Wollaston's observation of the yellow line, for it will be met with repeatedly, and will be of much significance in what follows.

Twelve years elapsed before the dark solar lines were independently discovered again in 1814 by Joseph von Fraunhofer, a young German optician employed in an optical-mechanical institute.[3] This time they

[1] W. H. Wollaston, "A method of examining refractive and dispersive powers by prismatic reflection," *Phil. Trans.*, 92 (1802): 365–80; p. 378.

[2] *Ibid.*, p. 380. Flame spectra had been known for at least half a century. See Thomas Melvill, "Observations on light and colours," in *Physical and Literary Essays* (Edinburgh, 1752), 2:35.

[3] Parts of Fraunhofer's papers are to be found translated in J. S. Ames, *Prismatic and Diffraction Spectra, Memoirs by Joseph von Fraunhofer* (New York and London, 1898). This is referred to below as Ames.

were not to be ignored and subsequently forgotten—primarily because of their usefulness in practical optics.

During the course of his work Fraunhofer had sought a means of measuring the dispersive powers of various kinds of glass for light of different colors.[4] For this it was necessary to isolate the latter, yet Fraunhofer did not succeed in finding colored liquids or colored glass which would allow only monochromatic light to pass. And colored flames, he found, did not yield monochromatic spectra corresponding to their color. However, he did find that the spectra of all flames, including oil and tallow flames, possessed in common a sharply defined orange streak, and this "homogeneous" source proved most useful.

Following a series of experiments in which lamplight was used, Fraunhofer commenced yet another series in which he allowed sunlight to pass through a narrow slit into a darkened room and through a prism placed on a theodolite. His own words best describe one of his motives in undertaking this experiment, and also his surprising discovery.

> I wished to see if in the colour-image from sunlight there was a bright band similar to that observed in the colour-image of lamplight. But instead of this I saw with the telescope an almost countless number of strong and weak vertical lines, which are, however, darker than the rest of the colour-image; some appeared to be almost perfectly black.[5]

Following a careful investigation, Fraunhofer concluded that the lines were "due to the nature of sunlight" and not to diffraction or illusion. As for the bright orange band of lamplight, Fraunhofer observed that it coincided with the dark line *D,* as he called it, of the solar spectrum. Later he discovered that in addition to being coincident, both were double.[6]

After Fraunhofer, this bright doublet found in most spectra was described as being yellow. Nevertheless, to Fraunhofer it was decidedly orange, for in the spectrum of the "light of electricity" he observed a line in the orange which at first seemed to have the same color as the bright line of lamplight. Yet, when its angle of refraction was measured it was seen to correspond more with the yellow rays of lamplight.[7]

[4] J. von Fraunhofer, "Bestimmung des Brechungs- und Farbenzerstreuungs-Vermögens verschiedener Glasarten, in Bezug auf die Vervollkommung achromatischer Fernröhre," *Denkschriften der Königlichen Akademie der Wissenschaften zu München,* 5 (1814–15): 193–226; in Ames, pp. 3–10; p. 3.

[5] *Ibid.,* p. 4.

[6] *Ibid.,* p. 10; and also J. von Fraunhofer, "Kurzer Bericht von den Resultaten neurer Versuche über die Gesetze des Lichtes, und die Theorie derselben," *Ann. der Physik,* 74 (1823): 337–78; in Ames, pp. 41–61; p. 58.

[7] J. von Fraunhofer, "Bestimmung des Brechungs- und Farbenzerstreuungs-Vermögens verschiedener Glasarten"; in Ames, pp. 9, 10.

Fraunhofer's method of producing "electric light" was to place two conductors half an inch apart and join them by means of a glass thread. One conductor was then connected to an electrical machine and the other to earth. While the current was passed, light appeared to stream continuously in a fine luminous line between the poles. A large electrical machine was found to produce many more lines than the "several" observed with a weaker machine.[8]

In all, Fraunhofer found 574 dark solar lines, the strongest of which he mapped. His primary interest in the lines was that they afforded him a means of attaining his original goal of determining refractive indices for most wavelengths. This he could do with great accuracy, as the majority of solar lines are sharply defined. Indeed, their usefulness in this respect, was what attracted attention to the lines, and once they were generally known they naturally demanded an explanation. This question, however, does not seem to have engaged Fraunhofer.

2. *Flame Spectra and Chemical Analysis*

Fraunhofer's work appeared at a time of intense interest and rapid progress in optics, when the rival wave and particle theories competed for supremacy and when many optical matters considered more important claimed attention. One of the most interesting phenomena of contemporary optics was polarization, discovered in the interval between the publication of Wollaston's and Fraunhofer's papers. This subject was significantly advanced by the Scotsman, David Brewster, who throughout his long and productive life maintained an active interest in most optical matters.

In 1822 Brewster published an account of a lamp designed to produce monochromatic yellow light.[9] This was an improvement upon Fraunhofer's method of producing this light useful in practical optics. However, Brewster's publication is important for another reason, namely, that it was the first of a series of related papers by himself and others, which appeared over the next twenty years and in which an explanation of the Fraunhofer lines was both arrived at and rejected, while a limited form of chemical analysis based on the spectra of colored flames was also attained.

That part of Brewster's work which drew the first response deals

[8] *Ibid.*, p. 9; J. von Fraunhofer, "Kurzer Bericht von den Resultaten neuerer Versuche über die Gesetze des Lichtes;" in Ames, pp. 41–61; p. 58.

[9] D. Brewster, "Description of a monochromatic lamp for microscopical purposes, etc., with remarks on the absorption of the prismatic rays by coloured media," *Trans. Roy. Soc. Edinburgh*, 9 (1823): 433–44.

with the absorption of sunlight by transparent colored media. This subject had previously mainly concerned astronomers (such as the celebrated William Herschel) in a practical way, but had also been of some interest to Thomas Young, champion of the wave theory, and, as we recall, to Fraunhofer.[10] Brewster's primary objective was "the discovery of a general principle of chemical analysis, in which simple and compound bodies might be characterized by their action on definite parts of the spectrum."[11] His procedure was to pass sunlight through different colored media and analyze the emergent light by means of a prism. He found, for example, that "blue glass attacks the spectrum in several points at the same time, and after absorbing all the middle rays, it leaves only the extreme red, and the portions of the blue and violet spaces which are contiguous."[12] Brewster did not succeed, however, in arriving at any general principle of chemical analysis.

The response to Brewster's observations came in the same year from John Herschel, then busy with astronomical observations.[13] However, while experimenting several years earlier "on the scale of tints developed by polarized light," Herschel had also used colored media in an attempt to obtain "tolerably homogeneous" rays from sunlight. Finding that the latter was a satisfactory source for all but red and yellow rays he had sought and found these in several sources, including luminous flames. His "few examples of remarkable flames" are of interest, as their spectra are described for the first time.[14] Sulphur, for example, when burning feebly, emits most rays, but principally violet and blue ones; when burning vigorously it emits a perfectly homogeneous and brilliant light, and when mixed with saltpeter and burned this latter definite color gives way to several others.[15]

Three years later, in 1825, when William Henry Fox Talbot, afterward to be associated with the development of photography, wrote on colored flames in the journal of which Brewster was

[10] W. Herschel, "On the power of penetrating into space by telescopes," *Phil. Trans.*, 90 (1800): 49–85; T. Young, "On the theory of light and colours," *Phil. Trans.*, 92 (1802): 12–48.

[11] D. Brewster, "Observations on the lines of the solar spectrum, and on those produced by the earth's atmosphere, and by the action of nitrous acid gas," *Trans. Roy. Soc. Edinburgh*, 12 (1834): 519–30; p. 519.

[12] D. Brewster, "Description of a monochromatic lamp for microscopical purposes." p. 439.

[13] J. F. W. Herschel, "On the absorption of light by coloured media, and on the colours of the prismatic spectrum exhibited by certain flames; with an account of a ready mode of determining the absolute dispersive power of any medium, by direct experiment," *Trans. Roy. Soc. Edinburgh*, 9 (1823): 445–60.

[14] Unfortunately, Herschel's drawings of these spectra were not published.

[15] J. F. W. Herschel, "On the absorption of light by coloured media," p. 455.

editor, these phenomena were "still unexamined, or imperfectly explained."[16] By impregnating the cotton wick of a spirit lamp with common salt Talbot had succeeded in producing a brighter homogeneous light than that given by Brewster's monochromatic lamp. He found it difficult, however, to determine precisely the source of the homogeneous yellow light.

I have found that the same effect takes place whether the wick of the lamp is steeped in the muriate, sulphate or carbonate of *soda,* while the nitrate, chlorate, sulphate, and carbonate of *potash,* agree in giving a blueish tinge to the flame. Hence, the yellow rays may indicate the presence of *soda,* but they, nevertheless, frequently appear where no soda can be supposed to be present.[17]

Talbot had confirmed Herschel's finding that yellow light was given by burning sulphur, a fact which he regarded as indicating "a very singular optical analogy between soda and sulphur, bodies hitherto supposed by chemists to have nothing in common."[18] Talbot also found that candles, and platinum touched by the hand or rubbed with soap, also gave the yellow light. Common salt sprinkled on platinum gave this light while the salt decrepitated, and the effect could be renewed at will by wetting the platinum. This latter circumstance led Talbot to suppose that the light was due to water of crystallization, rather than to sodium, the more so as it was also given by wood, ivory, and paper, whose only common constituent with sodium salts is water. But then there was the problem of explaining why, for example, potassium salts should not also produce the yellow light. Talbot finally concluded that water could not produce it as the light was also produced by sulphur, which was supposed to have no "analogy" with water.[19]

This provides an excellent illustration of the problem of the ubiquitous yellow line, which was to perplex spectroscopists for a considerable time to come and constitute a major obstacle to progress.

Talbot found that potassium salts displayed a characteristic red ray corresponding to the "characteristic" yellow ray of sodium salts, and on this basis he suggested that "whenever the prism shows a *homogeneous* ray of any colour to exist in a flame, this ray indicates the formation or the presence of a *definite chemical compound.*"[20] Thus a

[16] W. H. F. Talbot, "Some experiments on coloured flames," *Edinburgh J. Sc.,* 5 (1826); 77–81.
[17] *Ibid.,* p. 78.
[18] *Ibid.,* p. 79.
[19] *Ibid.*
[20] *Ibid.,* p. 81.

prismatic analysis of the "red fire of the theatres" would indicate from the bright yellow and orange lines the presence of sulphur (in spite of the yellow rays being characteristic of sodium!) and strontium. And he concluded that: "If this opinion should be correct and applicable to other definite rays, a glance at the prismatic spectrum of a flame may show it to contain substances, which it would otherwise require a laborious chemical analysis to detect."[21]

Talbot's expression is somewhat inconsistent—on the one hand he generalizes in terms of chemical compounds and substances, while on the other he speaks specifically of elements such as sulphur and strontium—yet he clearly expresses the basic idea of chemical spectrum analysis. Indeed, what we have just read finds a striking parallel in what Bunsen and Kirchhoff were to declare much later. Nevertheless, Talbot's analysis was restricted to only a few elements, and was consequently of little practical value. It did, however, mark an advance over the familiar flame analysis in which the salts of sodium, potassium, calcium, strontium, magnesium, lithium, barium, and copper, could be distinguished from one another by the colors which they imparted to flames.[22] In this analysis the presence of one salt could mask the presence of another, but with Talbot's analysis all of the salts present could be identified.

Talbot was aware of the need of extending his analysis, but this was either not easy or people were not sufficiently interested. In 1827 John Herschel described the spectrum of calcium salts as displaying a yellow and a bright green line, but while aware of Talbot's work he did not mention this observation as an addition to the latter's analysis.[23] Much later, Bunsen and Kirchhoff were to distinguish calcium from the alkali metals and from the other alkaline earths by its characteristic green line.[24]

The subject was not further advanced until 1834, some nine years later, when Talbot observed that while ordinarily it was difficult to distinguish the red lithium and red strontium flames, yet by using a prism the most marked distinction "that could be imagined" was apparent.

The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange, and a very definite

[21] *Ibid.*
[22] See J. Herschel's essay on light in *Encyclopaedia Metropolitana* (London, 1827), p. 438.
[23] *Ibid.*
[24] R. Bunsen and G. Kirchhoff, "Chemical analysis by spectrum observations," *Phil. Mag.*, 20 (1860): 89–109.