

Spectroscopy from 1916 to 1940

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During the first quarter century of The Optical Society (OSA), spectroscopy led to major insights into atomic and molecular physics and paved the way for important practical applications. Optical spectroscopy existed for decades before the formation of OSA, but it was empirical and descriptive in its nature. Spectroscopists had carefully measured the wavelengths of spectral lines associated with various elements, but the subatomic mechanisms that created these lines were not yet fully understood.

Twenty-four years later, as the world lurched toward the second all-encompassing war of the twentieth century, the spectroscopic fingerprints of atoms and molecules had provided vital evidence for the emerging quantum theory. Experimentalists refined their techniques and discovered previously unknown phenomena.

Spectroscopy and Quantum Mechanics

A few years before OSA was formed, Niels Bohr had proposed his model of the hydrogen atom, which explained the empirical Rydberg formula for the spectral lines of atomic hydrogen, at least to a first approximation. Theodore Lyman completed his investigations of the ultraviolet emission lines of hydrogen, beginning at 1216 Å in 1914.

Little happened in spectroscopy during World War I, but the field came raging back shortly after the armistice. In 1919, Arnold Sommerfeld, doctoral adviser to multiple Nobel Laureates, published *Atombau und Spektrallinien (Atomic Structure and Spectral Lines)*. William F. Meggers, who would become the 1949–1950 OSA president, opined that “spectroscopists were amazed that our meager knowledge of atomic structure and the origin of spectra could be expanded into such a big book” [1].

The same year, Sommerfeld and another German physicist, Walther Kossel, formulated the displacement law now named after them [1]. The law states that the singly ionized spectrum of an element resembles the neutral spectrum of the element preceding it in the periodic table. Likewise, the doubly ionized spectrum of an element resembles the singly ionized spark spectrum of the element preceding it, or the neutral spectrum of the element with atomic number two less than the designated element. The neutral spectrum was usually obtained by running an arc of current through a vapor; ionized spectra came from the light of an electric spark in a gas or vapor.

In 1922, the English physicist Alfred Fowler and the German team of Friedrich Paschen and Richard Goetze published tables of observational data on spectral singlets, doublets, and triplets without interpreting them according to the fledgling quantum theory. Later the same year, Miguel A. Catalán of Spain published his finding that the arc spectra of complex atoms have lines that occur in groups with certain numerical regularities [1]. He called these groups multiplets, and their discovery sparked a productive era of description and interpretation of the optical spectra of most complex atoms, except those of the rare-earth elements.

The following year, Sommerfeld [1] posited the “inner-quantum number,” now known as the azimuthal quantum number, represented by the script letter ℓ and the familiar subshells s , p , d , and f . In OSA’s journal, Sommerfeld also proposed a model for the neutral helium atom, which had perplexed scientists since Bohr explained the hydrogen atom [2].

Then in 1925, Americans Henry Norris Russell and Frederick A. Saunders examined the spectrum of calcium and discovered the type of spin-orbit coupling now known as LS coupling [3]. This breakthrough led to, in short order, an outburst of important theories of atomic structure and atomic spectra. Meggers [1] listed the astonishing output of a single year, 1925:

- Wolfgang Pauli's rule for equivalent electrons and his exclusion principle;
- Friedrich Hund's correlation of spectral terms with electron configurations and his correlation of multiplet components to series limits; and
- the determination by George Uhlenbeck and Samuel Goudsmit of the contribution of electron spin to the complexity of spectra, and their postulation of the half-integral quantum numbers of fermions.

Nearly simultaneously in 1925, Werner Heisenberg and Erwin Schrödinger formulated their matrix and wave mechanics formalisms, and quantum theory blossomed. Two years later, Heisenberg came up with his uncertainty principle, which partially explains spectral line broadening (but is certainly not the only cause of it).

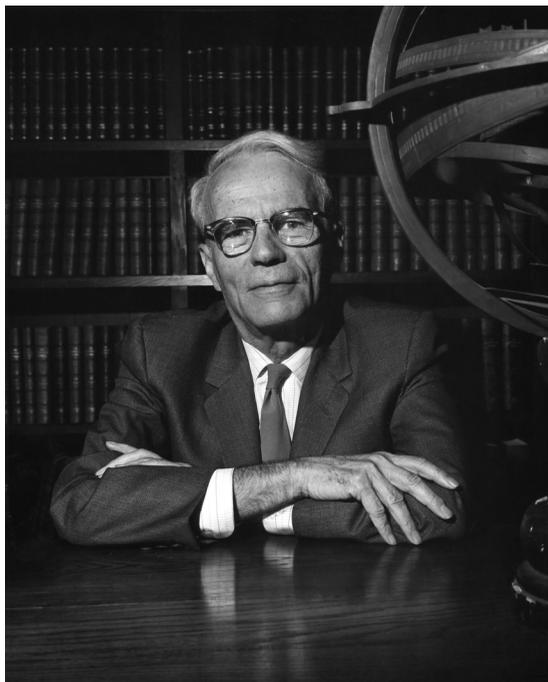
The Astronomical Connection

Some of the early spectroscopists, including Lyman, Russell, and Fowler, either worked as astrophysicists or had some background in the subject. The two specialties were synergistic: the discoveries of lines in the spectra of sunlight and starlight had motivated the birth of spectroscopy in the first place, and, as more atoms yielded their secrets in earthbound laboratories, astronomers learned about the chemical composition of the universe.

For instance, as a young man Frederick Sumner Brackett observed infrared radiation from the Sun at the Mount Wilson Observatory in California; in 1922, he discovered the series of infrared spectral lines, which bear his name, by studying the light from a hydrogen discharge tube [4]. In 1924, Ira S. Bowen (see Fig. 1) and OSA Honorary Member Robert A. Millikan modified their vacuum spectrograph to make it easier to record the extreme ultraviolet spectra of atoms heated by sparks [5]. Their work extended the range of spectroscopy into many light neutral atoms and multiply ionized heavier atoms. In turn, the lab work enabled Bowen to solve, in 1928, the mystery of the postulated element "nebulium."

Nineteenth-century astronomers had observed bright green emission lines in the object known as NGC 6543, popularly called the Cat's Eye Nebula. Since the lines matched those of no known element on Earth, they were attributed to a new substance named after the nebula. With his knowledge of both astronomy and spectroscopy, Bowen demonstrated that the emitting element was not nebulium at all, but doubly ionized oxygen giving off forbidden lines—spectral lines not normally permitted by the selection rules of quantum mechanics, but spontaneously occurring in the hard vacuum of a tenuous astrophysical gas cloud [6].

A decade later, astronomer-spectroscopists Walter Grotrian and Bengt Edlén identified the



▲ Fig. 1. Ira S. Bowen. (Courtesy of AIP Emilio Segre Visual Archives, W. F. Meggers Collection.)

true nature of “coronium,” another would-be element found in the solar corona 70 years earlier. Coronium turned out to be highly ionized iron, nickel, and calcium [7]. Every place astrophysicists have since looked, the rest of the universe consists of the same chemical elements that are found on Earth.

Advances in Molecular Spectroscopy

While some physicists occupied themselves with subatomic structures, other physicists and chemists investigated new spectroscopic phenomena in molecules. The nineteenth-century observations of fluorescence by G. G. Stokes led to the American R. W. Wood’s discovery of resonance radiation of vapors in 1918.

Wood (see Fig. 2), for whom an OSA award is named, began his career with detailed investigations of the spectra of iodine, mercury, and other elements in gaseous form. As a biographer wrote, Wood “discovered resonance radiation and studied its many puzzling features with great thoroughness and amazing experimental ingenuity” [8].

By far the biggest boost to molecular spectroscopy during this time period was C. V. Raman’s discovery of the inelastic scattering of light—the effect that came to bear his name. During his European trip in 1921, Raman (see Fig. 3), a native of India, spied the “wonderful blue opalescence” of the Mediterranean Sea and, as a result, was inspired to study the scattering of light through liquids [9]. In 1928, he and a colleague, K. S. Krishnan, discovered the inelastic scattering of photons now known as the Raman effect.

Lacking lasers, Raman and Krishnan had to use sunlight passed through a narrow-band photographic filter as a monochromatic light source. Early scientists who studied Raman scattering used mercury arc lamps or gas-discharge lamps as their sources. Nevertheless, in the 1930s scientists used Raman spectroscopy to develop the first catalog of molecular vibrational frequencies. The technique, however, would not reach its full flowering until the development of the laser in the 1960s.

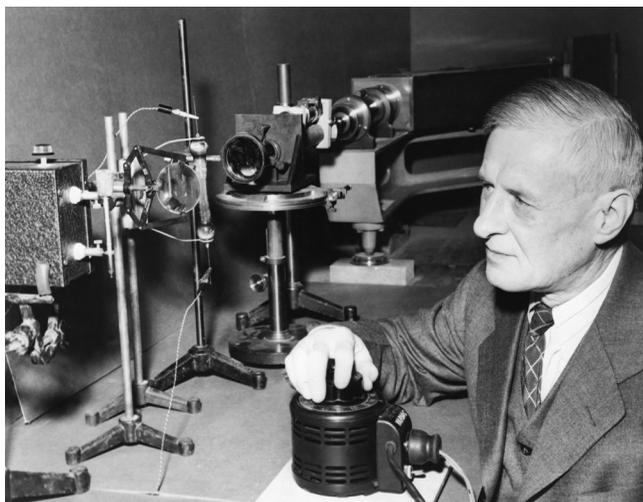
Optical spectroscopy also played an important role in the understanding of nuclear structure. Although A. A. Michelson had observed hyperfine structure as far back as 1881, it lacked an interpretation until 1924, when Pauli proposed that it



▲ Fig. 2. R. W. Wood. (Courtesy of The Observatories of the Carnegie Institution for Science Collection at the Huntington Library, San Marino, California.)



▲ Fig. 3. Chandrasekhara Venkata Raman. (Massachusetts Institute of Technology, courtesy AIP Emilio Segre Visual Archives.)



▲ **Fig. 4.** William F. Meggers with his laboratory equipment. (Courtesy of AIP Emilio Segre Visual Archives, W. F. Meggers Collection.)



▲ **Fig. 5.** George R. Harrison working with laboratory equipment. (Photograph by A. Bortzells Tryckeri, AIP Emilio Segre Visual Archives, W. F. Meggers Gallery of Nobel Laureates.)

In a major advance for pre-laser applied spectroscopy, Henrik Lundegårdh in 1929 developed a new flame-emission spectroscopy technique, which used a pneumatic nebulizer to spray a vaporized sample into an air-acetylene flame. This method made it easier for scientists to process many samples in a single day [14].

resulted from a small nuclear magnetic moment. In a 1927 article on the hyperfine structures of the spectral lines of lanthanum, Meggers and Keivan Burns pointed out the association between wide hyperfine splitting and spectral terms that arise when a single *s*-type electron manages to penetrate the atom's core [10]. "These penetrating electrons, so to speak, spy upon atomic nuclei and reveal in the hyperfine structure of spectral lines certain properties of the nuclei," Meggers wrote in 1946 [1]. "These properties are mechanical, magnetic, and quadrupole moments."

Spectral Analysis and Instrumentation

In parallel with the investigations into atomic and molecular structure, scientists of the 1920s and 1930s still had much to learn about the spectra of the various elements. They also made improvements to spectroscopic instruments and measurement techniques.

Before 1922, according to Meggers (see Fig. 4), scientists had only three ways to make quantitative spectrochemical analyses: the length-of-line method, the residual spectrum method, and the intensity-comparison with standards method [1]. During the following two decades, at least three dozen new techniques were published in the literature, although some were simply modifications of other procedures. Meggers and two of his colleagues at the U.S. National Bureau of Standards, C. C. Kiess and F. J. Stimson, published a 1922 monograph to bridge the gap between semiquantitative and quantitative spectroscopic analysis [11]. In 1926, Bowen published a detailed how-to article on vacuum ultraviolet spectroscopy [12], which David MacAdam later deemed one of the milestone articles in the history of the *Journal of The Optical Society of America* (JOSA) [13].

Since each chemical element can emit as many different spectra as it has electrons, the 92 naturally occurring elements can produce a total of 4278 spectra, according to Meggers [1]. Yet by 1939, according to a report by Allen G. Shenstone, only 400 or so had been analyzed in any great detail [15]. Scientists still kept plugging away at their analyses. George R. Harrison (see Fig. 5), OSA president in 1945 and 1946, once said that Meggers “determined the origins in atoms and ions of more spectrum lines than any other person,” though Harrison himself may have been a close second in that race [16].

With the data they did have, though, scientists vigorously advanced the field of spectrochemical analysis of mixed or complex substances. Meggers credited Harrison with spurring progress in this area by organizing 10 annual conferences on spectroscopy and applications, beginning in 1933. Researchers and technicians improved both prism spectrographs, which were favored in Europe, and grating spectrographs, by far the choice of Americans.

In 1938, Harrison invented a high-speed automatic comparator to record the intensities and wavelengths of spectral lines, and the following year he published the *MIT Wavelength Tables*, which listed the precise wavelengths of more than 100,000 individual spectral lines. Thanks to the economic circumstances of the era, Harrison procured funds from the U.S. Works Progress Administration to hire 143 workers to assist with the measurement of all those spectral lines. (A second edition, revised 30 years after its initial publication, is still in print.)

Toward the Future

During the first quarter-century of OSA’s existence, spectroscopy helped scientists consolidate the understanding of the structure of atoms and molecules, led to a greater understanding of the universe, and paved the way for many new practical applications.

As 1940 dawned, the laser—and the many new spectroscopy techniques it would spawn—was still two decades in the future. From a kindling pile of quantum-related hypotheses, however, scientists on three continents had assembled a coherent quantum theory largely resting on the evidence from optical spectroscopy, and this quantum knowledge would in turn spawn the optical revolution of the last 60 years.

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