7.2: A Very Brief History of Spectroscopy

Perhaps the first quantitative investigation that can be said to have a direct bearing on the science of spectroscopy would be the discovery of Snel's law of refraction in about 1621. I am not certain, but I believe the original spelling of the Dutch mathematician who discovered the law was Willebrod Snel or Willebrord Snel, whose name was latinized in accordance with the custom of learned scholars of the day to Snellius, and later anglicized to the more familiar spelling Snell.

Sir Isaac Newton's experiments were described in his *Opticks* of 1704. A most attractive illustration of the experiment, described in a work by Voltaire, is reproduced in Condon and Shortly's famous *Theory of Atomic Spectra* (1935). Newton showed that sunlight is dispersed by a prism into a band of colours, and the colours are recombined into white light when passed through an oppositely-oriented second prism. The infrared spectrum was discovered by Sir William Herschel in 1800 by placing thermometers beyond the red end of the visible spectrum. Johann Ritter the following year (and independently Wollaston) discovered the ultraviolet spectrum. In the period 1800-1803 Thomas Young demonstrated the wave nature of light with his famous double slit experiment, and he correctly explained the colours of thin films using the undulatory theory. Using Newton's measurements of this phenomenon, Young computed the wavelengths of Newton's seven colours and obtained the range 424 to 675 nm. In 1802 William Wollaston discovered dark lines in the solar spectrum, but attached little significance to them.

In 1814 Joseph Fraunhofer, a superb instrument maker, made a detailed examination of the solar spectrum; he made a map of 700 of the lines we now refer to as "Fraunhofer lines". (Spectrum lines in general are sometimes described as "Fraunhofer lines", but the term should correctly be restricted to the dark lines in the solar spectrum.) In 1817 he observed the first stellar spectra with an objective prism. He noted that planetary spectra resembled the solar spectrum, while many stellar spectra differed. Although the phenomenon of diffraction had been described as early as 1665 by Grimaldi, and Young had explained double-slit diffraction, Fraunhofer constructed the first *diffraction grating* by winding wires on two finely-cut parallel screws. With these gratings he measured the first wavelengths of spectrum lines, obtaining 588.7 for the line he had labelled D. We now know that this line is a close pair of lines of Na I, whose modern wavelengths are 589.0 and 589.6 nm. That different chemical elements produce their own characteristic spectra was noted by several investigators, including Sir John Herschel, (son of Sir William), Fox Talbot (pioneer in photography), Sir Charles Wheatstone (of Wheatstone Bridge fame), Anders Ångström (after whom the now obsolete unit the angstrom, Å, was named), and Jean Bernard Foucault (famous for his pendulum but also for many important studies in physical optics, including the speed of light) and especially by Kirchhoff and Bunsen. The fundamental quantitative law known as Kirchhoff's Law (see Chapter 2, section 2.4) was announced in 1859, and Kirchhoff and Bunsen conducted their extensive examination of the spectra of several elements. They correctly explained the origin of the solar Fraunhofer lines, investigated the chemical composition of the solar atmosphere, and laid the basic foundations of spectrochemical analysis. In 1868 Ångström published wavelengths of about 1000 solar Fraunhofer lines. In the 1870s, Rowland started to produce diffraction gratings of unparalleled quality and published extensive lists of solar wavelengths. New elements were being discovered spectroscopically:

Cs, Rb, Tl (1860-61); In (1863); He (1868 - in the chromosphere of the solar spectrum at the instants of second and third contact of a solar eclipse, by Lockyer); Ga (1875); Tm (1870); Nd, Pr (1885); Sm, Ho (1886); Lu, Yb (1907).

Michelson measured the wavelength of three Cd I lines with great precision in 1893, and Fabry and Pérot measured the wavelengths of other lines in terms of the Cd I standards. For many years the wavelength of a cadmium lines was used as a basis for the definition of the metre.

Although the existence of ultraviolet radiation had been detected by Richter, the first person actually to see an ultraviolet (UV) spectrum was Sir George Stokes (of viscosity and fluorescence fame), using a quartz prism (ordinary glass absorbs UV) and a fluorescent uranium phosphate screen. In 1906 Lyman made extensive investigations into ultraviolet spectra, including the hydrogen series now known as the Lyman series. Langley invented the bolometer in 1881, paving the way to the investigation of infrared spectra by Paschen. Balmer published his well-known formula for the wavelengths of the hydrogen Balmer series in 1885. Zeeman discovered magnetic splitting in 1896. Bohr's theory of the hydrogen atom appeared in 1913, and the wave mechanics of Schrödinger was developed in the mid 1920s.

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