"Do not several sorts of rays make vibrations of several bignesses, which according to their bignesses excite sensations of several colours, much after the manner that the vibrations of the air, according to their several bignesses excite sensations of several sounds? And particularly do not the most refrangible rays excite the shortest vibrations for making a sensation of deep violet, the least refrangible the largest for making a sensation of deep red, and the several intermediate bignesses to make sensations of the several intermediate colours?" (Newton 1730)

Introduction

The word 'spectrum' is from the Latin *spectrum* which means a vision, or something to behold. And the Greek *skopein* means 'to look at' (CharlestonWeb; PrincetonWeb), but in our context, a spectrum is a representation of the *entire* range of electromagnetic wavelengths, not just the visible section. Spectroscopy is the study of these spectra, a spectrograph is a tool used to manifest them, and spectrometry is the measurement of the various components of a spectrum (COSMOSWeb).

It is commonly regarded that modern spectroscopy began early in the 1700s with Sir Isaac Newton's 'Opticks'. The above quote is Query 13, Book 3 in the 4th edition of that landmark document, and describes his conclusions from experiments on splitting white light (refraction) into its component colours, to obtain a spectrum. Newton's work, while a watershed, was none-the-less, only a step in a long evolution of discovery.

The history of spectroscopy should be understood in context, as the meeting of several strands of human enquiry beginning millenia ago. There's a lot of ground to cover, and this essay will trace the history, from its roots in optics, electricity and magnetism, beginning some 4,000 years ago and going through discrete periods in history.

Ancient Optics

As far back as 2000 BC, Egyptians were using polished bronze to light the interior of their pyramids, and as personal mirrors (EgyptattractionWeb), and enquiry into the nature of light emerges with some amazing insights, as early as 500 BC. Mo Zi in China studied mirrors around that time, and the focusing power of lenses was known at least as far back as 423 BC when Aristophanes mentioned them in his play The Clouds (ArtOpticsWeb). Even Aristotle thought that colour couldn't exist without light (CharlestonWeb).

Thales of Miletus (624 – 547 BC) experimented with amber and lodestone, materials which displayed properties of (static) electricity and magnetism respectively (UVirginiaWeb) thus beginning the study of electromagnetism which ultimately converges with optics centuries later. None of this early interest was linked to the electromagnetic spectrum of course, but investigations of natural phenomena involving crystals as lenses was carried out by Seneca around 40 AD, and atmospheric refraction was studied by Clemedes c. 50 AD and by Ptolemy c. 140 AD. Nero even used an emerald as a lens to watch gladiators fighting (CharlestonWeb; OptimaWeb). These were the seeds of modern optics.

The Dark Ages and Renaissance

A thousand years passed, before Ibn-al-Haitham took up further study of refraction around 1010 AD (CharlestonWeb), allowing Monks to turn his science into the technology of a 'reading stone' which was a glass lens that sat on a page of text, magnifying it (DidyouknowWeb). By this time the Chinese were quite familiar with magnetism, constructing crude compasses for navigation (Mahan 1962).

Western science started to study light seriously in the early 13th century with Roger Bacon's work on the focal points of mirrors, and by the end of that century, glass and rock crystal lenses were being traded in Venice for use in eyeglasses (CharlestonWeb; OptimaWeb). Though the dark ages were devoid of much scientific progress in optics, the Renaissance re-invigorated science, and important work was carried out. Grosseteste c. 1200, John Pecham and Roger Bacon c. 1250, Theodoric of Frieberg c. 1275, Witelo c. 1300, and Henry of Hesse c. 1350, all studied and wrote on various aspects of vision, perception, reflection, refraction, lenses and rainbow production (Grant 1974).

The Enlightenment

This period saw extraordinary progress in the understanding of magnetism, electricity and light, the highlight for our topic being Newton's work and publications. In the bubonic, Shakespearean times of late 16th century London, William Gilbert wrote the definitive work on magnetism, De Magnete. Chiswick Press published it in 1600, and it provided groundbreaking work for subsequent scientists (GoddardDocWeb). Gilbert correctly described Earth's magnetic field and explained the alignment of compass needles. He was the first scientist to do a literature search (turning up little of benefit to him) but then set about experimenting and postulating about electricity and magnetism (Malin & Barraclough 2000), even developing a new piece of scientific equipment, the electroscope (UVirginiaWeb).

Rene Descarte's contribution at this point, around 1637, can't be exaggerated. His tireless efforts in natural philosophy (which then included science and metaphysics) produced many landmark documents such as 'the Geometry', 'the Optics', 'the Meteorology', 'the Discourse on the Method' and 'the Principles'. For our purposes, his mathematical description of what is now known as Snell's Law is pertinent: for light going from one medium into another, the sine of the incident angle and the sine of the refraction angle have a constant ratio:

$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

where n_1 is the refractive index of one medium, and
n_2 is the refractive index of the other medium, and
θ_i are the incident and refractive angles from the normal
(the 'normal' is at right angles to the surface of the medium)

Descarte would doubtless have read the material provided by Snell, who is generally credited with discovering the refraction law which bears his name, but Descarte was the one who published it (StanfordUWeb; WolframWeb).

Lenses, telescopes and chromatic aberration (differential bending of incident wavelengths causing coloured edges around images, which was solved by Hall in the mid 18th century) were hot topics in the literature late in the 17th century, with publications by Newton, Halley, Cassegrain, Hugens and Hooke (NASAADSABSWeb). Robert Boyle is a large figure in the history of chemistry, but in 1663 he also made contributions to optics with some comments about the phenomenon known as Newton's Rings which is an interference pattern created between overlapping light waves when a convex lens is placed in contact with a flat surface (UVirginiaWeb).

Around this time, there was conflict about the very nature of light – whether it was a wave form, or made up of particles. Some experiments could be explained if light was considered particulate (Newton's preference), but other observations needed light to be in wave form for an explanation. A clue to the duality of light, came in 1669 when Bartholinus discovered polarization (UVirginiaWeb). His experiments with passing a single light ray through a calcite crystal producing two exiting rays of light, showed that the original light ray was infact composed of two different parts, each being refracted by the calcite to slightly differing degrees. In the mid 17th century, Christian Huygens experimented with this, and found that the two rays were actually travelling at right angles to each other; he denoted them as the s- and p- polarization states, and subsequently published his seminal theory on the wave nature of light in 1690 (Collett 2005).

The pace picks up now, with studies in light and electricity coming thick and fast. This was around about the time that Danish astronomer Ole Roemer calculated the speed of light by noticing the difference in position of Jupiter's moon Io at different times of Earth's annual orbit around the Sun (UColoradaWeb). Skipping Newton for the moment, we also had work on chromatic aberration in lenses by Bradley, Moor-Hall and Dollond around 1728, Du Fay's 1734 proposition that there were two kinds of electricity, Benjamin Franklin's well known interest in electricity in mid 18th century, the 700-page The History and Present State of Electricity published by Joseph Priestley in 1767, and Galvani and Volta's work with electricity later in the same century (UVirginiaWeb).

Sir Isaac Newton (c. 1643 – c. 1727 depending on which calendar you use) published his Opticks in 1730. In Book I, Proposition I, Experiment I, he describes the use of a prism of solid glass to split an incoming ray of white light into its colours, the blue being refracted more than the red. Diagrams and supporting mathematics are included in the treatise (Newton 1730). Though spectra had been known about for some time, and discussed by Descarte, Grimaldi and Hooke, Newton was the first to systematically test the effect and project a spectrum on a wall, some 22 feet from the prism (Hearnshaw 1986). Newton used the word "spectrum" to describe his result, reporting his ongoing study to the Royal Society (Newton 1672), so this may be regarded as the point when spectrography officially began.

A significant step in the centuries-old path to spectroscopy, was taken by the Scottish physicist Melvill, who'd been working with excited gases by dropping various salts into a spirit flame, and observing the resultant colour. In 1752, he recorded the spectra which resulted when a slit of light from a flame was passed through a prism and projected on a surface. He experimented with various substances being introduced into the flame, finding that each substance had not a continuous spectrum but a unique set of (emission) lines in certain sections of the coloured spectrum (Cassidy et al 2002). Repeatedly, Melvill found the yellow, sodium emission line which would re-appear for him and many others. This was a confusing result because minute impurities causing a sodium emission were often seen, even when other species were introduced into the flame (Hearnshaw 1986).

Returning to our timeline and history, the first half of the 19th century saw many scientists working in the field of emission and absorption spectra for both celestial and earthly sources. It was a prolific period which coalesced many concepts into a general understanding of optics, but with only basic observational data on spectra; even though John Dalton proposed his atomic theory in 1806, the connection hadn't been made between atomic structure and spectral lines.

The fact that the electromagnetic spectrum extending beyond the visible red end, was uncovered by Herschel in 1800, who registered different temperatures for parts of the spectrum, the red part being the hottest and an even hotter recording outside the red end, but no heating beyond the violet end. Soon after, in 1801, Ritter and Wollaston found ultraviolet wavelengths by exposing silver bromide to that part of the spectrum, and Wollaston was actually the first to see absorption lines, which he saw in a solar spectrum in 1802 (Brashear 1914; King 1955), but thought they were simply gaps between the coloured parts of the spectrum, not actual absorption lines. Around this time, Young used a diffraction grating with 500 grooves per inch to measure the wavelength of several colours of light, thus beginning the concept of wavelength as an expression of the energy in a particular colour (Hearnshaw 1986).

The next big name in our history of spectroscopy is the German optical glass manufacturer, Joseph von Fraunhofer (1787-1826). Melvill's emission lines were complemented in 1814 when Fraunhofer's setup stretched (dispersed) the spectrum from the Sun, to reveal over 600 dark, absorption lines (Freedman & Kaufman 2005), which would eventually be known by his name (Fig. 1). He named the most distinct of these lines A, B, C…H and he counted some 574 lines between B and H. On studying other stellar spectra and spectra of reflected sunlight, Fraunhofer deduced that each star had a unique set of lines, and that they were actually a function of the star itself (King 1955). We now know that these lines indicate the presence of a cooler layer of gases in the chromosphere of the Sun (Lewis 2004). Infact, Fraunhofer came close to another discovery when he noted that his two, strong D lines were in exactly the same position as the emission lines from his sodium lamp (King 1955). He also guestimated the relative intensity of each colour with a curve drawn over the spectrum as also shown in Fig. 1. Fraunhofer also recorded absorption spectra for Sirius, Castor, Betelgeuse and other stars and planets, but solar spectra weren't to be widely studied for several more decades. Fraunhofer was also one of the first to use a diffraction grating (his was made of many thin wires placed in front of the telescope's objective lens) to calculate the wavelengths of his spectral lines (Hearnshaw 1986).

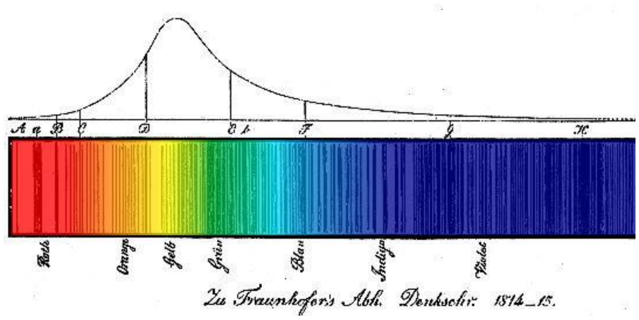

Fig. 1 The dark lines in this spectrum are absorption lines seen and drawn by Fraunhofer (HUJWeb)

French physicists Argo and Fresnel, were actively researching polarization around 1815, and before the century was half over, we had the discovery of the photo-sensitivity of silver bromide by Balard; Young's 3-colour vision theory; experiments with various salts sprinkled into a flame to produce different colours by Talbot & Herschel; a wave theory for diffraction by Schwerd;

Dopplers important 1842 work on the stretching and compression of light waves; and Faraday's observations with polarization and magnetic fields in 1845.

Recording spectral lines (particularly in the ultraviolet) took a leap forward in 1842, when the French physicist Becquerel, photographed Fraunhofer lines on a Daguerrotype plate (an early light-sensitive polished plate with silver iodide applied to the surface) mounted a metre away from a focussing lens, and the next year, the American, Draper repeated and extended Bequerel's work (Hearnshaw 1986).

This is all important 'support' science in terms of our spectroscopy history, but in 1848, the French physicist Foucault made the breakthrough discovery of an *absorption* line from an arc placed behind a sodium flame (UVirginiaWeb). In 1850, Foucault also developed an experiment which illustrated that light traveled faster through air, than water, matching the predictions of wave theory, and pretty much finishing Newton's ideas of particulate light (Cassidy 2002).

Flourescence was a pet study subject for Stokes of Ireland, and in 1852 he shone a solar spectrum through a quinine sulphate solution, which glowed blue, allowing more lines to be identified in the UV range (Hearnshaw 1986).

Ending the century was a discovery by Zeeman and Lorentz in 1896, that a static magnetic field will split a spectral line, a discovery which earned them a Nobel Prize in 1902, the result now called the Zeeman Effect which is used to augment many types of spectrometry (NobelWeb).

The Victorian Era

Another few decades of rapid discovery begins with Oersted's 1820 demonstration of induction of a magnetic field around a wire carrying electricity, and Ampere's corroboration of the interconnectedness of these two natural forces (CharlestonWeb), but Kirchhoff and Balmer were to stamp lasting impressions on Victorian, and the subsequent path of spectroscopy.

The German physicists Kirchhoff and Bunsen, worked together at the University of Heidelberg, and with Bunsen's newly designed flame tool (the Bunsen burner) and performed the first spectral analysis by noting the specific spectral lines of different chemicals sprinkled into a Bunsen burner flame. They went on to identify entirely new elements with the predictive nature of their spectra, and so discovered cesium and rubidium (Freedman & Kaufman 2005). This was the beginning of spectral analysis, and phenomena such as Fraunhofer lines could now be explained as selective absorption of parts of the Sun's spectrum by specific elements. Kirchhoff therefore, in 1859, had developed the theory that a gas with certain specific emission lines must absorb spectral lines at the same temperature. Stokes (1860) translated Kirchoff's findings which are important enough to quote here: "I conclude that the dark lines of the solar spectrum which are not evoked by the atmosphere of the earth exist in consequence of the presence, in the incandescent atmosphere of the sun, of those substances which in the spectrum of a flame produce bright lines at the same place." And he concluded that the sun is "surrounded by a gaseous atmosphere of somewhat lower temperature… From the occurrence of these lines (D), the presence of sodium in the atmosphere of the sun may therefore be concluded" (Stokes 1860). Spectral analysis had arrived, and spectroscopy could be used to determine and discover stellar chemical species from their spectra.

Around this time, we could say that the basic architecture of the optical spectroscope was developed. Today's optical spectroscopes consist of three basic parts: the collimator to convert all incoming light to parallel beams, the prism which disperses, and the telescope (James 2007). Though now a functional and predictive science, theoretical substantiation of spectroscopy was not yet developed.

Soon after Kirchhoff, scientific papers appeared, using the word spectroscopy. For example, Gassiot published a paper in the Proceedings of the Royal Society of London entitled 'On Spectrum Analysis; with a Description of a Large Spectroscope Having Nine Prisms, and Achromatic Telescopes of Two-Feet Focal Power' (Gassiot 1862).

Also around the 1860s, Fraunhofer had taken Young's previous observations of slit interference and developed the diffraction grating, which he used to accurately measure wavelengths. Michelson also investigated wavelength, but by looking at interference patterns of intersecting light waves. This 'interferometry' and wavelength calculation work would be important for spectroscopy and spectral analysis in the future.

While a huge amount of spectral data was being collected by many scientists, around 1862, attempts were being made by Rutherfurd and Secchi to classify stars by their spectra. Then Maxwell published his complete theory of electromagnetism 'A Dynamical Theory of the Electromagnetic Field' in late 1864. But, our strands of spectroscopic theory are still somewhat separate, with astronomers observing and collecting data, and chemists still identifying an array of materials by their spectra. Huggins & Miller's 1866 paper "On the spectrum of a new star in Corona Borealis" looked spectroscopically at a nova, with an insightful conclusion that the elements found in stars must surely be the building blocks of organic life! This was doubly important work, because it used the first specifically designed spectroscope, made by Huggins and Miller (Fig. 2)

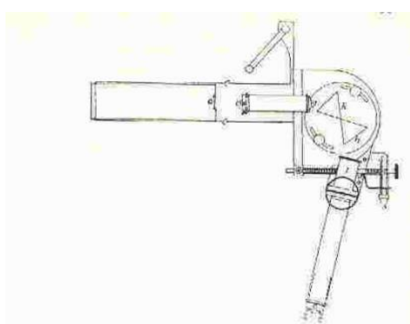

Fig. 2 Miller and Huggin's spectroscope. Source: Hearnshaw 1986

A total solar eclipse occurred in 1868, and emission spectral data taken from the solar prominances was analysed by the English astronomer Lockyer, who found lines near to, but distinct from the sodium lines. These were named helium (of the sun, helios) lines for a new element which was not manufactured on Earth for at least another 25 years (Hearnshaw 1986).

An important technical step was taken in 1872 when Draper was able to take the first photograph of a stellar spectrum. Recording eleven emission lines from the spectrum of Vega, his work was extensively developed by Londoner, William Huggins who analysed spectra from many stars, and would go on to receive many awards and accolades for his work in stellar spectroscopy (Hearnshaw 1986).

But it wasn't understood why an element, say hydrogen, only radiated at four certain wavelengths to produce four spectral lines, and not over a range. Enter Balmer in 1885, who by trial and error described spectral lines for hydrogen as a mathematical function of wavelength (Fig. 3).

Fig. 3 Hydrogen absorption lines H_α (656nm), H_β (486nm), H_γ (434nm), H_δ (410nm)

$$1/\lambda_n = R(1/2^2 - 1/n^2)$$

for n = 3, 4, 5 and 6

and R is a constant

This is known as the Balmer Series and equates to the four energies involved when an electron moves between the valence levels 3, 4, 5 and 6, and the 2nd level, in a hydrogen atom. This cause was not known at the time, however. Others in this field were Rydberg who elaborated relationships for spectral frequencies of other elements and compounds, and Pashen whose name is given to the transitions to the third level in hydrogen (Halliday et al 2005). This was all descriptive however, because the existence of the electron wasn't seriously postulated until 1895 by Larmor, nor proven until Thomson in 1897 (AIPWeb).

A succinct explanation of spectral lines became possible when in 1899, German physicist Max Plank presented his quantum theory of atomic structure which proposed that at the atomic level, energy exists in discrete packets or quanta, related to their wavelength and frequency (EAAWeb). This nicely meshed with Larmor's electrons, and the Balmer and Pashen series of quantum jumps.

The late 19th century and early 20th century saw two relevant works come to fruition. The English Lord Rayleigh (John Strutt) combined photography and the science of lenses and diffraction gratings, to derive a full theory of the optical spectroscope (James 2007). And, the Harvard College Observatory in Massachusetts stamped forever, it's mark on classification of stars by their spectra. Under the tireless direction of Harvard's Edward Pickering, millions of stellar spectra were recorded and classified, and with funds donated by Henry Draper's wife Anna, the observatory produced an enormous body of work which is still used today. Contributions from Williamina Fleming, Antonia Maury and Annie Jump Canon culminated in Canon's publication of the Harvard Classification system of stars, in 1924 (Hearnshaw 1986). In this system, stars are grouped according to their temperature, hot blue/white stars being class 'O' through to cooler red giants being class 'M'. Each class has a similar spectrum. See Fig. 4 below. But some theory was brewing around the same time.

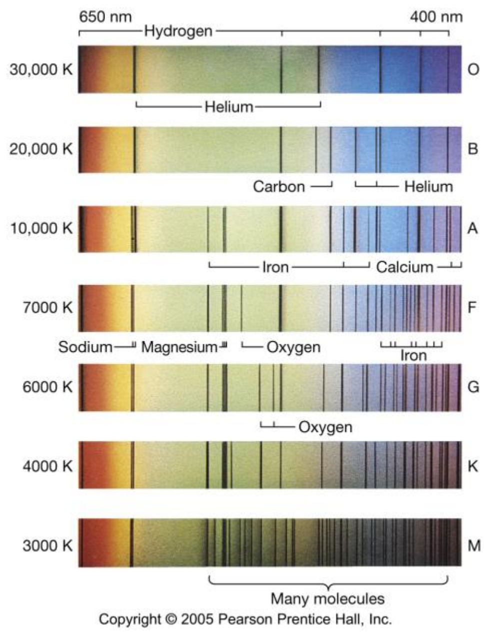

Fig. 4 The basic Harvard Classification showing subsequent Morgan Keenen Kellman spectra
Image credit: University of Oregon Physics Department

Theory and technology in the 20th century

Keeping pace with theory, H. Ebert broke the problem of increased resolution in spectrographs based on glass prisms, by substituting mirrors for the lenses of the collimator and camera. This idea was extended decades later by Fastie, who included more mirrors and a diffraction grating, developing the Czerny-Turner design for spectrographs. (James 2007)

The first half of the 20th century produced breakthroughs in the theory and understanding of atoms, which provides a background to understanding spectral lines. Perhaps the most significant work, was that of Neils Bohr who, in 1913 proposed that in Max Planck's atomic structure, electrons can occupy certain energy levels within an atom. This explained the existence of the discrete Balmer Series of absorption lines, and was the birth of Quantum Mechanics. Pauli, Heisenberg, Schrodinger, de Broglie, Born, Jordan, Bohr and Dirac all added to the theoretical and mathematical basis of quantum mechanics, and Pauli went on to derive his Exclusion Principle which states that only one electron may exist in any particular quantum state (Hearnshaw 1986).

So, a fuller explanation of the causes, and meaning of spectra was now available. The Harvard Classification system was adopted by the International Astronomical Union in 1922, but it soon became clear that stars with the same temperature could have different luminosities depending on their size, and so a refinement of the system was required. William Morgan, Philip Keenan and Edith Kellman went on to published their Atlas of Stellar Spectra in 1943, which subdivided Harvard classified stars originally into five spectral groups from I to V, subsequent study resulting in a more accurate classification, now referred to as the MK or MKK system (Hearnshaw 1986, Keenan 1987). This is now a cosmopolitan system in astronomy.

The second half of the 20th century was a period of extraordinary progress in the laboratory. Many techniques, theories and discoveries advanced our understanding of atomic and molecular behaviour. Perhaps the highlight was Charlotte Moore's publication of exhaustive tables of atomic energy levels in 1973 (CharlestonWeb).

Technologically, the 1950s offered the electronics of photomultipliers and semiconductors to vastly improve the detection, and resolution of optical spectra. With Fabry and Perot's interferometry work from the turn of the century, and improved diffraction grating production, the Fabry-Perot interferometer became the high end tool for optical spectroscopy. Also around this time, the ratio of 'light capture' to 'resolution' in a spectroscope was shown to be constant. This allowed astronomers to trade off one with the other, in order to tailor their inspection of high, or low temperature targets. (James 2007)

Spectroscopy today

Today, the whole spectrum of EM radiation is exploited to make enquiries of the universe. Telescopes are now spectrometers. And they've developed to spy targets in the infrared, ultraviolet, x-ray, gamma ray and radio wavelengths. But there's a difference in the format of the output compared to visible spectrography. Radio spectrometry doesn't use diffraction gratings, rather discrete frequency channels are analysed against certain functions such as frequency of momentum. A typical readout is shown in Fig. 5 below.

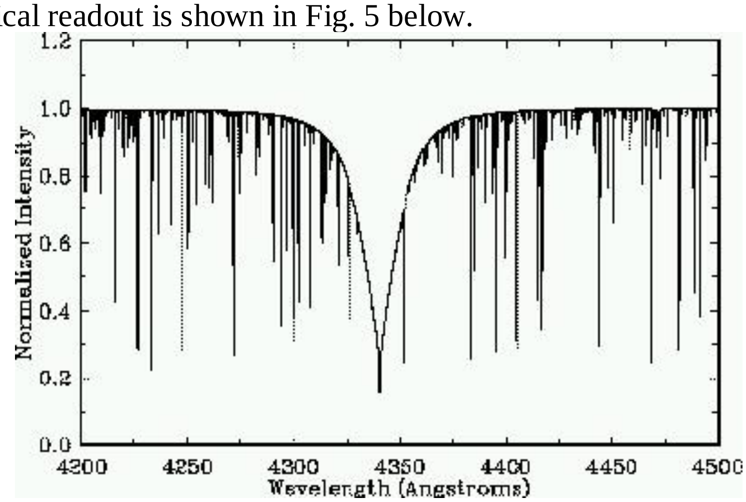

Fig. 5 Example of a non-optical spectrograph Source: AdduciWeb

Many types of spectroscopy are defined by their subject matter or their method, such as absorption, mass, fluorescence, x-ray, flame, plasma, spark, visible, UV, IR, NIR, Raman, CARS, NMR and Mossbauer. (The reader may wish to explore these further, I won't spend time elaborating here.) Furthermore, astronomers rely on the fact that electromagnetic spectra from astronomical targets usually contain lines of absorption and/or emission which can be analysed to reveal certain properties of the target.

Instead of the traditional method of splitting light with a prism and capturing the result on a photographic plate, modern spectrometers use diffraction gratings to disperse the spectrum, and electronics in the form of Charge-Coupled Devices (CCDs, which superceded earlier electronics in 1969) to digitally record spectra. The position, depth, height, width and general shape of spectral lines can be used to characterise the chemical content, age, movement and physical makeup of the observed body (COSMOSWeb). A typical modern spectrograph is shown Fig. 6

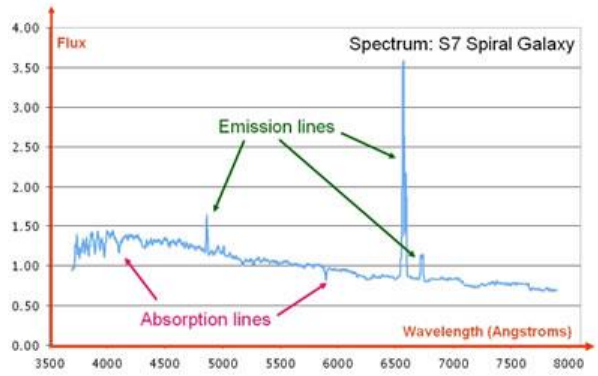

Fig. 6 Spectrograph of a Spiral Galaxy. Credit: (SAO COSMOS)

Summary

I have taken a slightly different approach in this history. I wanted to draw together the threads of spectroscopy that preceded the so-called ‘discovery’ of our topic. And present a contextualised view of it’s development. I traced the development of knowledge in optics, magnetism and electricity from ancient times. When humans were just finding philosophical thought and the properties of materials around them, through the dark ages and Renaissance when scientific enquiry was more formalised, and into the Enlightenment and Victorian eras where the landmark studies of Newton, Fraunhofer and Kirchhoff founded the basics of modern astrophysics. The modern era saw theoretical explanations, and technological production mature alongside voluminous charting of stellar spectra. Today, we use orbiting satellite telescopes which are really spectroscopes, peering into space without the interference of Earth’s atmosphere. We look at the range of electromagnetic spectra with broadband and narrow band dedicated equipment, and we’re making huge inroads into our understanding of the Universe.

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This research has made use of Swinburne University’s COSMOS online encyclopedia of astronomy.

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