A Brief (Incomplete) History of Light and Spectra

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In 1913, Niels Bohr explained why the lines in the hydrogen spectrum are arranged the way they are. His explanation places electrons in stable orbits which he called "stationary states" (violating well-known laws of science) and explains spectrum lines as the energy difference resulting from the movement of an electron from a higher-energy stationary state to a lower-energy one.

This moment not only ended almost 250 years of since the discovery of the spectrum, but was the beginning of fruitful ideas from one of the most profound intellects this world has ever seen. (L. Brillouin tells that he had entered the room just as Sommerfeld finished Bohr’s article in the July 1913 issue of Philosophical Magazine. Sommerfeld said "There is an extremely important paper here by N. Bohr which will be a milestone in theoretical physics.") Bohr’s work continues to have an impact on science today.

The best place to start, I suppose, is at the beginning.

Matter and energy interact. Take a lump of metal and heat it. It glows, giving off light. Burn some wood and one of the things it emits is light. Place an object in the sunlight and it gets hotter. Look at the sky after a rain and see a rainbow.

These things were known to the ancients. Today, we know that the energy given off by matter creates a spectrum. This spectrum and the behavior of its colors are so important to us that we have given it a name -- spectroscopy.

The use of spectroscopy has mushroomed since its roots in the early 1800s. Today, nearly 200 years after its beginnings, research using spectroscopy and research into improving the technique continues around the world.

What follows is in no way a complete history of spectral studies and the nature of light. These are only some highlights I have selected.

1666

Isaac Newton allowed sunlight from a small, circular hole to fall on a prism, producing a rainbow of color. Although the production of a rainbow by a clear crystal was known to the ancients, it was Newton who showed that the colors did not originate in the crystal, but rather were components of sunlight. This array of colors he called a spectrum.

Here is how the great man explained it:

"And so the true Cause of the Length of that Image was detected to be no other, than that Light is not similar or Homogenous, but consists of Difform Rays, some of which are more Refrangible than others."

Newton’s experimental arrangement is shown in the image below. It is from Voltaire’s Eléments de la Philosophie de Newton, published in 1738.
In addition, Newton was able to produce a spectrum from white light and then recombine the spectrum colors to get the white light back again.

Years later, in *Opticks*, Query 29, he gave the following mechanism for the fact that the colors refracted from the greatest amount (violet) through blue, green, yellow, orange (which he does not mention) and to the least amount (red):

"Nothing is more requisite for producing all the variety of Colours, and degrees of Refrangibility than that the Rays of Light be Bodies of different Sizes, the least of which may take violet the weakest and darkest of the Colours, and be more easily diverted by refracting Surfaces from the right Course; and the rest as they are bigger and bigger, may make the stronger and more lucid colours, blue, green, yellow, and red, and be more and more difficultly diverted."

This explanation is a particle-based one: light particles are of different sizes.

1676

In Paris, Olaf (Ole) Roemer, working with Giovanni Cassini (the head of the observatory), studies the variations in the calculated frequency of the planet Jupiter eclipsing its moon Io. To explain the variations, Cassini, in August 1675, writes:

"the second irregularity in the motion of the first Jupiter’s satellite may be due to [the fact] that light takes some time to reach us from the satellite, and it takes from ten to eleven minutes to pass the distance equal to half the diameter of the Earth’s orbit."

In September 1676, Roemer announced that the November 9 eclipse of Io by Jupiter would occur 10 minutes later than that predicted. He was shown to be correct. In December, he published a paper explaining his calculations, but is denounced by Cassini, who becomes his opponent. Roemer also suffered because he was a Protestant and, in France at that time, Protestants were just barely tolerated. In 1681, Roemer returned to his native Denmark and was given many responsibilities in science and political leadership. He is showered with many honors and awards.
and passed away September 19, 1710. Today he is known as the "Northern Archimedes" for his great range of contributions in science.

In his paper on the speed of light, he never calculated the actual value. Since that time, there have been speculative calculations based on Roemer’s paper, but their values are suspect. For example, one writer uses Roemer’s amount of time, but uses the modern distance to the sun. Another writer assumed Roemer might have used some values that, upon deeper analysis, he probably would not have. These two writers calculate that Roemer’s value for the speed of light (had he published one) would have been around 215,000 km/sec. The modern value is just under 300,000 km/sec.

In 1983, writing for the *Journal for the History of Astronomy*, Albert van Helden speculated, using clues in Roemer’s paper, that the calculated value - had there been one - would have been around 135,000 km/sec.

### 1704-1730

Issac Newton publishes four editions of *Opticks*. Query 29 asks:

"Are not the Rays of Light very small Bodies emitted from shining Substances?"

and Query 31 says:

"Even the Rays of Light seem to be hard bodies; for otherwise they would not retain different properties in their different Sides."

In *Opticks*, he develops the particle theory of light (also called the corpuscular theory of light). He is able to give plausible explanations for properties of light such as color, reflection, and refraction.

He was not able to explain everything about light, diffraction bands outside the geometrical shadow (discovered by Grimaldi in 1665) being one and Newton’s rings being another.

An extremely important prediction implicit in Newton’s particle theory is that, as light moves from air to water, it SPEEDS up.

A wave theory of light existed in Newton’s day. Its leading champion was Christiaan Huygens, but the theory was incomplete. It only addressed a small fraction of the phenomena Newton discussed and was difficult to understand. So, due to the wave theory’s poor explanatory power and Newton’s great authority within the science world, the particle theory of light reigned supreme.

### 1777

Carl W. Scheele (the discoverer of chlorine) investigated the effect of spectral colors on the darkening of silver chloride. It was already known that silver chloride darkened upon exposure to sunlight. Scheele found that, for the same exposure, the darkening was most rapid at the violet end.

### 1800

William Herschel, the famous astronomer, studied the heating effects of the colors of the spectrum. He did this by exposing thermometers to various colors of light. He found a steady
increase in heating power going towards the red. He also used a thermometer placed just outside the red color as a control. To his amazement, the dark region just outside the red color provided even more heating power than the red color.

In this manner, the infrared region was discovered.

1801

Johann Wilhelm Ritter verified Herschel’s results and extended them. He placed silver chloride outside the violet end of the spectrum and found even more darkening than Scheele did 24 years earlier.

In this manner, the ultraviolet region of the spectrum was discovered.

This year also saw the discovery (by Thomas Young) of interference patterns caused by light passing through a narrow slit. Up until this point, the wave theory of light (Huygens) had had nothing convincing to offer in opposition to the particle theory of light (Newton). Now it did, because you cannot explain interference using particles.

However, using waves, it was easy. Here is what Young said in the Bakerian Lecture, November 29, 1801:

"When two undulations, from different origins, coincide either perfectly or very nearly in direction, their joint effect is a combination of the motions belonging to both.

"Since every particle of the medium is affected by each undulation, wherever the directions coincide, the undulations can proceed no otherwise then by uniting their motions, so that the joint motion may be the sum or difference of the separate motions, accordingly as similar or dissimilar parts of the undulations are coincident."

However, despite the efforts of Young, the particle theory of light still remained the accepted view of light’s nature. In 1803, he writes:

"The experiment of Grimaldi on the crested fringes within the shadow, together with several others of his observations equally important, has been left unnoticed by Newton. Those who are attached to the Newtonian theory of light, . . ., would do well to endeavor to imagine anything like an explanation of these experiments derived from their very own doctrines; and if they fail in the attempt, to refrain at least from idle declamation against a system which is founded on the accuracy of its application to all these facts, and to a thousand others of a similar nature."

To me, Young sounds a bit frustrated!!

1802

While verifying Ritter’s results, William Wollaston also reported the existence of dark lines in the spectrum of sunlight

He passed sunlight through a very narrow slit (no more than 0.05 inch) so that it fell on the prism. (Up until this time, people had been using circular openings or relatively wide slits. This method resulted in very impure spectra.)
Projecting the light over a distance of 10-12 feet, Wollaston saw red, yellowish-green, green, blue and violet colors. He also reported seven dark lines. Five lines were reported as being on the boundaries between two colors, but two lines were within the color boundaries (specifically yellowish-green and blue).

1814-1823

Twelve years later, a young Joseph von Fraunhofer was looking for ways to check (and improve) the quality of telescopes he was making. He rediscovered the dark lines in the sun’s spectrum while measuring the dispersive powers of various kinds of glass for light of different colors. As he worked on this project, he noticed that a bright ‘orange’ line (due to sodium, but he didn’t know that) in the spectrum of the flame he was using was in the same position as the dark D-line (see below). This same line had been observed in flames from alcohol and sulfur as well as from candles.

Fraunhofer mapped out the 574 thin black lines that he observed in the sun’s spectrum. Eight of the most prominent lines were labeled A to G. Today, these lines are known as the Fraunhofer lines. The D-line was found to be two closely-spaced lines, subsequently called D₁ and D₂. Its position turned out to be in the yellow portion of the spectrum, not the orange that Fraunhofer wrote.

Here is what Fraunhofer drew:

![Fraunhofer's diagram](image)

In 1817 and 1823, Fraunhofer continued to report results from his research. He found:

1) the spectrum of the moon showed the stronger lines of the sun in the same places.
2) the spectra of Venus and Mars were faint, with some of the lettered lines being found.
3) Several star spectra showed differences from the sun, although some of the same lines in the sun were identified in other stars.

In 1821, Fraunhofer reported on his first efforts to use a diffraction grating (rather than a prism). Diffraction was discovered in 1665, but it received little attention until the early 1800s, when there was extensive discussion on the nature of light. The diffraction grating, a series of closely spaced thin lines, was destined to play an important role in future discoveries. Using his early diffraction gratings, Fraunhofer was able to measure the wavelengths of the two sodium lines, obtaining values very close to the modern ones.

However, he could not explain why the dark lines were there. In fact, although spectral research occupied him for much of his life, he never did find out how the lines that bear his name were made.
The modern term for what he saw is an "absorption spectrum."

1815-1819

Augustin Fresnel independently rediscovered interference and begins to study (and extend mathematically) the wave theory of light. In 1817, the French Academy of Sciences decided to offer a prize for the best essay covering the wave theory of light. In 1819, Fresnel (one of two entries) wins the prize with a stunning 135-page comprehensive treatment of the wave theory of light, refuting completely the particle theory of light.

On the judging panel was a mathematician of the first rank: Siméon Denis Poisson. He also happened to be a very strong believer in Newton's particle theory of light and was able, using Fresnel's mathematics, to derive a prediction he was sure would destroy the wave theory of light: the famous Poisson's Spot. Here is what he said:

"Let parallel light impinge on an opaque disk, the surroundings being perfectly transparent. The disk casts a shadow -- of course -- but the very centre of that shadow will be bright. Succinctly, there is no darkness anywhere along the central perpendicular behind an opaque disk (except immediately behind the disk). Indeed, the intensity grows continuously from zero right behind the thin disk. At a distance behind the disk equal to the disk’s diameter, the intensity is already 80 per cent of what the intensity would be if the disk were absent. Thereafter, the intensity grows more slowly, approaching 100 per cent of what it would be if the disk were not present."

The judging committee chairman, François Arago arranged for an experiment to see if the predicted spot was there. In his report, he wrote:

". . . Poisson has deduced from the integrals reported by the author the singular result that the centre of the shadow of an opaque circular screen must, when the rays penetrate there at incidences which are only a little oblique, be just as illuminated as if the screen did not exist. The consequence has been submitted to the test of a direct experiment, and observation has perfectly confirmed the calculation."

So, with a prediction intended to destroy the wave theory, Poisson has succeeded in advancing it greatly.

1826-1849

The next step in spectral analysis is due to John Herschel (son of William) and W.H. Fox Talbot. They demonstrated, when a substance is heated and its light passed through a spectroscope, that each element gave off its own set of characteristic bright lines of color. In 1826, they wrote "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." The modern term for a spectrum of bright colored lines is "emission spectrum."

In 1832, David Brewster suggested that the dark lines in the solar spectrum might be created by selective absorption of the light given off by the sun in its atmosphere. The obvious question then became which chemical substance emitted which line or lines.

In 1833, William Miller demonstrated, when sunlight is passed through gases in the laboratory, that additional dark lines appeared in the sun’s spectrum. It was suggested that the dark lines are due to the presence of gases on the sun. Miller also was one of the first to take photographs of
In 1834, Fox Talbot studied lithium and strontium, both of which give a red flame when burned. He then wrote "the prism betrays between them the most marked distinction which can be imagined."

In 1840, John Herschel discovered that the Fraunhofer lines extended into the infrared, the spectral region his father had discovered 40 years prior.

In 1842, A. Edmond Becquerel, photographed the solar spectrum plus its extension into the ultraviolet.

In 1849, Jean Foucault, investigating the spectrum of an arc between two carbon electrodes, noticed a line similar to the D line of the solar spectrum. He attempted to superimpose the two spectra by passing the sun’s rays through the arc and then through the prism. This demonstrated that the lines were in the same place, since they superimposed on each other.

He noticed something odd about the behavior of the D line. When the sunlight was shut off, the D line appeared as a bright line in the arc spectrum. However, he wrote this: "... the line D appears darker than usual in the solar light ... Thus the arc presents us with a medium which emits the D rays on its own account, and which at the same time absorbs them when they come from another quarter."

Devoting his time to other work, he fails to follow up on this observation. It is left to Gustav Kirchhoff, ten years later, to make the definitive discovery on the relationship between the emission (bright-line) spectrum and the absorption (dark-line) spectrum

1849-1850

Up until this time, the only measurements of the speed of light was astronomically-based, yielding only the speed of light in a vacuum. There was no way to test the implications of Newton’s 150-year-old particle theory of light, since it required comparing the speed of light going from air to water. Léon Foucault and Hippolyte Fizeau, both in France, were working independently on measuring the speed of light and thus be able to shed some light on this problem. Fizeau is the first (in 1849) to measure the speed of light on the Earth’s surface, but Foucault (in 1850) is the first to be able to compare the two values needed to test Newton’s particle theory for light.

The data is unequivocal: light travels SLOWER in water than it does in air. Newton’s particle theory cannot be true, as Fresnel so well demonstrated in 1819.

Foucault and Fizeau (younger by only 4 days) worked together in the early 1840’s, but parted ways without anger. Their competition was a model of scientific honesty and integrity. In 1862, Foucault determined the speed of light to be 298,000 ± 500 km/sec.

1859 - 1862: Gustav Kirchhoff (a physicist) and Robert Bunsen (a chemist)

Here is a brief discussion of the Bunsen burner.

The relationship between emission & absorption spectra (1859).

Kirchhoff passed sunlight of moderate intensity through a flame containing lithium chloride and observed the following:
"One sees at the specific position [of the lithium line] a bright line on a dark background; for a greater intensity of incident sunlight, however, there appears at the same place a dark line, having exactly the same character as Fraunhofer’s lines."

Kirchhoff also used incandescent lime, which was known to give off a continuous spectrum. He passed the light from the lime through a sodium flame and then through a prism. In the exact position of the D line of the solar spectrum, there appeared a dark line.

In this manner, he was able to demonstrate that hot gases absorbed the same wavelengths of light they emitted. He knew then that sodium vapor must be present in the atmosphere of the sun, absorbing the D line from the white light coming from the incandescent surface of the sun.

He wrote:

"... the dark lines of the solar spectrum, which are not caused by the earth’s atmosphere, originate from the presence of those substances in the glowing solar atmosphere, which cause bright lines at the same place in the spectrum of a flame."

However, with the lithium flame, a new line appeared between the B and C lines (remember these were labeled by Fraunhofer) that could not be associated with any of the known dark lines. Hence, no lithium was present in the sun’s atmosphere.

**Chemical Analysis by Producing Spectra**

Kirchhoff and Bunsen made a systematic survey involving many substances:

"We have compared the spectra produced by the above-mentioned chlorine compounds with those obtained when the bromides, iodides, oxides, sulphates, and carbonates of the metals are brought into the flames of sulphur, carbon dioxide, aqueous alcohol, illuminating gas, carbon monoxide, hydrogen, and detonating gas.

In this time-consuming, extensive research, which need not be presented here in detail, it came out that the variety of the compounds in which the metals were used, the differences in the chemical processes of the flames, and the great difference between their temperatures had no influence on the position of the spectral lines corresponding to the individual metals."

That is, every metal, no matter what compound it was in, gave the same spectrum.

Kirchhoff and Bunsen, in late 1860 discovered the element cesium by spectral analysis and in early 1861 they discovered rubidium in the same matter. Both are named for the color of the most prominent line in the spectrum (Latin *rubidus*, deepest red; *caesius*, sky blue)

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The story does not end here. Go to part 2.

**Brief Commentary before moving on**

Please do not get the impression that the above story is the complete story of spectral research or of the nature of light. I am only telling pieces of it as I build to Bohr’s explanation of the hydrogen spectra in 1913. For example, I am totally skipping over the discovery of band spectra. This is an extremely important type of spectra, but it does not fit into the story I am telling.
Line spectra, which I have been discussing above, were well-known to the scientific community of the 1860s. About the same time as K&B, a different type of spectra (today called 'band' spectra) was discovered. Of course, discussion arose as to how the two were different. By 1875, the correct answer was in hand. It simply was that line spectra are produced by free elements (atoms) and band spectra by compounds (molecules).

However, band spectra do not play a role in the direction I am going, so this is the last you’ll hear of them from me.

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