# The Story of Spectroscopy

Isaac Newton publishes Opticks

1704

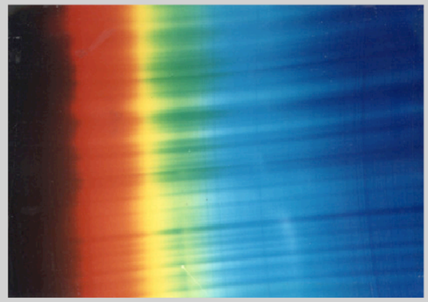
States that white light is made up of colors

Explains his Corpuscular theory of light

(light is made up of tiny packets)

Newton is the first to break light up into a spectrum. He is convinced through experimentation and observation.

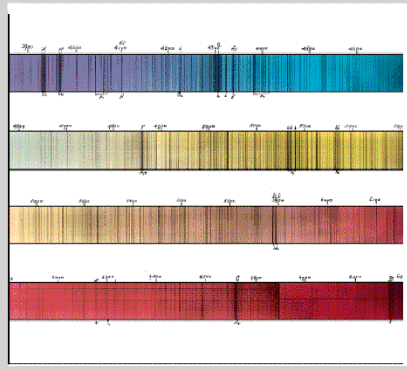
**William Hyde Wollaston**
**(1766-1828)**



**In 1802 Wollaston passes sunlight through a prisim & finds dark lines in the spectrum**

He was trained as a physician but only practiced 7 years. After that he did research. He contributed to many fields - chemistry, physics, botany, crystallography, optics, astronomy and mineralogy. In 1802 he discovered that the sun’s spectrum was not a continuous spectrum but was broken by many dark lines. He didn’t follow up on this discovery though.

Joseph von Fraunhofer
(1787-1826)



**In 1813 Fraunhofer independently rediscovers Wollaston's dark lines in the solar spectrum. Finds about 500 lines & labels the most prominent with letters.**

Joseph von Fraunhofer was the youngest of a poor glass grinder's ten children and was orphaned at the age of 11. He did not receive the luxury of a formal education, but was apprenticed to a Munich mirror maker and lens grinder. In 1801, an accident occurred that almost cost von Fraunhofer his life, but ultimately worked out to his great benefit. The building that he was working in collapsed and buried him alive for several hours. His dramatic rescue caught the attention of the court prince, as well as Joseph Utzschneider, a politician with an interest in optics. Von Fraunhofer's royal patron bestowed a fair sum of money upon him, which he used to buy himself out of his apprenticeship and to purchase a glass cutting and polishing machine. Utzschneider, however, gave friendship and books to the boy, which fueled his self-education.

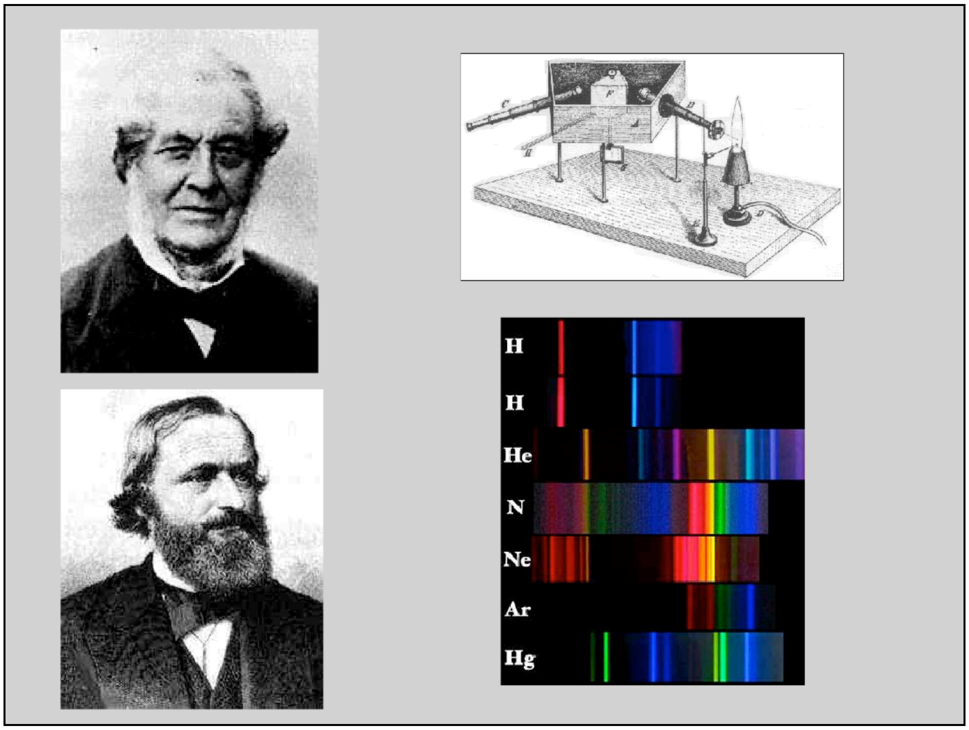
Employed at a Munich workshop that made scientific instruments, which was partially owned by Utzschneider, von Fraunhofer continued to develop his skills in optics. He become a very good lens maker.

By 1809, von Fraunhofer was made partner of the firm, assuming many of the business responsibilities. His designs continue to be used in microscopes and other fine optics.

In 1813, he independently rediscovered William Hyde Wollaston's dark lines in the solar spectrum, which are now known as Fraunhofer lines. He described a great number of the 500 or so lines he could see using self-designed instruments, labeling those most prominent with letters, a form of nomenclature that is still in favor. Fraunhofer lines would eventually be used to reveal the chemical composition of the sun's atmosphere.

Von Fraunhofer is also renowned for building the first diffraction grating, made up of 260 close parallel wires, in 1821. The rudimentary gratings were soon upgraded, possessing up to 10,000 parallel lines per inch. Von Fraunhofer was well versed in the mathematical wave theory of light and used the gratings to measure the wavelengths of specific colors and the dark lines in the solar spectrum. He also used them to develop the laws of diffraction.

The once uneducated apprentice advanced far from what might be expected from his humble beginnings. Von Fraunhofer was honored with membership to the Bavarian Academy of Sciences, given an honorary doctorate from the University of Erlangen, and is considered founder of the German optical industry. He taught at the University of Bavaria and was knighted in 1824. Von Fraunhofer may have achieved even greater heights if he had lived a longer life. However, the self made man contracted tuberculosis and died prematurely in 1826 at 39 years old.




Bunsen was a great teacher and his lecture courses were famous. He continued to research until he was 80. He admitted that he never found time to marry. Actually a better reason may be that he smelled terrible because of all the chemicals that he was working with. Emil Fischer's wife said of him: "First I would like to wash Bunsen and then I would like to kiss him because he is such a charming man."

Bunsen devoted much of his career to chemistry and organic and inorganic compounds. During this work he lost the sight of an eye and nearly died of arsenic poisoning. This convinced him to abandon that research.

With his fellow professor Kirchhoff he then moved on to spectroscopy.

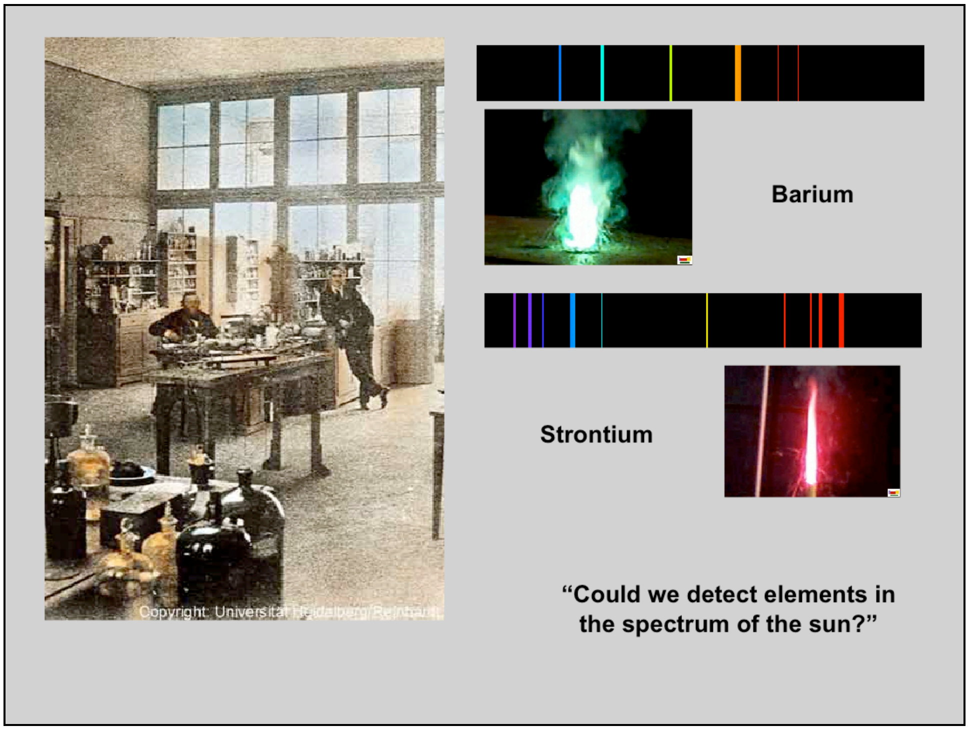
They work hard to catalog spectra for all the known elements

Gustav Kirchhoff (left) and Robert Bunsen.

**In the 1850s & 1860s they experiment with "Flame Tests" of the elements. Each element tested burns with its own color.**

**Determined Fraunhofer lines are caused by different chemical elements.**

Gustav Kirchhoff and Robert Bunsen, working together at Heidelberg studied spectra of elements during the 1850s and 1860s. (Bunsen invented the Bunsen burner) They determined that the dark Fraunhofer lines were caused by elements.

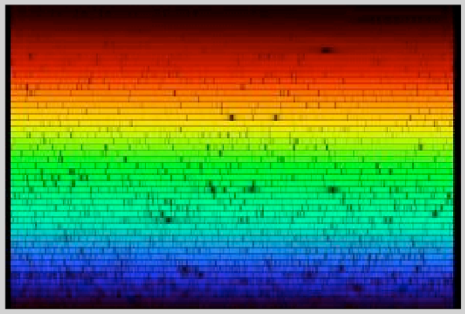



One evening they saw from the window of their lab in Heidelberg a fire raging in the port city of Mannheim 15 km to the west.

Using their spectroscope, they detected the lines of barium and strontium in the flames.

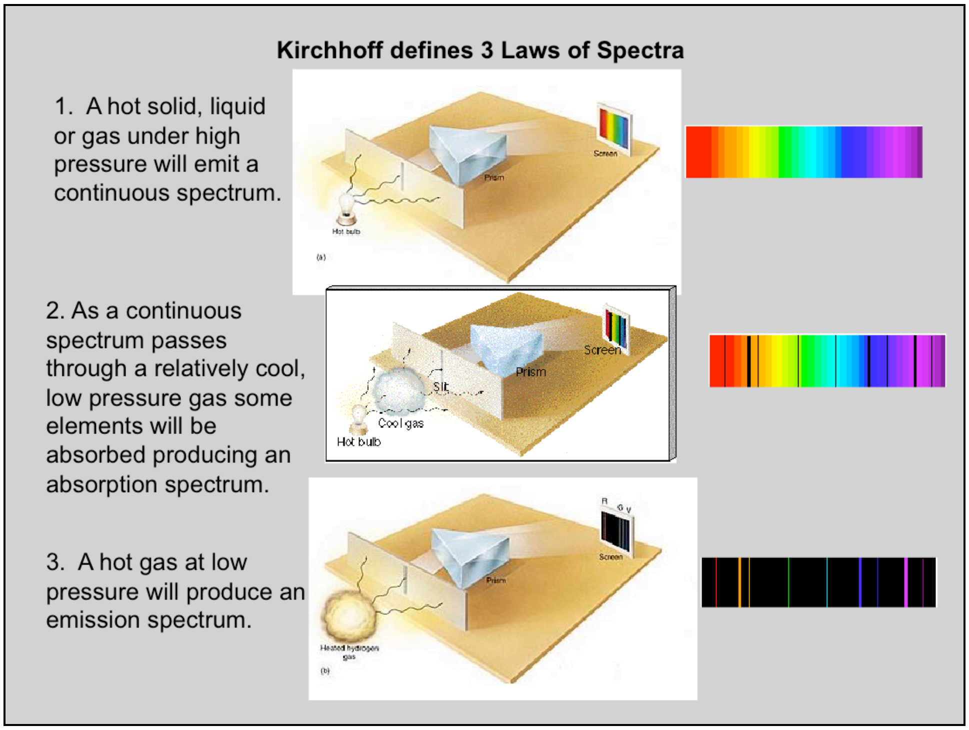
This set Bunsen to wondering whether they might be able to detect chemical elements in the spectrum of the sun.

**By 1861 Kirchhoff had identified 9 elements in the Sun's spectrum!**



**Sodium, Calcium, Magnesium, Iron, Chromium, Nickel, Barium, Copper, Zinc**

They were successful and by 1861 had discovered the elements sodium, calcium, magnesium, iron, chromium, nickel, barium, copper and zinc in the sun.

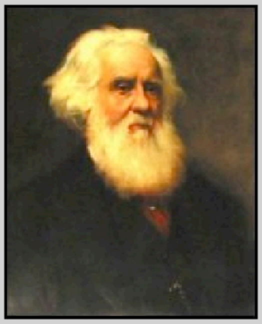


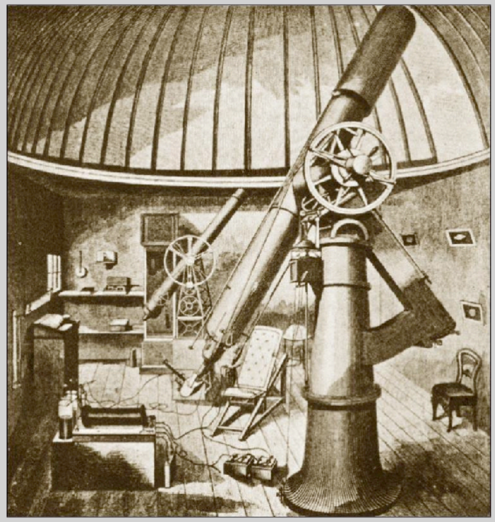

Kirchhoff developed 3 laws related to spectra.

1. Any object (solid, liquid, or gas) that is under high pressure will produce a continuous spectrum. No breaks.

2. If the continuous spectrum of an object is passed through a low pressure gas, some elements will be absorbed by the gas producing holes in the spectrum, seen as dark lines.

3. A gas under low pressure will emit only lines of color – an emission spectrum.





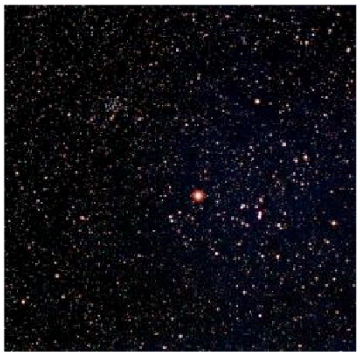
*"This news came to me like the coming upon a spring of water in a dry and thirsty land"*

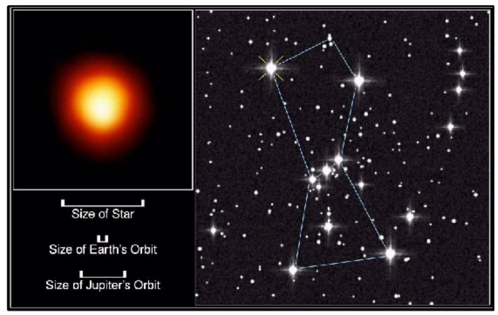
In England, William Huggins, a wealthy amateur astronomer, heard about Kirchhoff & Bunsen's work with elements in spectra. He had a private observatory in London.

He said " This news came to me like the coming upon a spring of water in a dry and thirsty land."

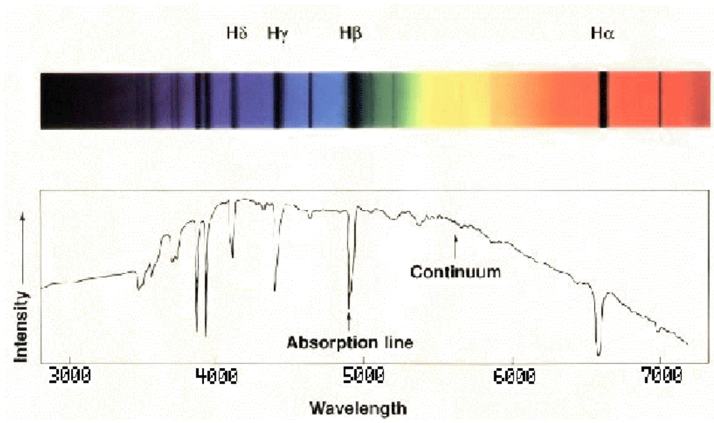
**In the 1860s Sir William Huggins uses a spectroscope on the stars Aldebaran and Betelgeuse.**

**He identifies iron, sodium, calcium, magnesium and bismuth.**






Huggins fitted a spectroscope to the telescope in his observatory. By carefully studying each spectrum until he could make sense of their many overlapping lines, he succeeded in identifying iron, sodium, calcium, magnesium and bismuth in the spectra of the bright stars Aldebaran and Betelgeuse.



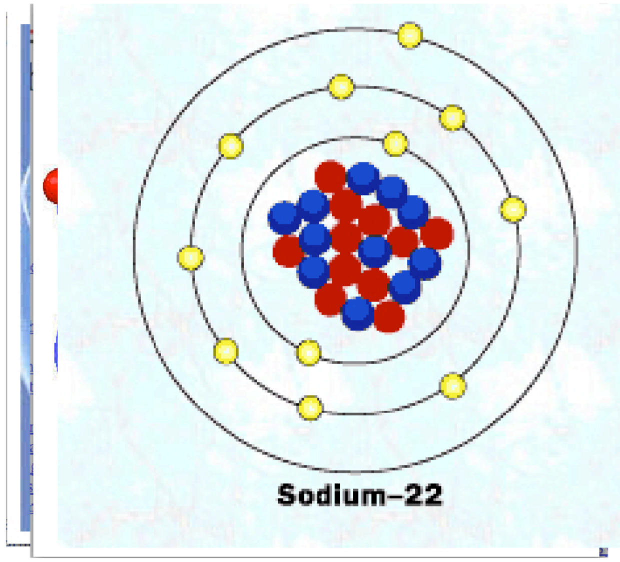

An absorption spectrum is produced when a continuum passes through "cooler" gas. Photons of the appropriate energies are absorbed by the atoms in the gas. Although the photons may be re-emitted, they are effectively removed from the beam of light, resulting in a dark or *absorption* feature. The atmospheres of stars act as a cooler blanket around the hotter interior of a star so that typical stellar spectra are absorption spectra.

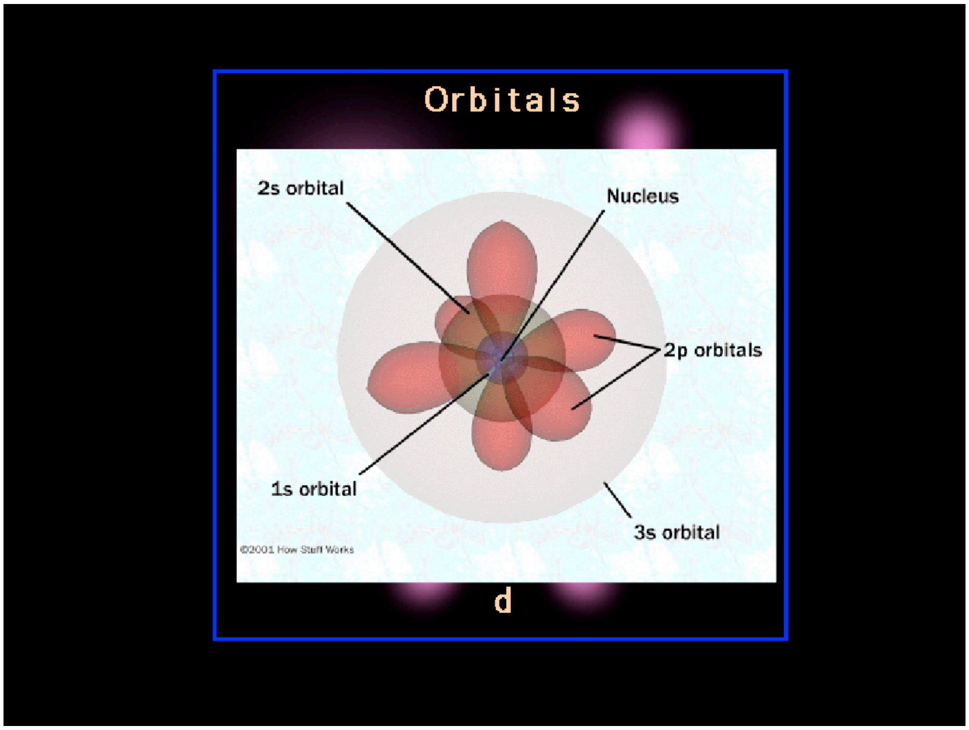
Break for stations

1. Flame Tests;  2. Glow slate;  3. Gas Tubes;  4. Sky

Then demo with dish of colored flame (element & ethyl alcohol)

# The Atom






Bohr's model of the atom is important because it introduced the concept of the quantum in explaining atomic properties. However, Bohr's model ultimately needed revision because it failed to explain the nature of atoms more complicated than hydrogen. It took roughly another decade before a new more complete atomic theory was developed - the modern atomic theory.

Traditional (classical) physics had assumed that particles were particles and waves were waves and thats that. However, de Broglie suggested that particles could sometimes behave as waves and waves could sometimes behave as particles - the wave/particle duality of nature.

Werner Heisenberg elucidated the Uncertainty Principle (1923)

Classical physics had always assumed that precise location and velocity of objects was always possible. Heisenberg, however discovered that this was not necessarily the case at the atomic level. In particular, he stated that the act of observation interfered with the location and velocity of small particles such as electrons. This is the case because observation requires light and light has momentum. When light bounces off an electron momentum exchange can occur between light and the electron which means the electrons location and velocity have been altered by the act of measurement. This scenerio has important implications to what we can measure at the atomic level.

Erwin Schrodinger took the ideas developed by de Broglie, Heisenberg and others and put them together in a single equation that is named after him. Solving this equation can in principle predict the properties and reactivities of all atoms and molecules.

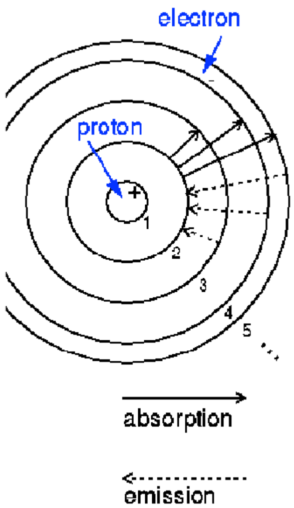
I)

**Energies are quantized:**

Atoms and molecules cannot have any energy but only certain energies. This means that energies are "quantized".

II)

**The orbitals, associated with each energy, determine where the electrons are located.**




**Bohr Model of Hydrogen Atom**

Ground State: Electron is in lowest energy level.

Absorption Spectrum: Electron absorbs light photons and jumps up to an excited state of higher energy .

Emission Spectrum: Electron emits light photon as it jumps down to a state of lower energy .

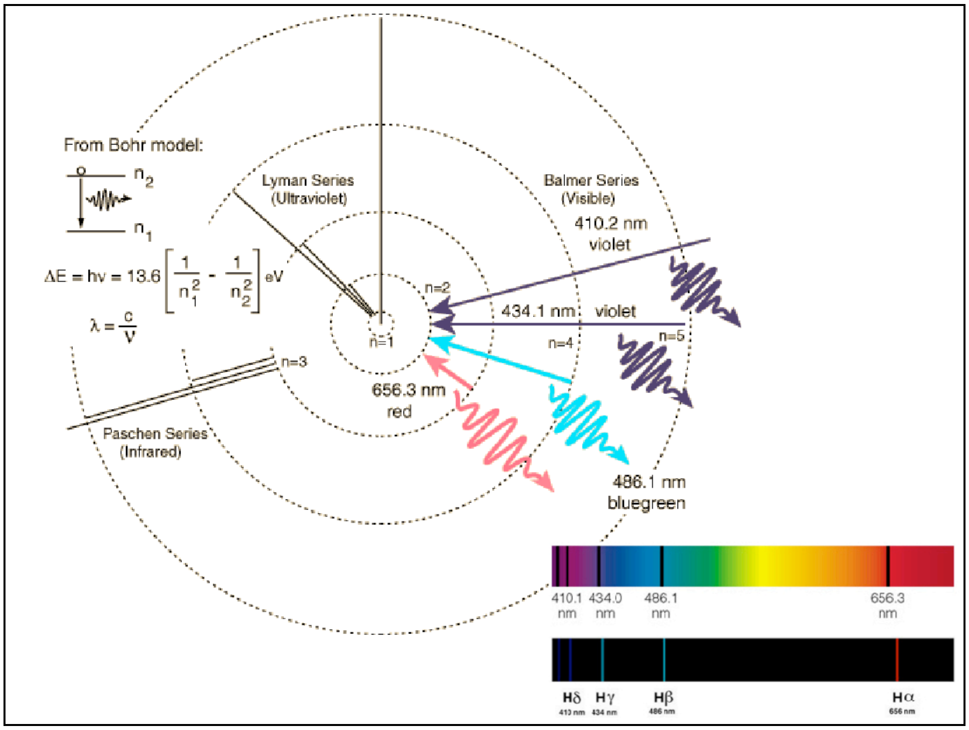
In 1913 Niels Bohr came to work in the laboratory of Ernest Rutherford. Rutherford, who had a few years earlier, discovered the planetary model of the atom asked Bohr to work on it because there were some problems with the model: According to the physics of the time, Rutherford's planetary atom should have an extremely short lifetime. Bohr thought about the problem and knew of the emission spectrum of hydrogen. He quickly realized that the two problems were connected and after some thought came up with the Bohr model of the atom. Bohr's model of the atom revolutionized atomic physics.

The Bohr model consists of four principles:

1)Electrons assume only certain orbits around the nucleus. These orbits are stable and called "stationary" orbits.2)Each orbit has an energy associated with it. For example the orbit closest to the nucleus has an energy E1, the next closest E2 and so on.3)Light is emitted when an electron jumps from a higher orbit to a lower orbit and absorbed when it jumps from a lower to higher orbit.4)The energy and frequency of light emitted or absorbed is given by the difference between the two orbit energies, e.g.,

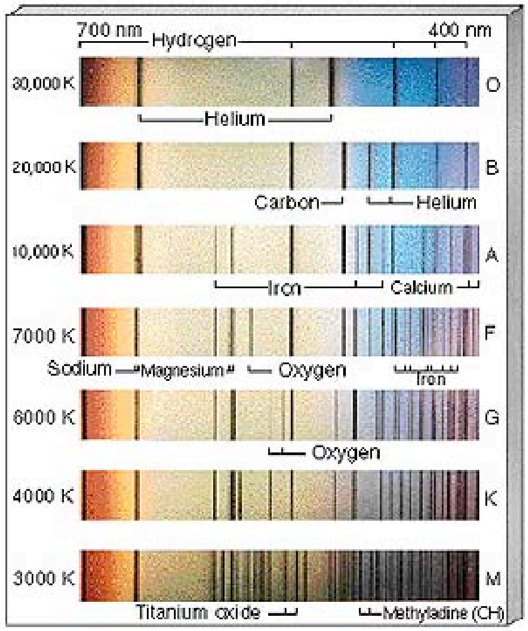
With these conditions Bohr was able to explain the stability of atoms as well as the emission spectrum of hydrogen. According to Bohr's model only certain orbits were allowed which means only certain energies are possible. These energies naturally lead to the explanation of the hydrogen atom spectrum:

Bohr's model was so successful that he immediately received world-wide fame. Unfortunately, Bohr's model worked only for hydrogen. Thus the final atomic model was yet to be developed.




Different names (lyman, balmer, etc) are named for the energy level where the electron is either falling back to (emission) or moving from (absorption)

We can only see Balmer Series = visible light




**Very Hot stars**

***See absorption lines from ions**

*** Too hot for nucelus to hold unto electrons**

**Hot stars**

***Only see absorption lines from atoms**

***Bonds between molecules broken**

**Cooler stars**

**•Can see absorption lines from molecules**

***Not hot enough to break bonds**

The temperature of the stellar photosphere determines the rate and severity of collisions between molecules, atoms and ions which in turn determines:

*1. the molecular equilibrium* - if the star is too hot, fragile molecular bonds will be broken apart. Most molecules such as TiO are seen only in spectra of the coolest stars ( T = 3000 -- 4000K). Strong molecules such as CH and CN can be seen in somewhat hotter stars like the sun.

*2. the ionization equilibrium* - the hotter the temperature, the higher the ionization state of the atoms in the stellar atmosphere will be. Atoms are ionized (or partially ionized) when they lose or gain an electron. In cool stars most atoms will be neutral. At higher Temperature, easily ionized atoms such as Na, Ca, etc, will be ionized; above T = 10,000K hydrogen becomes ionized and above about 15,000K helium becomes ionized.

*3. the number of atoms in excited states*. At low T, almost no H atoms are in the n=2 orbit, capable of absorbing "Balmer" photons, but as T increases the n=2 population increases and we see the hydrogen features, reaching a maximum in stars with T = 10,000.

O >33,000

B 10,500 – 30,000

A 7500 – 10.000

F 6000 – 7000

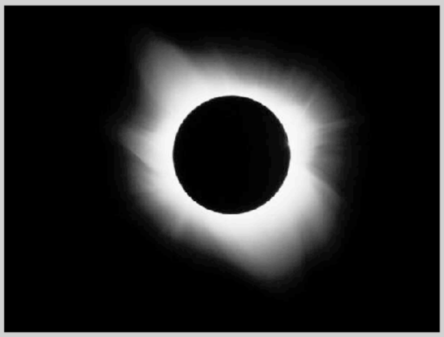
G 5500 – 7000

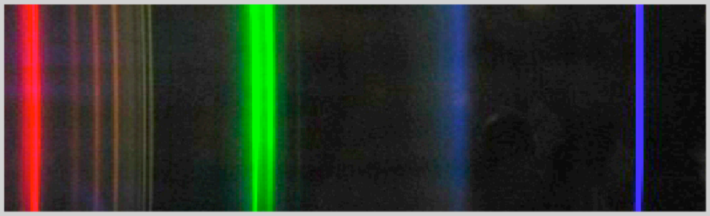
K 4000 – 5000

M 2600 - 3500

**By 1868 the spectra of all known elements is known**

**During the 1868 solar eclipse, Norman Lockyer & Pierre Jansen found a unknown pattern of lines in the solar spectrum.**





**Lockyer names the new element "Helium" after helios, the Greek word for the Sun. Helium wasn't found on Earth until 1895, 27 years later.**

In 1868 the French astronomer Pierre Janssen first detected helium as an unknown yellow spectral line signature in light from a solar eclipse.

Since then large reserves of helium have been found in the natural gas fields of the United States, who is by far the largest supplier of the gas.

On 26 March 1895 British chemist William Ramsay isolated helium on Earth by treating the mineral cleveite with mineral acids. Ramsay was looking for argon but, after separating nitrogen and oxygen from the gas liberated by sulfuric acid, noticed a bright-yellow line that matched the $D_3$ line observed in the spectrum of the Sun.[14] These samples were identified as helium by Lockyer and British physicist William Crookes.

It was independently isolated from cleveite the same year by chemists Per Teodor Cleve and Abraham Langlet in Uppsala, Sweden, who collected enough of the gas to accurately determine its atomic weight.[15]

Helium was also isolated by the American geochemist William Francis Hillebrand prior to Ramsay's discovery when he noticed unusual spectral lines while testing a sample of the mineral uraninite. Hillebrand, however, attributed the lines to nitrogen. His letter of congratulations to Ramsay offers an interesting case of discovery and near-discovery in science.