

Atomic Spectroscopy

Johannes could still remember when he saw his first rainbow. It was at his uncle's farm just north of his hometown of Halmstad, Sweden. As he studied the arch of brilliant colors that stretched over the fields of grazing cattle on that misty morning, he wondered how such a thing of beauty could exist. Now he was a professor at the prestigious University of Lund, and he was still studying rainbows.

But in the laboratory, Johannes Rydberg was looking at a very different rainbow than what he had witnessed as a boy. He was looking at the light given off from a tube filled with hydrogen gas, and he observed this light as it passed through a prism and was *refracted*, or bent. In 1855, Heinrich Geissler invented a gas discharge tube that was similar to the tubes used in today's "neon" signs. A glass tube is evacuated under vacuum, then gas is pumped in at low pressure. Electrodes are placed at the ends of the tube. When an electrical voltage is applied, the gas in the tube glows with a characteristic color. In the late 1800's, gas discharge tubes were manufactured solely for the purpose of research so that people like J. R. Rydberg and J. J. Balmer could study their physical phenomena. When the light from these tubes is refracted, the result is a *line spectrum*, a series of thin lines of different colors that are separated by darkness. In contrast, when white light, such as that given off by the sun or an incandescent bulb, is passed through a medium that refracts the beam, the human eye sees a *continuous spectrum* of colors, like a rainbow. (See Tro, pp 277-302.)

What is happening inside a gas discharge tube? The energy supplied by the voltage causes the electrons in the atoms of the gas to become "excited"; that is, they jump to a higher energy level. The excited electrons then fall to a lower energy level, releasing a photon of energy. Light can be related to energy by the following expression:

$$E = \frac{hc}{\lambda} \quad \text{Eq. 1}$$

where E = energy (J), h = Planck's constant (6.63×10^{-34} J•s), c = the speed of light (3.00×10^8 m/s) and λ = wavelength (m). Electrons fall only between very specific energy levels for a given element. Therefore, only very specific wavelengths are observed, resulting in the appearance of single lines in the spectrum of a single element.

Both Rydberg and Balmer developed an equation that relates the electron transitions that take place in a hydrogen discharge tube to the wavelengths observed in the line spectrum:

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{Eq. 2}$$

where R_H = the Rydberg constant, and n_1 and n_2 are whole numbers (integers). The energy levels of the emission series for the hydrogen atom are shown in Figure 1 on the next page. The transitions of the Balmer series fall in the visible range of wavelengths. Thus, for the visible spectrum of hydrogen, n_1 always equals 2. You will deduce the Rydberg constant, R_H , by measuring the wavelengths in the hydrogen spectrum.

To measure the wavelengths of the lines, you will use a *spectroscope*. A spectroscopy contains a diffraction grating that separates light into its components, like a prism does. Light that enters the spectroscopy through a small slit bends around opaque areas

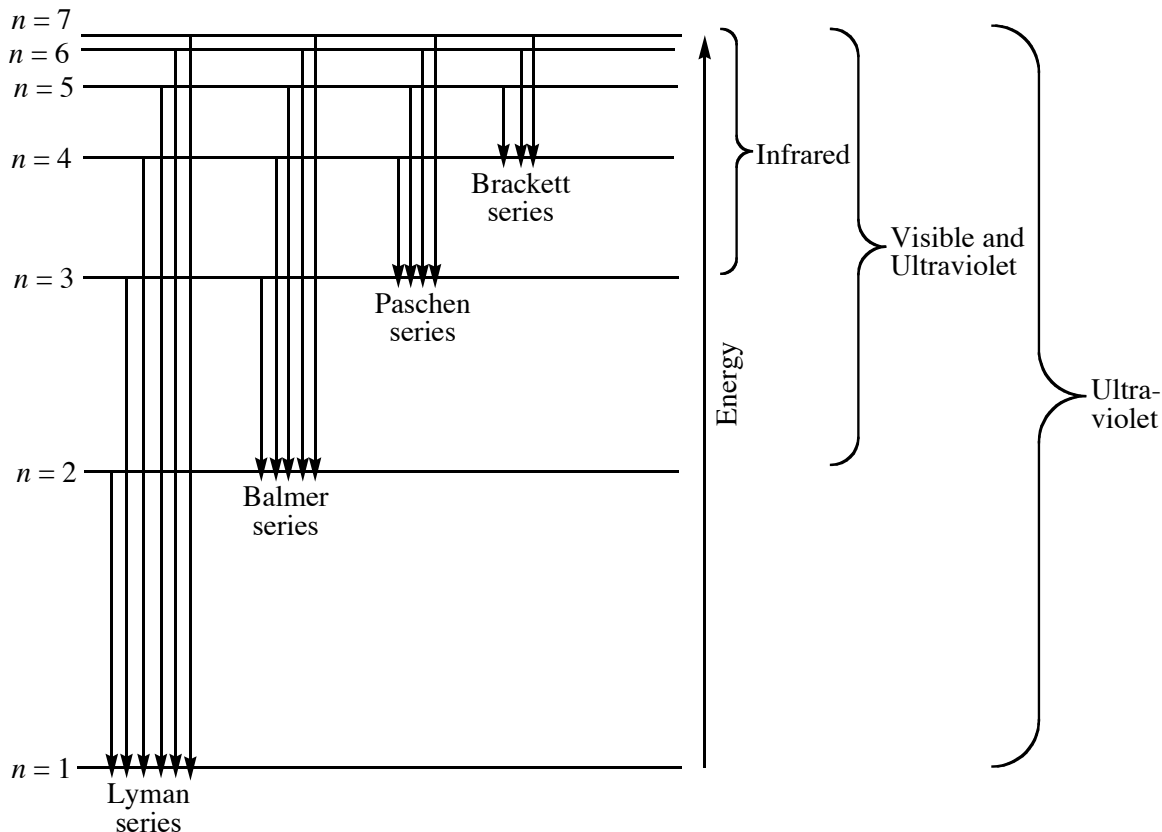


Figure 1. Electron transitions in the hydrogen atom

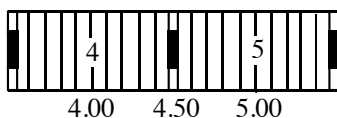
of the diffraction grating. The amount of bending which occurs depends in part on the wavelength of the light. The resulting spectrum is superimposed on a scale mounted inside the spectroscope. Before measuring the hydrogen spectrum, the spectroscope will first be calibrated using a mercury vapor lamp so that the relationship between the scale position and the wavelength can be determined.

In this experiment, you will also observe the line spectra of elements other than hydrogen with the spectroscope. In these cases, the light being studied will come from placing a solution that contains the ionic form of the element into a flame.

Procedure (you do not need to outline this procedure)

Using the spectroscope

Point the slit of the spectroscope toward the light source while looking through the square at the opposite end, which contains the diffraction grating. On the right hand side, you will see a scale with numbers and divisions.



Underneath the scale, you should see several brightly colored lines. Write down the location of each line to the nearest hundredth of a division (three significant figures).

Calibrating the spectroscope

Your instructor will insert the mercury discharge tube into the power source for you. View the tube through your spectroscope. You should see four colored lines. Note the locations and colors of the four lines in your notebook.

Measuring the atomic spectrum of hydrogen

Your instructor will insert the hydrogen discharge tube into the power source for you. Write the locations and colors of the lines that you see through the spectroscope in your notebook.

Observing the atomic spectra of Li^+ , Ca^{2+} , and Sr^{2+}

Work with a partner. Go to one of the flame test stations. At the station, you will find a Bunsen burner, a solution that contains a metal ion, wooden splints, wire loops and black paper taped to the wall. Light the Bunsen burner (if it is not already lit). Pull one of the wooden splints or wire loops out of the solution, then place the wet end into the flame near the tip of the blue cone. Your partner should observe the flame through his or her spectroscope while you hold the splint or loop in the flame. When your partner has been able to successfully observe the line spectrum for the ion, switch positions. It will be easiest to see the spectrum against the black backdrop. *Sketch* the line spectrum that you observe in your notebook. You will not be able to measure the lines accurately for these flame tests. Move on to each of the other two stations.

Calculations

The calibration data for the spectroscope is used in conjunction with wavelength values from the literature for the mercury line spectrum. The wavelengths of the lines found in the mercury spectrum are:

405 nm (violet)
436 nm (blue)
546 nm (green)
579 nm (yellow)

The relationship between the scale position and the wavelength is linear. Plotting the scale position as a function of wavelength will allow for the determination of the slope and y-intercept of the line. These values can then be used to calculate the wavelengths that correspond to the scale positions measured for the hydrogen spectrum. An Excel spreadsheet template can be found on the laboratory computers that will construct a calibration plot and find the hydrogen wavelengths using your data. Simply type the scale positions that you recorded into the appropriate columns found on **Sheet1** of the template.

To find the Rydberg constant, you need to match up the wavelengths from the hydrogen spectrum with the three lowest energy transitions:

$n_2 = 3$ to $n_1 = 2$
 $n_2 = 4$ to $n_1 = 2$
 $n_2 = 5$ to $n_1 = 2$

Remember that $E = hc/\lambda$. Type the wavelengths into the appropriate column found on Sheet2 of the template (click on the tab at the bottom of the screen). Rearranging **Eq. 2**, we have:

$$\frac{1}{\lambda} = -R_H \left[\frac{1}{n_2} \right] + \left[\frac{R_H}{n_1} \right]$$

A plot of $1/\lambda$ as a function of $1/(n_2)^2$ will result in a straight line with a slope equal to $-R_H$. The actual value for R_H can be found in your textbook, Tro, on page 289.

Print out two copies of the spreadsheets, and hand one set in to your TA along with the notebook pages that contain your sketches of the atomic spectra for lithium, calcium and strontium.

Note: If you do not complete this experiment, two points will be deducted from your third performance grade.