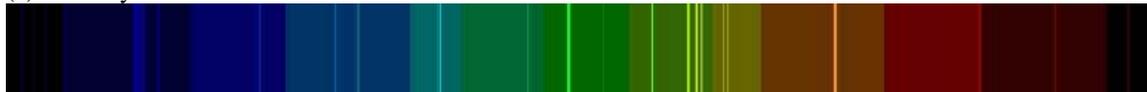


Emission Line Spectra and the Rydberg Constant

(a) Mercury



(b) Helium



(c) Hydrogen



Figure 1

Visible line spectra for (a) helium, (b) hydrogen and (c) neon.

<http://astro.u-strasbg.fr/~koppen/discharge/>

Introduction:

In spectroscopic analysis, two types of emission spectra are observed: continuous spectra and line or discrete spectra. The spectrum of visible light from an incandescent source is a **continuous spectrum** or band of merging colors, and contains all the wavelengths of the visible spectrum. However, when the light from a gas discharge tube (e.g., mercury or helium) is observed through a spectroscope, only a few colors or wavelengths are visible. The colored images of the spectroscope slit appear as bright lines separated by dark regions: hence the name **line** or **discrete spectra**.

Each gas has a characteristic spectrum. Thus, spectroscopy provides a method of element identification. The discrete lines of a given spectrum arise from electron transitions between energy levels that depend on the structure of that specific atom. The line spectrum of hydrogen was explained by Bohr's theory of the hydrogen atom. However, before this, the line spectrum of hydrogen was explained by an empirical formula involving the Rydberg constant. In this experiment, line spectra will be observed and the relationship of the empirical Rydberg constant to the theoretical quantities of the Bohr theory will be investigated. The Bohr model fails when applied to atoms more complicated than hydrogen. In this lab we will also explore the nature of the electron energy levels in Helium. To do this, we will determine the wavelength of the spectral lines of Mercury (for calibration), Hydrogen, and Helium using two different methods. The first (part I) will involve the use of a spectroscope and diffraction grating. The second method will use only the vernier spectrometer. Once you have determined the wavelengths emitted by Hydrogen and Helium sources, you will fit your data to the Rydberg equation and experimentally determine the Rydberg constant. Along the way you will also determine the upper and lower

Theory:

Hot gases within the spectrum tubes you will use produce discrete line spectra because the gases are not ionized—the electrons are still bound in the atoms. Collisions between atoms, caused by the oscillating potential difference, will excite atoms to higher energy levels. When they de-excite, photons with specific wavelengths are emitted.

The characteristic color of light from a gas discharge tube is indicative of the most intense spectral line(s) in the visible region. For example, light from a hydrogen discharge tube has a characteristic red glow resulting from an intense emission line with a wavelength of 656nm. When table salt (sodium chloride) is vaporized in a flame, it appears yellow because of intense emission lines in the region of the sodium spectrum.

The hydrogen spectrum is of particular theoretical interest because hydrogen, having only one proton and one electron, is the simplest of all atoms. Niels Bohr (1885 – 1962) developed a theory for the hydrogen atom that explains the spectral lines as resulting from electron transitions between energy levels or discrete electron orbits (Figure 2), with the wavelengths of the spectral lines being given by the theoretical equation

$$\lambda = \frac{hc}{\Delta E}$$

The Hydrogen Atom

The wavelength of each emission line depends on the difference between the energy that an electron starts and ends at as it changes from one energy level to another. Each energy level is described by the “principal quantum number” of the electron, n . The wavelength of emitted light obeys the formula

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{Eq. 1}$$

where R is the **Rydberg constant**, n_f is the quantum number of the final energy level of the electron, and n_i is the quantum number of the initial energy level of the electron. Note that the Lyman series is associated with a final principal quantum number of 1, the Balmer series with 2, and the Paschen series with 3. Only one of these series produces emission lines in the visible spectrum.

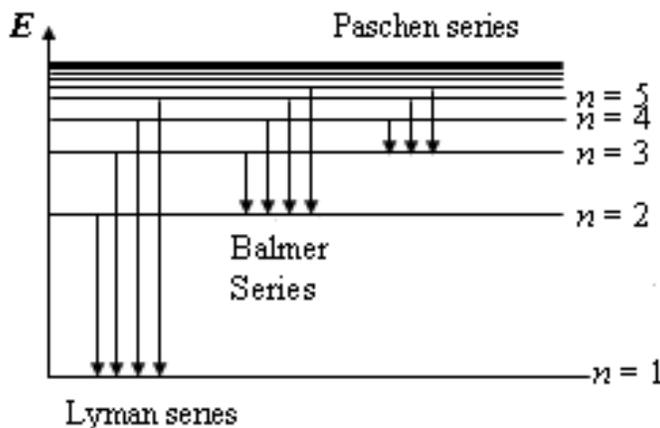


Figure 2
The energy-level transitions for the hydrogen atom.

The Helium Atom

Because the helium atom contains two electrons, matters become more complicated. In order to understand the energy transitions in the helium atom, one must take into account the spins of the two electrons. If the spins are aligned (parallel), the electrons in the helium atom will obey the para-Helium diagram below. If they are opposed, they will obey the ortho-Helium diagram below. Furthermore, one must also take into account the electron's angular momentum quantum number. According to convention, $s = 0$, $p = 1$, $d = 2$, and $f = 3$. In the energy levels displayed below, the number on the left refers to the principal quantum number, n , while the letter on the right refers to the angular momentum quantum number, l . This quantum number for any electron can range from 0 to $n-1$. For example, the $3s$ state on the para-Helium diagram refers to an electron with $n = 3$ and $l = 0$ in a helium atom where the spins of the two electrons are parallel. It is important to note that only one of the two electrons can ever be excited, while the other will be in the lowest, $1s$, state. If both electrons were excited, the total energy would surpass the ionization energy of the helium atom. The numbers next to the lines between energy levels indicate the wavelength in nanometers of photons emitted during transitions between those states.

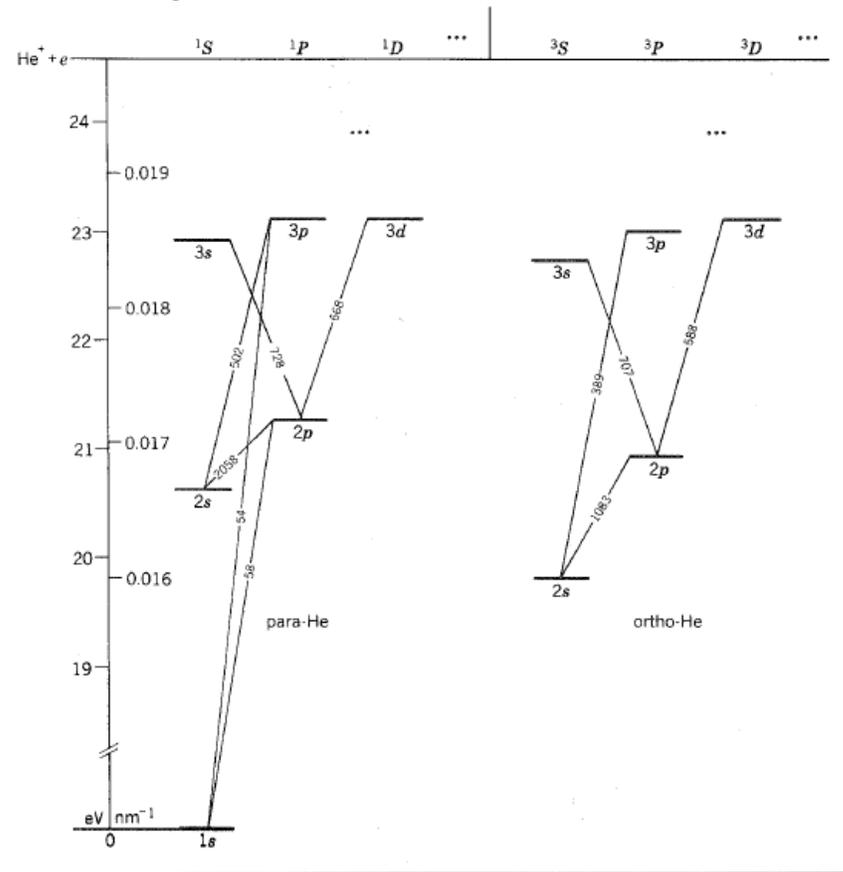


Figure 2

Selected energy-level transitions in the Helium atom (*Introduction to the Structure of Matter*. John Brehm and William Mullin. John Wiley and Sons, 1989.)

Experiment Part I - Using the Spectrometer

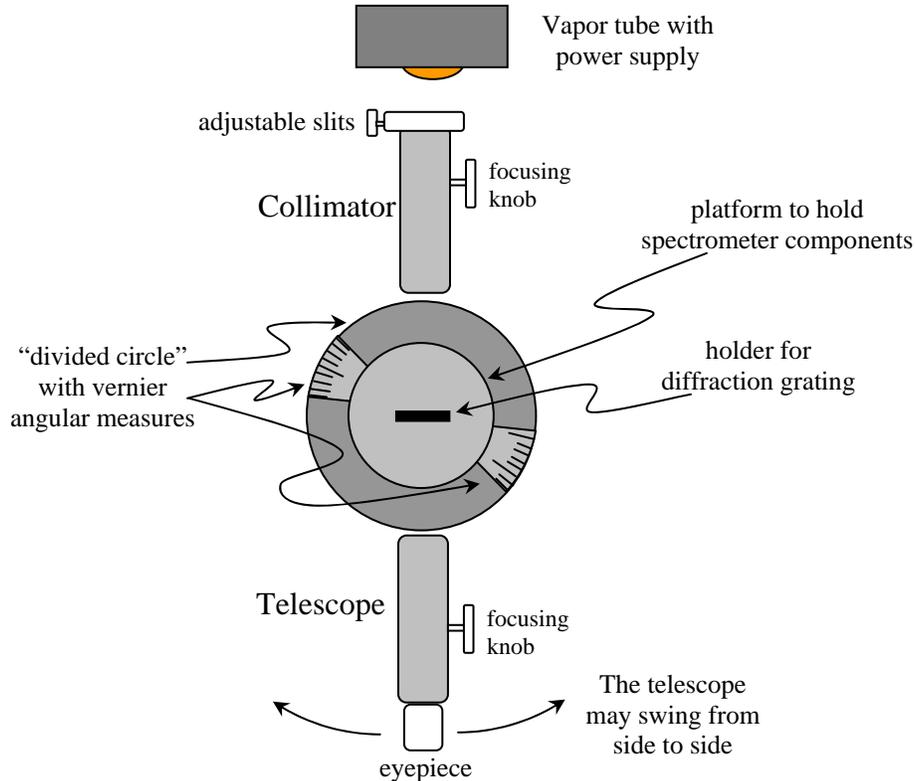


Figure 3
Spectrometer and Vapor Tube

Equipment:

- Spectrometer
- Diffraction Grating
- Spectrum Tube Power Supply
- Hydrogen Spectrum Tube
- Mercury or Helium Spectrum Tube
- Two Unknown Spectral Tubes
- Red reading Lights

Caution: The spectrum tube power supplies operate at 5000V, 10mA. This voltage can produce a dangerous and nasty shock. You must follow these guidelines:

- A. Do not EVER stick your fingers in the sockets under any circumstances.
- B. Do not insert, remove, or adjust the spectral tubes while the power supply is turned on.

- C. Turn the power supplies off and unplug them as soon as you are finished making observations.
- D. Do not keep liquids anywhere near the power supply. Drinks are not allowed in this lab.
- E. Do not operate the power supplies with wet hands.

Procedure:

1. Set up spectrometer with the slit facing mercury vapor tube in its power supply. With no diffraction grating in place, line up the telescope, collimator, and spectral tube in a straight line, as shown in Figure 3. Insert the eyepiece in the telescope and focus on the slit. Narrow the slit so that only the discharge tube can be seen. Adjust the angle measure so that it reads zero when you are looking straight through the apparatus, and increases as you rotate the telescope.
2. Carefully mount the diffraction grating on the platform, at right angles to the collimator axis. Before you insert it, make sure that you can “eyeball” the spectral lines – you should see different color parallel images of the tube when you look through the grating, and off to the side (Figure 4). If not, you will need to rotate the grating 90° . Raise or lower the grating support so that the entire slit can be seen in the telescope.

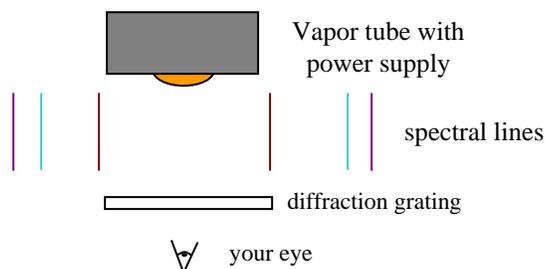


Figure 4 As you look through the diffraction grating at the vapor tube, spectral lines appear “in mid air” off to the sides. To see them, look through the grating at an angle. You will not see them if you look directly at the tube!

3. With the telescope, scan from left to right until you can see the first order spectrum lines. Note that if you scan past the first order, the colors repeat. These are the second order lines.
4. Measure the angle, 2θ , between the same color lines right and left, for each of the first order spectral lines. Read the angular vernier scale carefully to provide the maximum number of significant figures in your measurement. Record the vernier reading. Calculate θ , the angular displacement from the vertical for each line. Repeat for at least one line of the second order spectrum.

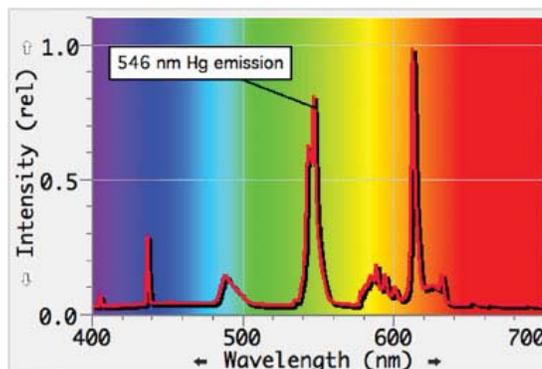
5. From your observations, calculate the wavelength of the spectral line using the equation

$$m\lambda = d \sin \theta \quad \text{Eq. 2}$$

where $m = 1$ for the first order spectra, and $m = 2$ for the second order. You'll need to calculate the spacing between lines on the diffraction grating, which has 600 lines per mm. The wavelengths for the brightest mercury spectral lines are: 435.835 nm (blue), 546.074 nm (green), and a pair at 576.959 nm and 579.065 nm (yellow-orange).

6. Replace the mercury light source with a hydrogen vapor tube and measure the angles for each of the bright spectral lines. Using equation 2, and the value of d you determined from step six, calculate the wavelength of each of these lines. You will need to measure the angles to the right and left for each line, and then average them to cancel out any misalignment of the spectrometer.
7. Replace the Hydrogen vapor tube with a Helium tube and repeat step 6.

Experiment Part II – Measuring the Spectra using the Vernier Spectrometer.



Equipment:

- Vernier Spectrometer
- Computer with Logger Pro
- Hydrogen & Helium Spectrum Tube
- Red reading Lights

Procedure

Caution: The spectrum tube power supplies operate at 5000V, 10mA. This voltage can produce a dangerous and nasty shock. You must follow these guidelines:

- A. Do not EVER stick your fingers in the sockets under any circumstances.
- B. Do not insert, remove, or adjust the spectral tubes while the power

supply is turned on.

- C. Turn the power supplies off and unplug them as soon as you are finished making observations.
 - D. Do not keep liquids anywhere near the power supply. Drinks are not allowed in this lab.
 - E. Do not operate the power supplies with wet hands.
1. Place the hydrogen spectrum tube in the power supply.
 2. Connect the Vernier spectrometer to your computer via the USB cable. Open Logger Pro. To set up the spectrometer, click on Experiment → Change Units → Intensity. You are now ready to make measurements.
 3. Use a lab stand and right angle clamp to position the end of the optical fiber probe next to the spectral tube.
 4. Turn on the spectrum tube power supply.
 5. View the hydrogen spectrum through a diffraction grating or spectroscope to get a feel for the colors that are present.
 6. Carefully record the wavelengths of the emission lines.
 7. Turn off the power supply, replace the hydrogen tube with helium and repeat steps 4-6.
 8. Repeat steps 4-6 for at least two unknown elements.

Analysis(use data from parts I and II to determine separate results) :

1. Determine whether the lines in the hydrogen atom that you observed are part of the Lyman, Balmer, or Paschen series. To do this, you must calculate a set of values for the factor $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$ for $n_f = 1, 2, \text{ and } 3$ and $n_i = \text{several numbers larger than } n_f$.

For each n_f , plot the reciprocal of wavelength, $1/\lambda$, vs. the factor $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$.

Assume that the longest visible wavelength is associated with the smallest n_i in each case. You should have three plots, each with one data point per observed wavelength. Only one of these plots should be linear, and this will reveal which series you are dealing with. Before you make the plot complete table 1 on the following page.

Table 1 – quantum numbers and associated wavelengths.

n_f	n_i	$\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$	Possible Associated Wavelength
1	2		
1	3		
1	4		
1	5		
2	3		
2	4		
2	5		
2	6		
3	4		
3	5		
3	6		
3	7		

- Do a linear fit to the chosen plot from step one, and use it to determine the Rydberg constant.
- Using the helium atom energy levels table, determine the starting and final quantum numbers for each of the emission lines that you observed in the helium atom. Repeat step one for Helium to see if a “rydberg constant for Helium” exists. In other words, is there a linear relationship for $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ vs $1/\lambda$ for Helium?

Results:

- Which series of the hydrogen atom were you observing? (Lyman, Balmer, or Paschen) Does your measured value of the Rydberg constant agree with the theoretical value within the percent uncertainty of the experiment?
- Did your analysis of the helium spectra produce similar results to that of Hydrogen? If not, why not?
- Make a neat table explaining the quantum numbers, measured wavelength, and accepted wavelength for the transitions in the helium atom.
- How did your results from using the spectrometer compare with your results from using the spectroscope? Are there advantages and disadvantages to each method?