Atomic Emission Spectra

Modern Physics Lab - Rochester Institute of Technology*

Introduction

In this experiment two different diffraction-grating spectrometers are used to measure the wavelengths of the emission lines of hydrogen. These wavelengths are then used to calculate a value of the Rydberg constant R_H and compare both results against the known value.

Emission Spectra

An atom in an excited state returns to its ground with the emission of electromagnetic radiation. The emission spectrum, the distribution of the wavelengths of the emitted light, may consist of discrete lines if they result from transitions between bound states or a continuous band of all wavelengths if it results from transitions from unbound states to a bound state.

In an absorption spectrum, the white light given off by an object passes through a material and then into a spectrometer. As the light passes through the material, the atoms and molecules will selectively absorb energy from the continuous spectrum at specific frequencies. The resulting spectrum, when analyzed with a spectrometer, will appear as a continuous band of colors with black lines where the material absorbed energy.

The sources of the emission spectra you will study are gases under a very low pressure. The tube containing the gas is connected to the ends of a high voltage power supply. The voltage difference creates an electric field, which accelerates electrons in the gas. When these electrons collide with electrons bound in the gas molecules, the collisions raise the electrons of the gas molecules to higher energy states. When the electrons return to a lower state, the atom emits energy at discrete wavelengths, often in the form of visible light. Because the emitted light is the result of transitions between many different states, many different frequencies are observed. Since the gas emits light at various wavelengths, the light that we see with our naked eye is a combination of all the different wavelengths. The actual spectrum is observed with a diffraction grating spectrometer.

Balmer Lines of Hydrogen

In an empirical study of the spectrum of hydrogen, Johann Balmer discovered that the four wavelengths (or "lines") of light produced by a hydrogen-filled discharge tube could be described by a simple mathematical equation. Balmer later extended his result to describe the entire spectrum of hydrogen, including the ultra-violet and the infrared spectral lines. Balmer's formula, published in 1885, is:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \tag{1}$$

where R_H is the Rydberg constant and n is an integer greater than 2. The lines corresponding to the different values of n are referred to as the Balmer lines. A theoretical understanding of the origin of these emission lines and the precise mathematical formulation described by Balmer's formula remained a mystery until Bohr's semi-classical theory of the one-electron atom was published in 1913.

Bohr model of the one-electron atom

According to the Bohr model, the electron orbiting the proton in a hydrogen atom can only exist in certain orbital states in which the angular momentum is an integer value of $\hbar$; specifically, where the quantum number $n = 1, 2, 3, ...$ When the electron is in an orbit described by n, the total energy of the hydrogen atom is given by:

$$E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = \frac{-13.6\text{eV}}{n^2} \tag{2}$$

where m_e is the electron mass and ϵ_0 is the permittivity of free space. The $n{=}1$ state is the lowest possible energy state and is called the ground state. The Bohr model assumes the nucleus is infinitely massive and does not move. If this assumption is not valid for a particular system, m_e should be replaced by the reduced mass of the system.

When an electron makes a transition from an initial state of higher energy E_i to a final state of lower energy E_f, the atom emits a photon of energy $E_\gamma = E_i - E_f$. For a photon $E_\gamma = \frac{hc}{\lambda}$. Combining the last two equations,

$$\frac{1}{\lambda} = \frac{13.6\text{eV}}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \tag{3}$$

which is Balmer's formula with $n_f{=}2$.

Diffraction Grating

A diffraction grating is a thin piece of glass or plastic which has a series of very fine scratches or grooves cut in its surface. The grooves are perfectly straight and parallel and are equally

spaced so that there are a fixed number of grooves per millimeter. If the number of grooves per unit length is n, then the separation between adjacent slits is $d = 1/n$.

When a beam of monochromatic light strikes a grating at normal incidence, each groove or slit scatters the light in all forward directions. However, in only certain directions will the light scattered from different grooves interfere constructively, producing a strong beam. The criteria for constructive interference is

$$d \sin \theta = m\lambda \qquad (4)$$

where λ is the wavelength of the light, θ is the angle the diffracted beam makes with respect to the incident light and m is an integer (referred to as the order of the reflection). Only at certain angles θ defined by $m=0,\pm 1,\pm 2,...$ will the rays from all the slits interfere constructively, producing a bright beam in that direction. In any other direction, the rays from the various slits interfere destructively and produce no light intensity.

An incident light beam made up of a several distinct wavelengths will be split by the grating into its component wavelengths, with each separate wavelength constructively interfering in different directions, determined by Equation 4. Thus, the various wavelengths can be determined by measuring the angles of diffraction.

Week 1 Pre-Lab

1. Sketch an energy level diagram of the hydrogen atom with the various levels labeled with the proper value of the quantum number n. Indicate on your diagram which transitions cause the four lines of the Balmer series.

2. The colors of the four lines of the hydrogen spectrum are: red, blue-green, blue-violet and violet. Which initial state $n_i = 3$, 4, 5, 6 corresponds to each color?

3. Transitions to the $n = 1$ (ground state) level from higher levels in the hydrogen atom do not produce visible wavelength photons. Are the wavelengths produced by transitions to the $n = 1$ level longer or shorter than visible wavelengths? Explain.

4. What is the longest possible wavelength for a transition to the ground state?

5. What is the relation between the wavelength λ and the frequency ν of a photon? What is the relation between the energy E and the frequency ν of a photon?

6. Like most things in introductory physics, the simplified Bohr model (Eqn. 2) is not entirely correct. This derivaiton assumes that the mass of the proton is infinitely larger than the mass of the electron. In reality they orbit each other (just like astronomical bodies) and the mass of the electron, m_e, has to be replaced by the reduced mass of the system, μ:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (5)$$

Thus two atoms differing only in the mass of their nucleus will have different energy levels, and thus different atomic spectra. Deuterium (a hydrogrenic atom with both a proton and neutron) was actually discovered due to this fact.

(a) Calculate the $n = 3 \rightarrow n = 2$ transition wavelength for hydrogren using the reduced mass equation

(b) Do the same for deuterium.

(c) What is the percent difference between these? Comment on whether you could expect to **easily** see the difference between these isotopes.

7. Is the Balmer formula (Eqn. 1) useful in calculating the emission lines for Helium? Why or why not?

Week 1 - Manual Spectrometer

Spectrometer

Despite its simplicity, a diffraction grating spectrometer is a very precise measuring instrument and is still the most commonly used device for measuring the wavelengths of spectral lines. A schematic of a diffraction grating spectrometer is shown in Figure 1.
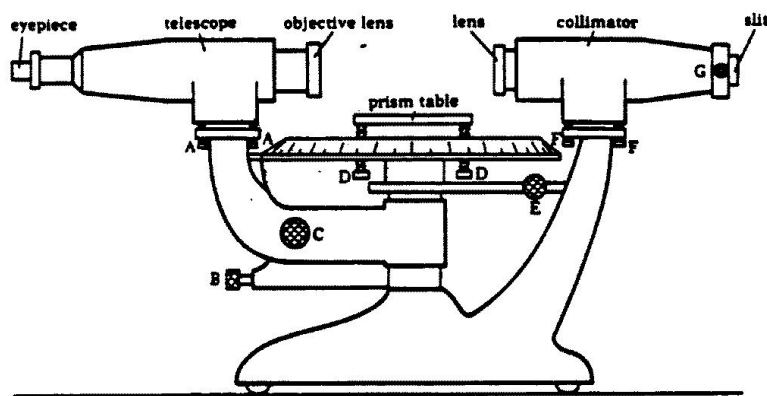

Figure 1: Spectrometer diagram

A: Screws to level or align the telescope
B: Knob to fix the position of the telescope. This knob must always be loosened before moving the telescope by hand and locked only to make fine adjustments with knob C.
C: Fine adjustment knob.
D: Screws to level or raise the prism table.
E: Knob to fix the position of the graduated disc and prism table. When readings are taken with the telescope, this knob must be in the locked position.
F: Screws to align the collimator.
G: Knob for adjusting the slit width.

The spectrometer has around its base a scale graduated in degrees with a least count of 0.5 degrees (30 arcminutes). There is also a vernier scale above the main (outer) one which measures arcminutes. Recall that there are 60 arcminutes in a degree.

Reading the Angle

In order to determine the angle at which the spectrometer is set

1. Read the main (outer) scale: read the number opposite the marking "0" on the vernier (inner) scale. Make sure you choose the half-degree which is to the left of the "0" on the vernier scale. This is the angle to the nearest half-degree.

2. Read the vernier scale. To do so, pick the line on the vernier scale which lines up with some line on the main outer scale (there should be only one line that is perfectly lined up, although others will look very close). Read the vernier scale for this line. This gives the number of arcminutes away from the half-degree determined above.

3. Add this number of arcminutes, divided by 60, to the main reading in degrees.

For example, if the value 162.5 on the main scale is closest to the "0" on the vernier (without going past the "0") and 16 is the best match on the vernier scale, then the correct angle is 162.77 degrees (=162.5 degrees plus (16/60) degrees). See Figure 2.
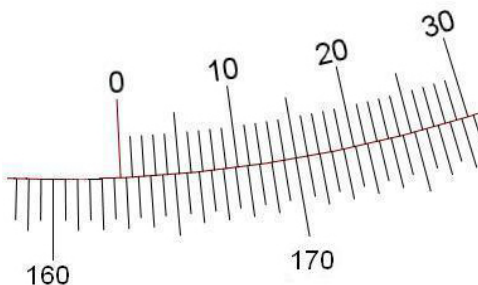

Figure 2: A reading of $162.5 + 16/60 = 162.77°$

Procedure

1. Wearing gloves, install a hydrogen tube in the power source.

2. Arrange the hydrogen lamp and the diffraction grating on the spectrometer. Before using the spectroscope, the telescope must be adjusted to focus parallel rays, and the collimator must be adjusted to give parallel rays. These adjustments have been made already. All you need to do is adjust the eyepiece so that the cross hairs are in good focus.

3. Place the diffraction grating on the spectrometer table. The number of lines per unit length is marked on the grating. From this, you can calculate the slit spacing d. Be sure to record the number of lines/mm.

4. Align the plane of the grating to be perpendicular to the axis of the collimator. Observe the hydrogen source through the grating provided. In the first order spectrum ($m=1$), you should clearly see three lines: red, blue-green (teal), and blue-violet; if the room is dark enough and/or the source intense enough, you can see a violet line as well.

5. Set the telescope cross hairs on the central image produced by the grating. This is the zero angle reference needed for future measurements. Make sure that the telescope is adjusted so that both the cross hairs and the slit are in focus. Adjust the location of the light source by moving it slightly side to side, in front of the slit; your goal is to get the brightest possible image.

6. Measure the angular position (with uncertainty) of the first order maxima for the red, blue-green, and blue-violet lines of the hydrogen spectrum (and the violet line, if it is visible). Measure the angles on both sides of the central maximum, that is, swing the spectrometer arm both to the left and to the right. Be sure to use the vernier when measuring angles. Include the observed line color when recording the angles. The angle for one color line is the average of the deviation from $180°$, that is, the average of the "left side" and the "right side" values. Thus if you see a red line at $157°$ and $207°$, these are $23°$ and $27°$ from $180°$ respectively, thus your red line lies at $25°$. Alternatively, you can ignore the $180°$ entirely, and simply calculate $(207° - 157°)/2 = 25°$. Of course with the vernier, you will have more digits of accuracy in your angles, this calculation is only for an example.

7. Measure the angular position (with uncertainty) of the second order maxima for as many lines as you can detect.

8. Using all the observed orders for a given line, calculate the weighted average wavelength of the light. Repeat the calculation for all three (or four) lines. Include an estimate of the uncertainty of the wavelengths. When propagating the uncertainty in the wavelength from the uncertainty in the angle, the uncertainty $\delta\theta$ has to be in radians (not degrees).

9. Wearing the thermal glove (the tube is likely very hot), replace the hydrogen tube with a neon or a helium tube. Visually look at the lines and record what colors you see. Qualatatively compare these to the wavelengths listed on a reference page `http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/atspect.html`. You will use helium next week to calibrate the digital spectrometer.

Week 1 Check In

For the $m = 1$ order data, use Equation 1 to plot $1/\lambda$ vs $1/n_i^2$ to determine the Rydberg constant R_H from the slope of this graph.

Week 2 Pre-Lab

In order to operate the digital spectrometer you will have to download free software to your computer. Please visit `https://www.oceaninsight.com/support/software-downloads/oceanview-downloads/oceanview-form/` to download a free version of the OceanView software. This version of OceanView contains a lite version of the software that despite its name will work indefinetly (and no need to "activate" the trial).

You will use this software in other labs so it's worth it to put the (lightweight) software on your personal laptop. While you won't be able to test the software with a spectrometer, please get this installed before coming to lab.

We will model the emission spectrum with a gaussian. This will enable us to obtain not only the center of the peak but also its width. Gaussians are used everywhere in science, especially when it comes to analyzing light emission. This is true in this case for intensity vs wavelength, but is also true anytime you are locating spots in an image (think astrophysics and biophysics).

While the Gaussian is extremely useful for characterizing the features of the signal, it is sometimes used for phenomenological reasons. That is, it's used because it works, not because there are fundamental equations that say the output must have the gaussian shape. Although more correctly, the Gaussian function is the probability density function of the normal distribution.

In general, Gaussians have the following form:

$$f(x) = ae^{\frac{-(x-b)^2}{2c^2}} \tag{6}$$

Before you use the gaussian, you should determine how the varaibles a, b, and c modify the curve. Create python code to plot the Gaussian curves for different values of these variables. Use these plots to describe what they represent, at least qualatatively.

Check the `SampleCode.py` file for the code snippits you might want to use. (Basically you want to use `linspace` to create an array of your x values, and then create another variable to calculate the gaussian at each individual x value. Then plot these and change the a, b, and c variables to see how it changes).

Note: For us because we have *real* data you may or may not have to add in a $+d$ to your function to deal with any offsets generated by the equipment or background noise.

Digital Spectrometer

The Ocean Optics spectrometer records wavelegnths from the visible into the near UV, so five Balmer lines at minimum (and possibly up to seven) can be observed. This spectrometer is fully computerized. It plugs into the computer via a USB cable. The blue "cable" is not actually a cable, but a fiber optic line. The small box is the actual spectrometer. It contains

two mirrors and a reflection grating; it is exactly the same as the big spectrometer you will or have already used in the Photoelectric Effect, except much shorter path length (poorer resolution) and computer controlled.

1. You will first use the helium tube to calibrate the digital spectrometer. Mount the helium tube into the power supply, turn it on, and align the fiber optic cable in order to achieve a good signal on the software. You should see multiple peaks. Make sure the peaks are not saturated, as these will be useless for obtaining the center of the peak.

2. Use the software to identify the centers of each peak, and compare these to the list of helium wavelenghts linked above. State to what level of precision your measured wavelengths agree with the expected values.

3. Mount a hydrogen tube, and align it with the spectrometer.

4. Save a copy of the spectrum. The easiest way to do this is to click "Copy data to clipboard" and then paste it into a blank .txt file.

5. Again make sure the peaks are not saturated. You will have to save multiple sectra in order to see every peak. Some allignments will cause the stonrger peaks to be saturated in order to see the weaker ones.

6. Using python, fit the peaks of the hydrogen data to gaussians, as it is more accurate than just finding the highest point. Since the entire data set is not just one Gaussian, you will have to create subarrays of for each peak. Check the `SampleCode.py` file for how to use `np.where` to do this.

   When it comes to fitting Gaussians (or anything that is not a staight line) you have to give the software an initial guess to get it started. Gaussians in particular are very sensative to the guess for the b varaible so make sure you get that one as close as possible (usually rounding to a whole wavelength is enough). The other guesses have to be in the same ballpark, but it is vital to get b fairly close.

Analysis

1. For the manual grating spectromter you should have two measurements for each wavelength, one for the $m = 1$ diffraction and one for the $m = 2$. You need to account for this data, either plotting them as additional points in the next step or by finding a weighted average for each wavelength.

2. For both Hydrogen data sets (from the grating spectrometer and from the OceanOptics spectrometer), use Equation 1 and plot $1/\lambda$ vs $1/n_i^2$ to determine the Rydberg constant R_H. You should be able to determine R_H from both the slopt and intercept.

3. State your final value for the Rydberg constant from all your measurements, with overall uncertainty. How many uncertainties (sigma) are your experimental values from the expected value?