Spectroscopy: Calibration, Rydberg's Constant, and Identification of an Unknown Gas

Abstract:
This spectroscopy experiment looks into the calibration of a spectrometer, determination of the Rydberg constant, and the identification of an unknown gas employing the Bohr model of the atom. The calibration process involves measuring y-values of known spectral lines from helium and hydrogen, allowing the determination of calibration parameters m and b. The calibrated spectrometer is then employed to identify an unknown gas by comparing its emitted spectral lines with known gas spectra. Furthermore, the experiment calculates the separation of spectral lines in the yellow doublet of sodium.

The Rydberg constant is determined by applying the Bohr model and comparing the experimental wavelengths of hydrogen's spectral lines with the calculated values. The calculated Rydberg constant closely matches the known value, affirming its significance in understanding hydrogen's energy levels.

The spectrometer's resolution is assessed by comparing the experimentally determined wavelengths of the sodium doublet lines to their known values, revealing high precision but some accuracy deviation. The experimental data exhibit commendable precision, as the closely spaced sodium doublet lines illustrate. However, a notable discrepancy in accuracy is observed, as the experimentally determined wavelengths deviate from the known values by approximately 12 nm.

Lastly, the unknown gas is identified as neon based on its spectral lines, macroscopic color, and spectral distribution, supported by comparisons with known neon spectra.

Introduction:
The Bohr model of the atom[1] was proposed by Danish Physicist Niels Bohr in 1913 and it was a significant advancement in our understanding of atomic structure. It was developed to explain the spectral lights that Hydrogen gas emits when charged with high voltage. It introduces the following key concepts:

1) Quantized Energy Levels: Bohr model states that electrons could only exist in specific, discrete energy levels or orbits. These energy levels are represented by whole numbers (n = 1, 2, 3, ...) and are often referred to as "shells." Electrons in lower energy levels are closer to the nucleus.
2) Radiation Absorption and Emission: Electrons can transition between energy levels by absorbing or emitting energy in the form of photons. When an electron moves to a lower energy level, it emits a photon with a specific energy corresponding to the energy difference between the levels.
3) Central Nucleus: The model retained the concept of a central nucleus containing protons and neutrons, with electrons orbiting around it.

The Rydberg constant is used to calculate the energy levels and wavelengths of the spectral lines in hydrogen and hydrogen-like ions. It is approximately equal to 1.097 x 10^7 per meter (1/m).[2]

---

[1] Bohr, Niels. On the Constitution of Atoms and Molecules. Philosophical Magazine July 1913 [4]
[2] Michelle Faust, LibreTexts. Bohr's Hydrogen Atom [3]

The following equation is used to calculate the wavelength of light emitted or absorbed as electrons transition between energy levels:

$$\frac{1}{\lambda} = R * (\frac{1}{n_1^2} - \frac{1}{n_1^2})^3$$

Where:
- λ is the wavelength of light
- R is the Rydberg constant.
- n1 and n2 are integers representing the initial and final energy levels.

Even though Bohr model is great for explaining the emission spectrum of hydrogen-like atoms, it has significant limitations being:
1) Limited Applicability: The Bohr model primarily worked well for hydrogen and hydrogen-like ions with only one electron. It couldn't explain the spectra of atoms with more than one electron or complex molecules.
2) Lack of Explanation for Quantization: The model didn't provide a theoretical basis for the quantization of energy levels; it was essentially an ad hoc assumption.
3) Neglect of Electron Motion: The model treated electrons as particles following circular orbits, which contradicted the emerging wave-particle duality concept in quantum mechanics.
4) No Explanation of Fine Structure: The model fails in accounting for fine details in spectral lines, such as the splitting of lines in a magnetic field (Zeeman effect) or the fine structure splitting due to electron spin (Spin-Orbit coupling).
5) Wave-Particle Duality: The Bohr model didn't incorporate the dual nature of electrons as both particles and waves, which is a fundamental aspect of quantum mechanics.[4]
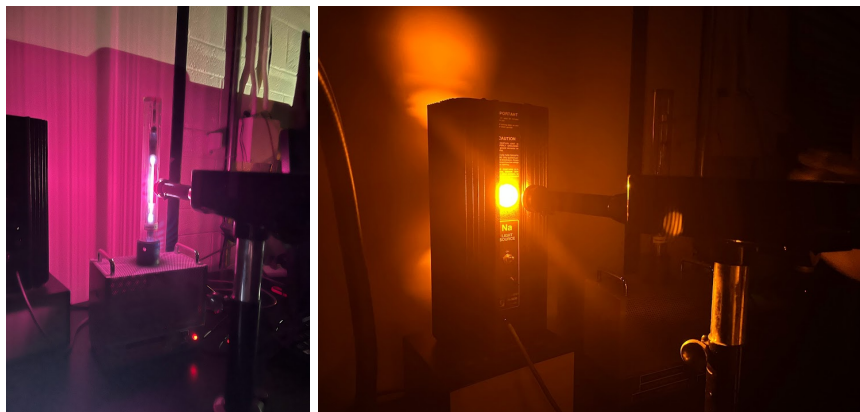
Setup:

Figure 1: Lab setup for Hydrogen and Sodium lamp spectroscopy.

The equipment used in this experiment are as follows:

---

[3] Rydberg Constant Lab Handout [1]
[4] Michelle Faust, LibreTexts. Bohr's Hydrogen Atom [3]

- Spectrometer with $\lambda_0 = 282.8 \pm 0.4$ nm. This instrument allows the experimenter to visually see and measure the wavelengths of stronglines of gasses
- Sodium lamp. This instrument powers up a tube of sodium gas which then emits yellow doublet
- Samples of helium, hydrogen and an unknown gas in discharge tubes
- Power supply for the discharge tubes. This instrument applies a high voltage across discharge tubes that contains gasses, and makes them emit certain wavelengths of light.

Experimental Procedure:
Calibration of the Spectrometer
The y values gathered from the spectrometer are related to the wavelength of the strong line according to the following equation:

$$y = \frac{m}{\lambda - \lambda_0} + b \qquad\qquad (1)$$

Where m and b are calibration parameters we have to determine during the calibration process and λ_0 is a value specific to the spectrometer used in measurements and should be given to the experimenter.

Calibrating the spectrometer first requires measuring y values of predetermined strong-lines of hydrogen and helium with known wavelengths. In order to do that, the following procedure should be followed:
1. Adjust the knob so that the crosshair of the spectrometer would sit on the strong-line
   a. Make sure to adjust the focus of the spectrometer so that the strong-lines would be as thin as possible. Neglecting this would cause strong-lines to appear very wide and increase the uncertainty in measurements.
2. Record the y value by following the procedure outlined in the lab handout.
3. Iterate for the next strong-line

After gathering the y values for specific wavelengths, plot the y vs. $(\lambda - \lambda_0)^{-1}$ graph and apply a linear fit to it. The slope of the fit would be the m value while the y intercept would be the b value.

Identification of the Unknown Gas
Now that the spectrometer is calibrated, it can be used to identify an unknown gas through the following procedure
1. Attach the tube with the unknown gas to the spectrometer
2. Record the color of the light it emits that you can see with your naked eyes
3. Record as many y values for strong-lines as necessary by following the procedure outlined in lab handout
4. Convert the y values to wavelengths with equation 1 and the values we gathered during calibration
5. Compare the color of the light emitted by the tube and the wavelengths of the strong-lines with the colors and wavelengths of the gasses from a lookup table.

Calculating the Separation of Spectral Lines in the Yellow Doublet of Sodium

1. Turn on the sodium lamp and wait for the lamp to warm up, which can be identified with its color changing to yellow.

2. Measure the y values of the two yellow lines.
3. Convert the y values to wavelengths with equation 1 and the calibration parameters we gathered during calibration
4. The difference of the wavelengths are the separation of spectral lines in the yellow doublet of sodium
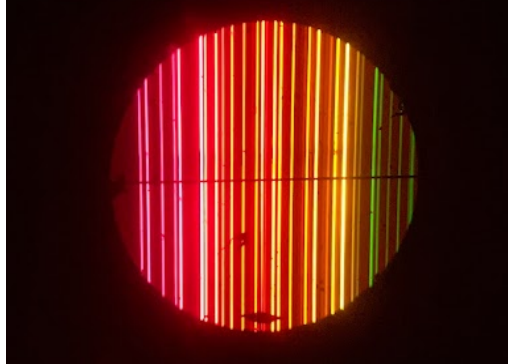

Figure 2: Image taken from lens of spectroscope for unknown gas.

Data and Analysis: Calibration Curve

	Helium strong lines						Hydrogen Strong Lines			
λ,nm	447.1	471.3	492.2	501.6	587.6	667.8	410.2	434.0	486.1	656.3
Color	Blue	Blue	Blue	Cyan	Yellow	Red	Violet	Violet	Blue	Red
y	14.15	12.57	11.49	11.12	8.42	6.11	17.64	15.21	11.81	7.18
$(\lambda\text{-}\lambda_0)^{-1}$	0.00609	0.00531	0.00478	0.00457	0.00328	0.00260	0.00785	0.00661	0.00492	0.00268

Figure 3: Established wavelengths λ of Helium and Hydrogen spectral lines with observed color, measured values on the Vernier scale y and data prepared for fit using calibration constant $\lambda_0 = 282.8 \pm 0.4$ nm.
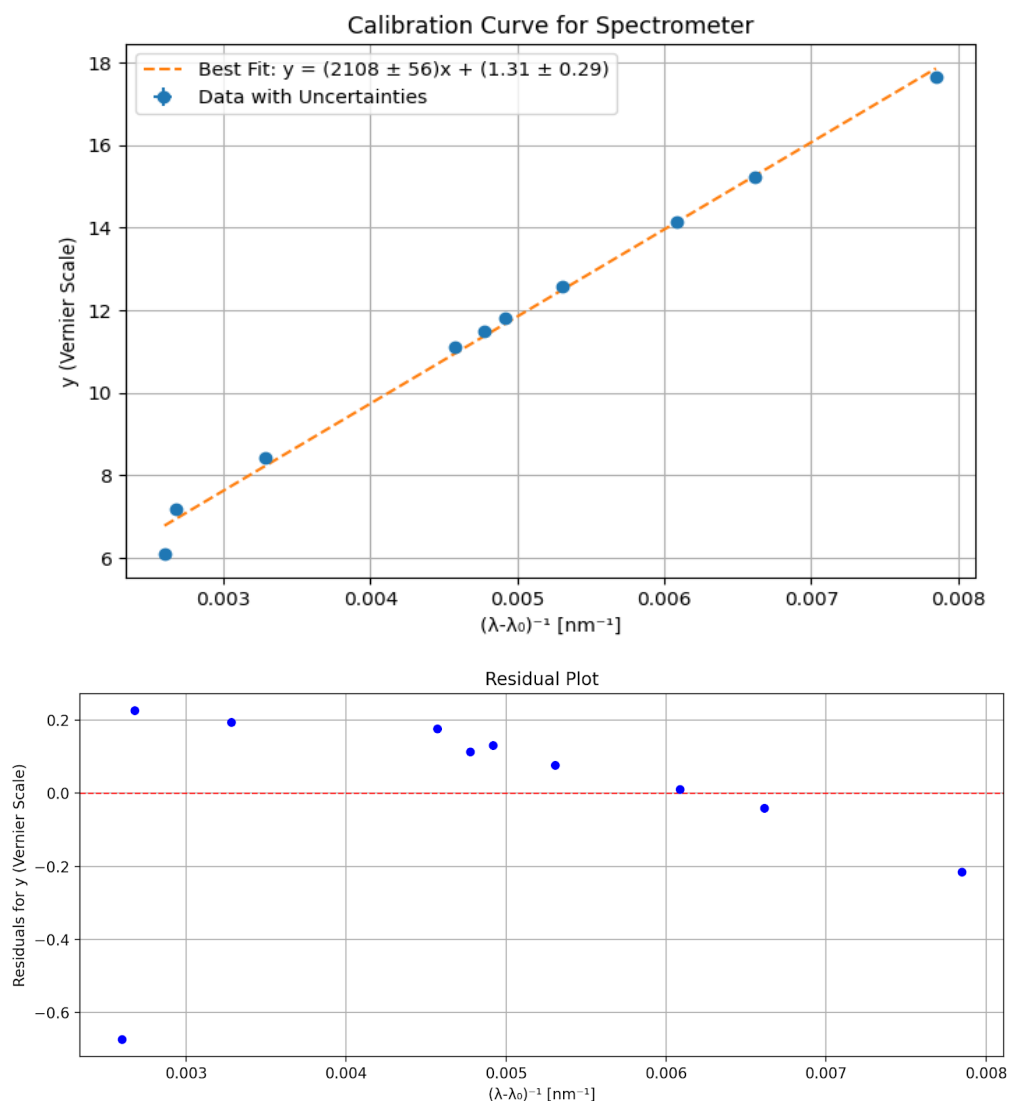

Figure 4: Calibration curve and residual plot for Spectrometer used in this experiment determined using Python Numpy Curve_Fit function. Uncertainties are plotted, but small enough to not show on the figure.

The measurements on the Vernier scale for the strong lines of both Helium and Hydrogen were input into a linear fit with the dependent variable being the inverse of the established spectral lines' wavelengths minus the calibration constant of the spectrometer used in the experiment as according to Equation 1 seen previously. No error was assumed for the accepted values of the spectral line wavelengths and the uncertainty in the Vernier measurements was ±0.005. The fit, found in Figure 4, yielded the values for the constants m = 2108 ± 56 and b = 1.31 ± 0.29. This is a reasonable fit for the data, with an R^2 value of 0.999978[5] and a relatively low chi squared value of 6.83[6]. However, we can see one possible outlier in this data at roughly 0.0025 on the x-axis which might have been caused by random error.
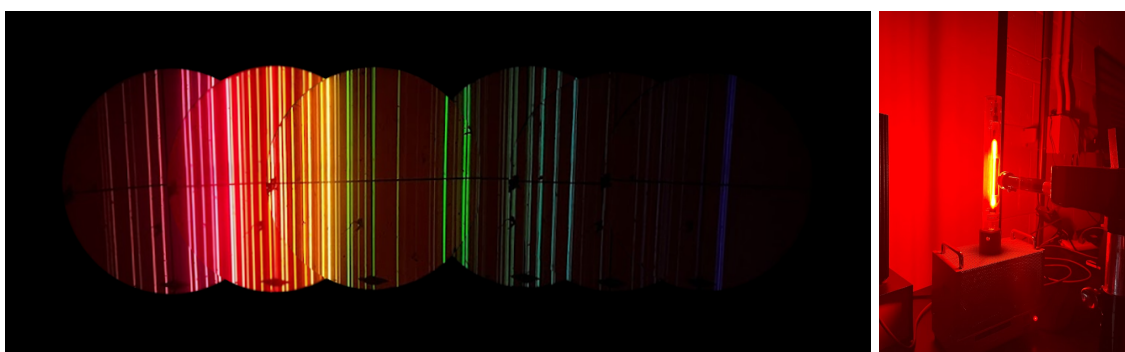
Data and Analysis: Unknown Gas

Figure 5: Images spliced together showing full spectrum of unknown gas and discharge tube macroscopically.

Unknown Gas Strong Lines									
λ,nm	626.08	620.58	615.78	615.25	598.81	585.21	573.13	533.73	500.33	469.83
Color	Red	Red	Red	Red	Orange	Yellow	Yellow	Green	Cyan	Violet
y	7.45	7.55	7.64	7.65	7.98	8.28	8.57	9.71	11.00	12.58

Figure 6: Observed color and measured Vernier scale values y of multiple spectral lines of unknown gas as well as calculated wavelengths λ based on equation 2.

Data for the wavelength of the Unknown Gas Strong Lines was calculated using Equation 2 below, the inverted version of Equation 1 with established fit constants from the calibration process.

$$\lambda \ = \ \frac{m}{y-b} + \lambda_0 \tag{2}$$

---

[5] R Squared Calculator. Ncalculators.com [6]
[6] Chi Squared Calculator. Graphpad.com [5]

Data and Analysis: Sodium Lamp

Yellow Doublet of Sodium Lines		
λ, nm	577.18	577.59
y	8.47	8.46
Color	Yellow	Yellow

Figure 7: Observed color and measured Vernier scale values y of Sodium doublet lines as well as calculated wavelengths λ based on Equation 2.

Similarly as with the analysis for the Unknown Gas Strong Lines, the wavelength values of the Yellow Doublet in Sodium were calculated using Equation 2.

Discussion: Rydberg Constant

Using Equation 3 where λ is the wavelength for a particular principle quantum number n of the state that is responsible for the given λ, R_H can be solved for. The principle quantum numbers for the wavelengths of 410.2 nm, 434.0 nm, 486.1 nm, and 656.3 nm are 6, 5, 4, 3 respectively, with the lower energy waves corresponding to jumps from lower energy states. Error in the values of the wavelengths will be assumed to be ±0.05 nm and there is no error value for the quantized integers.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n^2} \right) \qquad (3)\,[7]$$

Then rearranging:
$$R_H = \frac{1}{\lambda} \left(\frac{1}{4} - \frac{1}{n^2} \right)^{-1}$$

Solving: $R_{H,3} = 1.097059 \cdot 10^7 \pm 8.4 \cdot 10^2 \, m^{-1}$, $R_{H,4} = 1.09717 \cdot 10^7 \pm 1.1 \cdot 10^3 \, m^{-1}$,

$$R_{H,5} = 1.09721 \cdot 10^7 \pm 1.3 \cdot 10^3 \, m^{-1}, R_{H,6} = 1.09703 \cdot 10^7 \pm 1.3 \cdot 10^3 \, m^{-1}$$

And then taking the average: $R_H = 1.097117 \cdot 10^7 \pm 5.8 \cdot 10^2 \, m^{-1}$

Then modifying Equation 4 to solve for R_{EH} where h is Planck's constant and c is the speed of light in a vacuum:

$$\frac{R_{EH}}{hf} = R_H \lambda \qquad (4)\,[8]$$

$$R_{EH} = R_H hc$$

---

[7][8] Rydberg Constant Lab Handout. University of Toronto Department of Physics [1]

$$R_{EH} = 2.17936 \cdot 10^{-18} \pm 1.2 \cdot 10^{-22} J = 13.60247 \; eV \pm 7.2 \cdot 10^{-4} eV$$

The calculated value of R_{EH} is extremely close to the documented value of 13.605693 eV. Unfortunately it is not within the uncertainty of the calculated value which could be a result of different rounding in the calculations.

The value described by R_{EH} also has physical significance as it is approximately equal to the ionization energy of atomic hydrogen[8]. This means that if an atom of hydrogen absorbs exactly R_{EH} of energy, an electron present in the lowest orbital of hydrogen will be expelled from the atom.

Discussion: Resolution of the Spectrometer

The values of the yellow double that were found in this experiment were 577.18 nm and 577.59 nm, compared to the actual values of 588.9950 nm and 589.5924 nm [1]. The distance between the first two is 0.41 nm and the difference between the second two is 0.5974. These values are quite close, showing that the precision of the spectrometer is quite good. However, it appears the accuracy of the experimentally determined wavelengths was off by around 12 nm. This is presumably a failure of the calibration fit used to determine these wavelengths from the Vernier Scale. Looking at Figure 4, a possible outlier in the fit can be seen, possibly leading to this error in accuracy of the Sodium Doublet.

Discussion: Identification of Unknown Gas

The unknown gas in this experiment has been determined to be Neon. This is supported by similarities in the spectral lines with Neon's recorded values, as well as a qualitative similarity to the distribution of spectral lines and macroscopic color and intensity of the unknown gas.

Shown in Figure 5, the unknown gas exhibited an extremely bright red-orange color, very similar to the established color of excited Neon seen below in Figure 8. The only gasses in the lookup table that would emit such light are Helium and Neon. However, after comparing the spectral lines in Figure 5 with the number and distribution of spectral values in Figure 8, it becomes clear that Neon appears to match better than Helium.

Figure 8: Emission spectrum and macroscopic view of Helium above and Neon below. [1]

In addition, among the measured spectra values seen in Figure 6, several line up with the values seen in Figure 8 within a certain margin of error. The most notable being the two values of the yellow spectral lines measured at 585.21 nm and 573.13 nm. If is assumed that our fit overestimated the actual values by

---

[8] Ionization Energy. Britannica [2]

around 12 nm in this range of values as previously stated, these measurements would line up quite well with two of the most intense documented spectral lines, 585.2 nm and 596.5 nm.

NEON

WAVELENGTH nm	RELATIVE INTENSITY	COLOUR
724.5	1	RED
717.4	1	RED
703.2	5	RED
702.4	3	RED
692.9	6	RED
667.8	7	RED
659.9	7	RED
653.3	7	RED
650.7	7	RED
609.6	5	ORANGE
607.4	7	ORANGE
603.0	5	ORANGE
596.5	4	ORANGE
588.2	6	YELLOW
585.2	10	YELLOW
540.1	5	GREEN

Figure 9: Table of Wavelength and Intensity Data for Neon [1]

Therefore, through this combination of qualitative and quantitative data, the identity of the unknown gas can be confidently assumed to be Neon.

Works Cited

[1] "University of Toronto." *Rydberg Constant Lab Handout*, Department of Physics, www.physics.utoronto.ca/~phy293lab/experiments/rydberg.pdf . Accessed 17 Oct. 2023.

[2] "Ionization Energy." *Encyclopædia Britannica*, Encyclopædia Britannica, inc., 15 Sept. 2023, www.britannica.com/science/ionization-energy.

[3] "Bohr's Hydrogen Atom." *Chemistry LibreTexts*, Libretexts, 30 Jan. 2023, chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Quantum_Mechanics/09._The_Hydrogen_Atom/Bohr%27s_Hydrogen_Atom.

[4] Bohr, Niels. "On the Constitution of Atoms and Molecules - UB." *University of Barcelona*, 1913, ffn.ub.es/luisnavarro/nuevo_maletin/Bohr_1913.pdf.

[5] "Compare Observed and Expected Frequencies." *GraphPad by Dotmatics*, www.graphpad.com/quickcalcs/chisquared1.Chi-square/ . Accessed 17 Oct. 2023.

[6] "R-Squared (R^2) Calculator." *Ncalculators.Com*, ncalculators.com/statistics/r-squared-calculator.htm. Accessed 17 Oct. 2023.