Rydberg Constant

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1 Introduction

The purposes of this experiment were to explore the relationship between a spectrometer's scale reading with the wavelengths from certain gases' emission spectra and to calculate various Rydberg constants using experimental values. In this experiment, a current was accelerated through a discharge tube — an evacuated glass tube filled with gas or vapour — causing collisions between electrons and neutral atoms of the gas in the discharge tube. In doing so, the gas becomes ionized, promoting the electron(s) in the valence shell to an excited state[1]. When the excited electron transitions to a lower energy level, a photon—the energy of which is equal to the difference in the energies of the two states—is emitted [2]. This separation between energy levels, as outlined by the distinct shell structures which characterize Bohr's model of the hydrogen atom, consequently results in the quantization of energy. However, there are several limitations with Bohr's model of the hydrogen atom. For instance, his model violates the Heisenberg Uncertainty Principle, since it posits that both the position and momentum of electrons can be simultaneously known. Additionally, Bohr's model of the atom is unable to predict the relative intensities of spectral lines[3]. Despite these limitations, the Bohr model of the atom has proven to be useful in the field of atomic theory and quantum mechanics; namely, Bohr correctly predicted that energy of electrons quantized - an idea that leads into this first equation. For the hydrogen atom, the relationship between the energy of the emitted photon and the energy level transition between two states of quantum numbers m and n is given by the following equation:

$$hf = R_{EH}(\tfrac{1}{m^2} - \tfrac{1}{n^2}) \quad (1)$$

where $R_{EH} = 13.60593$ is the Rydberg constant for hydrogen, m and n are the different principal quantum numbers denoting the energy states, and hf represents the change in energy between the two levels. Similarly, the following equation relates the wavelength of a photon emitted by hydrogen with the principal quantum number responsible for the energy at the excited state:

$$\tfrac{1}{\lambda} = R_H(\tfrac{1}{2^2} - \tfrac{1}{n^2}) \quad (2)$$

where λ is the wavelength of the emitted line, n is the principal quantum number of the excited state, and R_H is a different Rydberg constant. Equation (2) specifically denotes the change in energy between two energy levels where the electron falls to the $n = 2$ level: the photons emitted in this case are classified as the Balmer Series. Two other formulas of note are as follows:

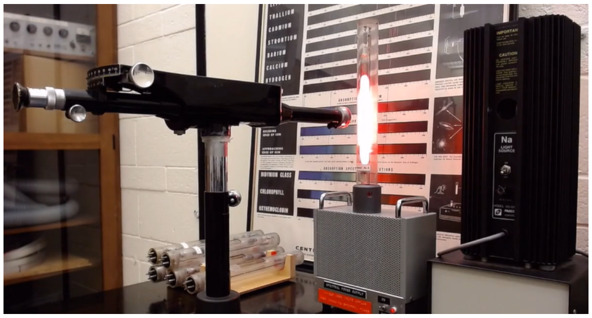


Figure 1: Experimental setup. The rectangular prism attached to the vertical pole is the spectrometer. The gray rectangular prism is the discharge tube power source and the tube protruding from this prism is one of the discharge tubes. The apparatus on the far right of the figure is the sodium lamp

$$E_f = hf = \tfrac{hc}{\lambda} \quad (3)$$

where $h = 6.626070040x10^{-34} J \cdot s$ is Planck's constant, c is the speed of light in a vacuum, f is the frequency of a photon, and λ is the wavelength of a photon.

$$y = \tfrac{m}{\lambda - \lambda_0} + b \quad (4)$$

where y is the scale reading of the spectrometer, λ is the wavelength of the observed photons, and λ_0, m, and b are constants. Equations (3) and (4) describe the energy of a photon and the relationship between the spectrometer's scale reading with an observed photon's wavelength, respectively.

2 Materials and Experimental Setup

- Tri-prism spectrometer. To properly set up the spectrometer, a cross-hair, visible through the eyepiece, was precisely aligned with the image of the spectral line. To obtain a clearer picture of the emission spectrum, the main focus on the spectrometer was adjusted. The slit width was also tweaked in order to change the width of the spectrum lines.

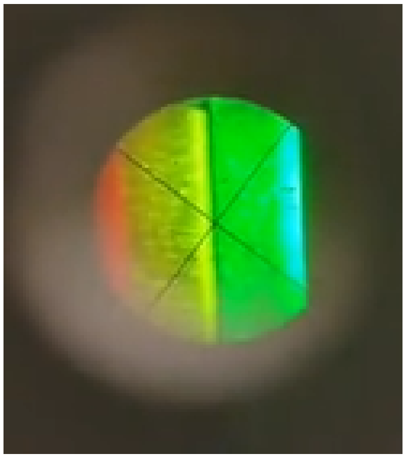
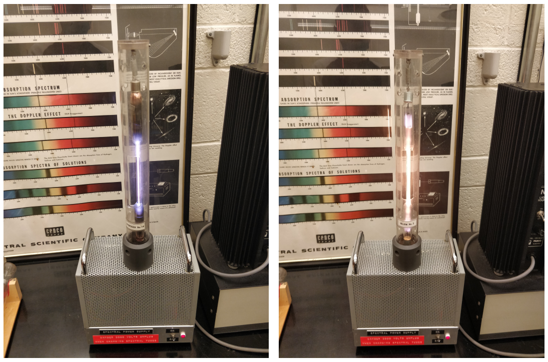
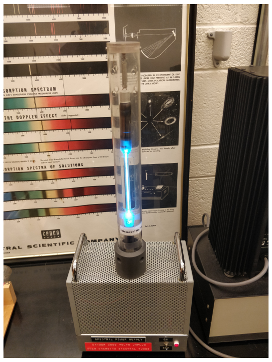


Figure 2: Image of the cross-hair as seen through the spectrometer's lens



(a) Hydrogen tube. (b) Helium tube.



(c) Discharge tube with unknown gas.

Figure 3: Discharge tubes.

- Discharge tubes (Figure 3). Two of these discharge tubes contained hydrogen and helium gas and a third tube contained an unknown gas.
- Sodium lamp
- Discharge tube power source

3 Procedure

3.1 Spectrometer Calibration Using the Hartmann Relation Method

The spectrometer's cross-hair was precisely aligned with the image of one of the spectral lines. Once this was done, the value on the Vernier scale (y value in Table 1) was recorded into Table 1. Data detailing the wavelength (λ) values of Helium were taken from the lab manual. Using a MATLAB script, y was plotted against $(\lambda - \lambda_0)^{-1}$ in order to determine the relationship between λ and y and to approximate the m and b values in Equation (4), thereby calibrating the tri-prism spectrometer.

3.2 Identifying the Unknown Gas

The calibration gas tube used in section 4.1 was replaced by the discharge tube containing an unknown gas. Using an identical spectrometer setup as in section 4.1, the y-values of the unknown gas for different sections of the spectrum line were recorded. Then, using Equation (4), the wavelengths of the unknown gas were determined. The identity of this unknown gas was concluded by comparing the calculated λ values with those given in the APPENDIX 2 section of the lab manual[4].

3.3 Calculating the Rydberg Constant

The wavelengths of Hydrogen's spectral lines were plugged into Equation (2) in order to calculate the Rydberg constant, R_H. Using Equations (1) and (3), RH was converted to R_{EH}.

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

The power supply for the discharge tubes was shut off and the sodium lamp was turned on. An identical spectrometer configuration, as in sections 4.1 and 4.3, was set up. Once the colour of the discharge became yellow, the separation between the two yellow lines was calculated. The λ values for the two yellow sodium lines were then calculated. These λ values were compared to those provided in the lab manual in order to gauge the accuracy of the spectrometer as well as the accuracy of the calibration performed in Part 1 of this lab.

Table 1: Hydrogen and helium spectral line wavelengths and their corresponding colours and vernier scale readings from the spectrometer.

λ (nm)	Colour	Scale reading (y)
Hydrogen spectral lines		
410.2	Violet	15.5
434	Violet	14.55
486.1	Blue	12.13
656.3	Red	7.53
Helium spectral lines		
447.1	Blue	14.46
471.3	Blue	12.89
492.2	Blue	11.82
501.6	Cyan	11.4
587.6	Yellow	8.76
667.8	Red	7.41

4 Results and Discussion

4.1 Spectrometer calibration using the Hartmann Relation method

The known wavelengths of hydrogen and helium spectral lines and the vernier scale readings given by the lab manual [4] are shown in Table 1. The values of λ have no uncertainty in the context of this lab since it is a provided value. The scale readings have an instrumental uncertainty of ± 0.005. By plotting the values of the scale readings against the values of $(\lambda - \lambda_0)^{-1}$ and fitting the data to a linear function using MATLAB (shown in Figure 4), we can estimate the values of the coefficients m and b from Equation (4).

4.1.1 Fitting procedure and determining the calibration function

The MATLAB *lsqcurvefit* function was used to determine the unknown parameters m and b of the linear fit. We wrote a MATLAB script that produced three fits: one for the hydrogen data set (Figure 4a), one for helium (Figure 4b), and one that fitted both data sets together (Figure 4c). We decided that the fit for both data sets was the most suitable result to use for the calibration function since it treats every data point measured with equal importance. Since the calibration function is independent of the element and only dependent upon the spectrometer, it is logical to fit both data sets together. Using this method, the values for m and b were determined to be $1619nm \pm 3nm$ and 3.6 ± 0.005, respectively. Therefore, the calibration function described by Equation (4) is determined to be

$$y = \frac{1619}{\lambda - \lambda_0} + 3.6. \quad (5)$$

To calculate the uncertainties in these values, the error propagation formula was used. Below is an example of the uncertainty calculation for the value of m (the same process was used for

b):

$$\delta m = m\sqrt{\sum_{k=1}^{10}(\frac{\delta y_k}{y_k})^2}$$
$$= 1619\sqrt{\frac{0.005^2}{7.53^2}+\frac{0.005^2}{12.13^2}+\frac{0.005^2}{14.55^2}+\dots}$$
$$= 3nm$$

4.1.2 Goodness of fit

We first test the goodness of fit using the Chi-Squared criterion. We use the formula:

$$\chi^2 = \sum_{i=1}^{N} \frac{[y_i - f(x_i)]^2}{\sigma_{y_i}^2}. \quad (1)$$

The reduced χ^2 value of the fit was calculated to be around 15443. This value is extremely large compared to the ideal value of 1, indicating that the uncertainties were much too small. Therefore, based on the Chi-Squared goodness of fit criterion, the fitted function is not a good fit for the data sets.

We then test the goodness of fit by examining the residuals of the data, shown in Figure 5. Since there is no obvious pattern in the residuals of the data, a systematic error in the setup is unlikely; the error is likely due to random error. Therefore, in this respect, the fit satisfies the criterion for a good fit.

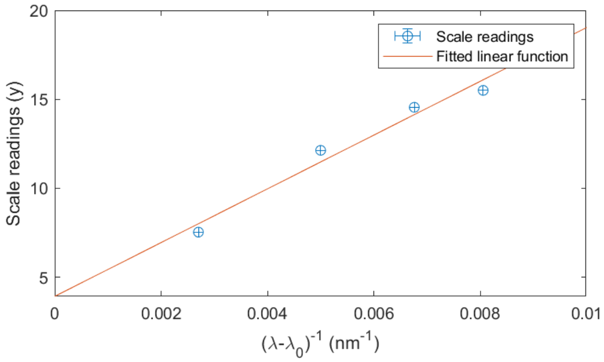
4.2 Identification of the unknown gas

Scale readings on the spectrometer correspond to wavelengths of light. Using the calibration function determined in Section 4.1, we are able to determine a given scale reading's corresponding wavelength by simply rearranging the equation to isolate λ:

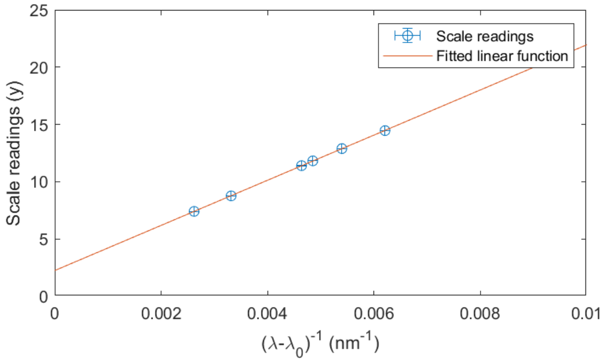
$$\lambda = \frac{m}{y-b} + \lambda_0, \quad (6)$$

or, subbing in the calculated values for m and b:

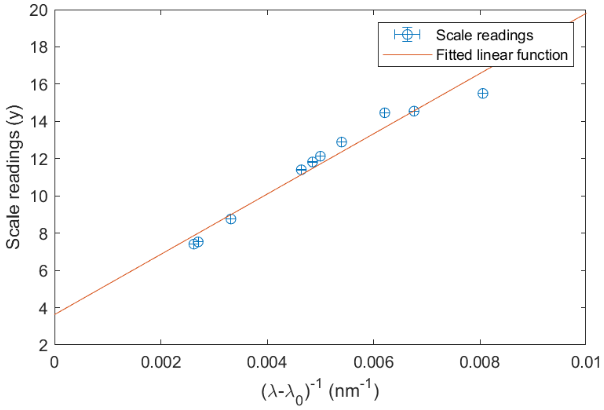
$$\lambda = \frac{1619}{y-3.6} + \lambda_0. \quad (7)$$



(a) Hydrogen spectral lines plot. $m = 1512nm \pm 1nm$ and $b = 3.9 \pm 0.004$.



(b) Helium spectral lines plot. $m = 1971nm \pm 2nm$ and $b = 2.2 \pm 0.003$.



(c) Plot of both hydrogen and helium spectral lines. $m = 1971nm \pm 2nm$ and $b = 2.2 \pm 0.003$.

Figure 4: Plot of the scale readings against the values of $(\lambda - \lambda_0)^{-1}$ and the fitted linear functions for hydrogen (a), helium (b), and both (c) spectral lines. The equation of the fits are given by $y = m(\lambda - \lambda_0)^{-1} + b$. Error bars are too small to be seen in the plots. The x error corresponds to the uncertainty in λ (0 nm) and y error corresponds to the uncertainty in scale readings (±0.05).

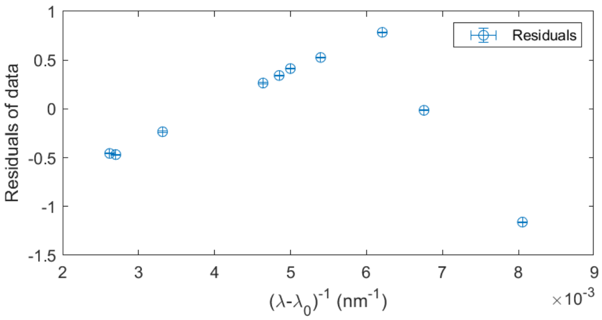


Figure 5: Residuals of the hydrogen and helium data sets. There is no obvious trend or pattern in the residuals, implying no systemic error - a good fit.

Table 2: Scale readings and calculated corresponding wavelengths and colours of the unknown gas.

y Reading	8.36	8.99	9.86	15.47
λ	626.1	586.4	544.6	422.4
Colour	Orange	Yellow	Green	Violet

The scale readings and the calculated corresponding wavelengths are shown in Table 2. Based on the unknown gas' spectral line wavelengths and referring to Appendix 2 and the figure on page 4 of the lab manual [4], we can guess that the unknown gas is likely mercury vapour.

4.3 The Rydberg Constant

By rearranging Equation (2) to isolate R_H, we obtain an expression for the Rydberg Constant in terms of the wavelengths of the spectral lines of hydrogen and the principal quantum number (n):

$$R_H = \left[\lambda\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\right]^{-1}. \quad (8)$$

Table 3: Values of the Rydberg Constant calculated from the spectral lines of hydrogen.

λ	n	R_H
656.3	3	10970592.7
486.1	4	10971679.4
434	5	10972130.8
410.2	6	10970258.4
Average		10971165.3

Using the four spectral lines given in the lab manual for hydrogen, we calculate the Rydberg Constant for each line and average the values to obtain an estimate of the constant. These values are shown in Table 3. The average value for the Rydberg Constant is calculated to be $R_H = 10971165.3m^{-1}$ using the spectral lines of hydrogen. Since there are no given uncertainties in this process of calculating Rydberg's Constant, we report its value using the smallest number of significant digits used in its calculation. Therefore, $R_H = 10970000m^{-1}$. To convert R_H to R_{EH} in electronvolts, we first isolate R_{EH} in Equation (1):

$$R_{EH} = \frac{hf}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)}. \quad (9)$$

Substituting in Equation (3), we obtain

$$R_{EH} = \frac{hc}{\lambda\left(\frac{1}{m^2} - \frac{1}{n^2}\right)}. \quad (9)$$

and notice that the denominator is equivalent to the denominator of the expression for R_H in (8). Substituting in Equation (8), we get an expression that allows us to convert R_H to R_{EH}:

$$R_{EH} = hcR_H. \quad (10)$$

Substituting values into this expression, we arrive at a value of $R_{EH} = 13.602483eV$. Again, since there were no uncertainties in the calculation process, we report the final value with the smallest number of significant digits used in the calculation. Therefore, $R_{EH} = 13.60eV$. Compared to the value presented in page 2 of the lab manual ($R_{EH} = 13.605693eV$), this value differs by only a few thousandths of an electronvolt. Given that the precision of the least precise values used in the calculation were to the nearest ten-thousands digit (the calculated value of R_H), this discrepancy is negligible and we can conclude that the two values agree with each other. This value is equivalent to the ionization energy of atomic hydrogen and physically represents the amount of energy required to remove hydrogen's electron.

4.4 Calculating separation of spectral lines in the yellow doublet of sodium

The scale readings of the yellow doublet of sodium were 8.77 and 8.75. Using Equation (7) from Section 4.2, we can convert scale readings to wavelengths. We also calculate the uncertainty of the results using the error propagation formula used in Section 4.1 when calculating the uncertainty in m and b. The scale readings (8.77 and 8.75) correspond to the wavelengths $599.1528nm \pm 1.4289nm$ and $600.3689nm \pm 1.4320nm$, respectively. The expected values of 588.9950 nm and 589.5924 nm lie well outside of the calculated values. This implies a low accuracy in the spectrometer's measurements and/or the accuracy of the calibration detailed in Section 3.1 in the procedure. Furthermore, the two calculated values both lie within each other's uncertainties, meaning that given the device's error, we are unable to confidently distinguish the two lines. We therefore conclude that the spectrometer does not have good resolution.

5 Conclusions

In this lab, we used a tri-prism spectrometer to explore the relationship between the spectrometer's Vernier scale and the wavelengths of certain gases' emission spectra. In doing so, we were able to predict the identity of an unknown gas by comparing known values of wavelengths corresponding to certain colours of light with experimentally derived values. Some portions of this lab, such as our calculation and subsequent confirmation of the value of the Rydberg constant, produced results that were, as per the lab manual, expected. However, there were other sections of this experiment where our experimental results did not align with expected values. For instance, our wavelength measurements for the yellow doublet of sodium did not agree with the values provided in the lab manual. Such discrepancies may have occurred due to a low accuracy in using the spectrometer or faulty calculations in calibrating the device. For future labs, the quality of data could be improved by ensuring that the spectrometer is clearly focused on the images that are to be viewed - as outlined in Section 2 - and by taking multiple measurements of nearby portions of an emissions spectrum in order to account for a wider range of wavelength values for varying intensities of light.

6 Appendix

6.1 MATLAB code

The MATLAB script written for fitting the data sets can be accessed here: `https://drive.google.com/file/d/1tbYxAMEsk5XWpIa7eecJ6gYjs3xlbJR6/view?usp=sharing`.

7 References

References

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[3] M. Faust. "Bohr's hydrogen atom." (), [Online]. Available: `https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_`

Chemistry) /Quantum _ Mechanics / 09 . _The _ Hydrogen _ Atom / Bohr ' s _ Hydrogen _ Atom# : ~ : text = The % 20Bohr % 20Model % 20is % 20very , presence % 20of % 20a % 20magnetic % 20field.. (accessed: 08.15.2020).

[4] *Lab manual: Rydberg Constant and Emission Spectra of Gases*. 2017.