Analysis of the Emission Spectra of Ionized Gases - Calibration, Gas Identification, and Calculation of the Rydberg Constant

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Abstract

We provide an analysis of the emission spectra of gases to calibrate a prism spectrometer, identify an unknown gas, calculate the Rydberg constant, and measure the separation of the yellow sodium doublet. Calibration was performed by applying the Hartmann dispersion relation to known hydrogen and helium spectral lines for the conversion of vernier scale readings to wavelengths. The Hartmann dispersion relation was highly representative of the data set, with an R-squared value of 0.90. The curve fit parameters allowed us to calculate the wavelengths emitted by the spectral lines of an unknown gas. Calculations and spectral line matching led to the identification of Neon gas. The Rydberg constant $R_{\rm H}$ was calculated to be $R_{\rm H} = 1.097 \times 10^5$ cm⁻¹, and the $R_{\rm EH}$ was calculated to be $R_{\rm EH} = 13.60$ eV, with a percent error of -0.07%, demonstrating high accordance with literature values. The measured sodium doublet separation was 1.50 ± 0.13 cm⁻¹. This is significantly lower than the accepted separation of 7.20 cm⁻¹, suggesting significant calibration errors.

1. Introduction

This experiment studies the emission spectra of gases to determine the Rydberg constant ($R_{\rm H}$) by analyzing spectral lines of hydrogen. In this section, we provide a brief background on established equations used to calibrate the spectrometer, identify the unknown gas, and calculate the Rydberg constant. These equations are sourced from the lab manual provided by the University of Toronto department of physics [1].

When a gas in a discharge tube is excited, its atoms emit photons due to electron transitions between discrete energy levels. The energy of an emitted photon (E_f) is given by:

$$E_f = hf = hc / \lambda \tag{1}$$

where h is Planck's constant $(6.626 \times 10^{-34} [J/s])$ and c is the speed of light $(3.00 \times 10^8 [m/s])$, and λ is the emitted wavelength [1]. The empirical Rydberg equation relates the photon energy to the quantum states involved in the transition:

$$hf = R_{EH}(\frac{1}{m^2} - \frac{1}{n^2}) = T_m - T_n,$$
 (2)

where $R_{EH} = 13.605693$ [eV] = $2.179872x10^{-18}$ [J] is the Rydberg constant, m and n are principal quantum numbers, and T_m and T_m are energies [1]. As per the lab manual [1], it is useful to note that the conversion between electronvolts [eV] to joules [J] is given by:

$$1[eV] = 1.60218 \times 10^{-19} [J] \tag{3}$$

For the visible hydrogen spectrum, the Balmer formula [1] is used:

$$\frac{1}{\lambda} = R_H (\frac{1}{2^2} - \frac{1}{n^2}) , \tag{4}$$

where $R_H = 1.097 \times 10^7 \, [m^{-1}]$. In this equation, m = 2 because the Balmer series corresponds to electronic transitions to the second energy level in hydrogen [B]. The spectrometer must be calibrated using known spectral lines of helium and hydrogen. This is done using the Hartmann dispersion relation [1]:

$$y = \frac{m}{\lambda - \lambda_0} + b \,, \tag{5}$$

where y is the scale reading, m and b are calibration constants, and $\lambda_0 = 282.8 \pm 0.4 [nm]$.

2. Experimental Method

This section details the four key experiments performed. The experimental methods used have been applied using the lab manual provided [1], and summarized below. We additionally provide labelled images of the lab set-up in figures 1 and 2 below.

- 1. Calibration of the Prism Spectrometer: A helium discharge tube was placed in the power supply (Figure 1.), and the spectrometer was used to observe the strongest spectral lines. For each spectral line, the readings from the spectrometer scale and Vernier scale were recorded, and added together as the total scale reading. This procedure was then repeated for the hydrogen discharge tube. Using the known wavelengths of both gases, the Hartmann dispersion relation was used to create a calibration curve. This provided the calibration constants m and b used to convert our scale readings into wavelengths.
- 2. *Identification of Unknown Gas*: After calibration, a discharge tube with an unknown gas was placed in the power supply. With the same process as for the helium and hydrogen tubes, the total scale readings for the brightest spectral lines were recorded, and converted into wavelengths using the calibration function obtained in *Step 1*. The measured wavelengths were compared to a list of reference spectra of known gases to identify the unknown gas.
- 3. Determination of the Rydberg Constant: The wavelengths of the hydrogen spectral lines were inputted into Eq. (4) to calculate the Rydberg constant $R_{\rm H}$. Then Eq. (1) and Eq. (2) were used to express $R_{\rm H}$ in electronvolts, resulting in another value for the Rydberg constant $R_{\rm EH}$
- 4. Measuring the Sodium Doublet Separation: The sodium lamp was turned on, and two closely spaced yellow spectral lines were observed using the spectrometer. After summing their scale and Vernier readings to get the total scale readings, the calibration function was used to convert them into wavelengths. The calculated wavenumber separation of the lines ($\Delta \sigma$) were compared to the expected value, which allowed us to assess the accuracy of the spectrometer's resolution.



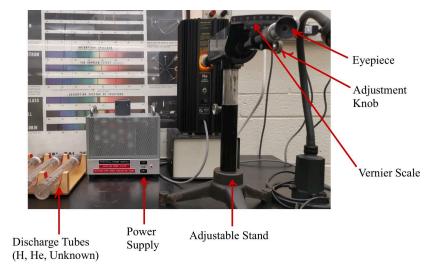


Figure 1. Helium discharge tube after being placed on the power supply.

Figure 2. Experimental setup.

3.1 Calibration with the Hartmann Relation Method

In this section we demonstrate the calibration of the vernier scale readings by relating the observed scale readings of known wavelengths of Hydrogen and Helium. This is performed using the Hartmann dispersion relation (Eqn. 6), where the separation of the spectral lines as measured using the vernier scale can be linearly related to the inverse of the difference between each line's wavelength.

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

 λ_0 is a function of the optics of a spectrometer and is provided to be 282.8 ± 0.4 nm. We take a scale uncertainty of half of the smallest reading (\pm 0.005) and include the measured scale readings in Table 1 below. Calculations of $(\lambda - \lambda_0)^{-1}$ for each of the spectral lines' wavelengths is also included in Table 1 below.

Table 1: Scale Readings for Known Wavelengths of Light Emitted from Prism Spectrometer for Hydrogen and Helium

Gas	Colour	λ, nm	Total Scale Reading (± 0.005)	$\frac{1}{(\lambda - \lambda_0)} \left[m^{-1} \right]$
Не	Blue	471.3	12.55	0.0053
Не	Blue	492.2	11.55	0.0048
Не	Cyan	501.6	11.08	0.0046
Не	Yellow	587.6	08.95	0.0033
Не	Red	667.8	07.15	0.0026
Н	Violet	410.2	14.10	0.0078
Н	Violet	434.0	15.15	0.0066
Н	Blue	486.1	11.85	0.0049
Н	Red	656.3	7.50	0.0027

The scale readings ("y") were plotted against $(\lambda - \lambda_0)^{-1}$ ("x"), and fit to a line as per the Hartmann dispersion relation as shown below in Fig. 3.

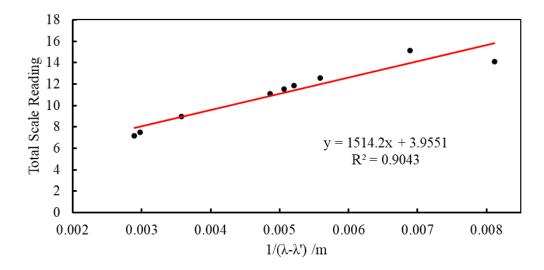


Figure 3: Calibration Curve for Known Wavelengths of Light

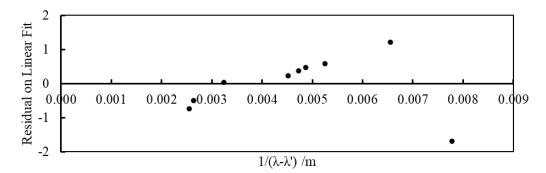


Figure 4: Residuals on the Linear fit of Known Wavelengths using the Hartmann Dispersion Relation

Vertical error bars with an uncertainty of \pm 0.005 were included however the high precision of the instrument resulted in the error bars being too small to be visually significant. The line of best fit was produced using Excel's least squares estimator, and shown to be $y = 1514.2 (\lambda - \lambda_0)^{-1} + 3.96$. The fit was accurate with an R² value of 0.9043, demonstrating the Hartmann dispersion relation was representative of the observed data points for the Hydrogen and Helium spectral lines. There appeared to be more deviation between the line of best fit and the observed data points at the longest and shortest wavelengths, possibly representative of non linear dispersion at the tail ends of the visible light spectrum. We evaluate a second criterion of best fit using the residual values plotted in Fig. 4 to calculate the root mean squared deviation (RMSD) of the data set [7].

$$RMSD = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x - f(x))^2} = 0.808$$

The RMSD should reflect or be approximately close to the experimental uncertainty [3]. The discrepancy between the assumed uncertainty based on the smallest vernier scale reading (0.005) and the RMSD (0.808) is visually represented by the fact that none of the error bars fall on the line of best fit. This suggests that the uncertainty we took was unreasonably low, and that the calibration check we performed using the sodium yellow doublet lines should have been prepared more carefully (further discussed in Section 6).

We calculate the wavelength λ for each of the spectral lines of the unidentified gas by taking the inverse of the linearly fit function to calculate $(\lambda - \lambda_0)^{-1}$ as shown below.

$$\frac{1}{(\lambda - \lambda_0)} = \frac{y - 3.96}{1514.2} \Rightarrow \lambda = \frac{1514.2}{y - 3.96} + \lambda_0, \tag{6}$$

where y is the total scale reading.

We include the calculated λ values for the unidentified gas in a table below.

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	Expect Range of Wavelengths	Total Scale Reading, "y"	Calculated			
	λ for Observed Colour (nm)	(±0.005)	Wavelength λ (nm)			
Blue	450 - 495	10.40	518 ± 242			
Green	495 - 570	9.71	546 ± 274			
Yellow	570 - 590	9.00	583 ± 327			
Yellow-Orange	570 - 620	8.74	599 ± 354			
Orange	590 - 620	8.45	620 ± 394			
Red	620-750	7.60	698 ± 592			

Table 2: Wavelengths Calculated for the Spectral Lines of an Unknown Gas "X".

The values calculated all fall within the expected range given the colours qualitatively observed except for the blue line. The blue line was calculated to have a wavelength of 518 nm, which was longer than expected. This shade of blue might have been a blue-green, or the calibration curve might be less accurate at shorter wavelengths.

3.2 Uncertainties and Errors in Calibration

The uncertainty in an instrument is typically half of the smallest readable value [4]. The smallest readable unit on the Vernier is 0.01 divisions. Therefore, the uncertainty in the scale reading, Δy , is given below by equation 7.

$$\Delta y = \frac{0.01}{2} = \pm 0.005 \text{ divisions} \tag{7}$$

Here we note that the separation of the sodium doublet lines was entirely clear, making it reasonable to take the equipment's specificity as our uncertainty. We further comment on our uncertainty calculations under section 6, on the calculation of the separation of the spectral lines for the yellow doublet of sodium, a common resolution optimizing technique.

Given we depended on the linear fit parameters for our calculations of λ , we first calculated the uncertainty on the fit parameters (Figure 3). The uncertainty for the slope and the y-intercept were determined to be ± 0.25 and ± 0.0032 , respectively, with their calculations demonstrated below. All formulae for uncertainty propagation and error calculations have been sourced from the uncertainty propagation guide [5] and the uncertainties on linear fits guide [6] respectively.

The slope uncertainty s_m and the y-intercept uncertainty s_b can be calculated using the following 2 formulae [6].

$$s_m^2 = N \frac{s_{yx}^2}{\Delta}$$
 and $s_b^2 = \frac{s_{yx}^2 \sum x_i^2}{\Delta}$

The Δ component of the slope uncertainty was calculated as follows.

$$\Delta = N \sum x_i^2 - (\sum x_i)^2 = 7 \times 1.69 \times 10^{-4} - 0.032^2 = 1.88 \times 10^{-4}$$

where N ranges from 1 to 7 due to the 7 data points we have collected. Then, the variance of y(x) was calculated using the formula,

$$s_{y,x}^{2} = \frac{1}{N-2} \sum [y_i - (b + mx_i)]^2 = \frac{1}{7-2} [13.25 - (6.8411 + 844.9 \times 0.0078)]^2 = 0.429.$$

Using the values obtained, the standard deviation of the slope s_m is taken as the square root of

$$s_m^2 = N \frac{s_{y,x}^2}{\Delta} = 7 \times \frac{0.429}{1.88 \times 10^{-4}} \rightarrow s_m = 0.25,$$

and the standard deviation of the y-intercept s_h as the square root of

$$s_b^2 = \frac{s_{yx}^2 \sum x_i^2}{\Delta} = \frac{0.429 \times 1.69 \times 10^{-4}}{1.88 \times 10^{-4}} \rightarrow s_b = 0.0032$$
.

We propagate the uncertainties to our calculations of λ using the standard uncertainty propagation formula.

$$\lambda = \frac{m}{y-b} + \lambda_0 \Rightarrow \Delta \lambda = \lambda \sqrt{\left(\frac{s_m}{y-b}\right)^2 + \left(\Delta y \frac{-m}{(y-b)^2}\right)^2 + \left(s_b \frac{m}{(y-b)^2}\right)^2 + \left(\Delta \lambda_0\right)^2}$$

$$\frac{\Delta \lambda}{\lambda} = \sqrt{\left(\frac{0.25}{y - 3.96}\right)^2 + \left(0.005 \frac{(-1514.2)}{(y - 3.96)^2}\right)^2 + \left(0.0042 \frac{1514.2}{(y - 3.96)^2}\right)^2 + (0.4)^2}$$

$$\frac{\Delta \lambda}{\lambda} = \sqrt{\frac{0.0625}{(y - 3.96)^2} + \frac{97.76}{(y - 3.96)^4} + 0.16}$$

4. Identification of the Unknown Gas

In this section we qualitatively identify the unknown gas by matching the spectral lines observed to the known emission spectra of gases provided in figure 7 [1]. The calculated wavelengths for each spectral line observed are included in Table 2.

Figure 6. shows the spectrum of the unknown gas in which we have observed through the prism spectrometer. As shown, there are vibrant red, orange, yellow, and some green lines. Compared to the reference spectra provided by the Lab manual and shown by Figure 7 [1], we guess that our unknown gas is neon based on the strong match with the emission spectrum of neon shown. According to the provided spectral data, neon exhibits several distinct lines in the red and orange regions, particularly around 703.2 nm, 667.8 nm, 659.9 nm, 653.3 nm, and 650.7 nm. These wavelengths correspond closely to the dominant colors of the spectral lines of the unknown gas shown in Figure 7. Moreover, when observing the discharge tube of the unknown gas shown in Figure 7., both our observed tube and the neon tube in Figure 5. have the similar intense red, almost molten glow, which further reinforces our guess that the unknown gas is neon.



Figure 5. Unknown gas inside the discharge tube is excited using a high-power voltage source.

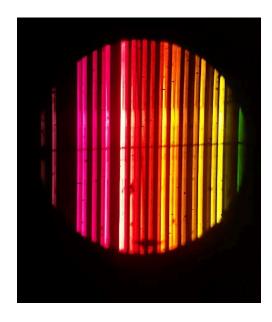


Figure 6. Spectral lines of unknown gas.

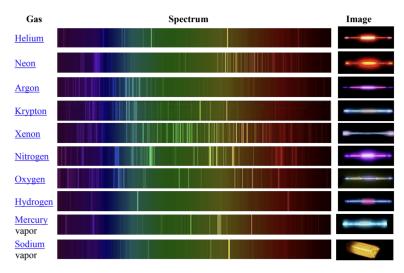


Figure 7. Emission spectra of gases and vapors under low pressure. Image extracted from Lab Manual [1].

5. Calculating the Rydberg Constant

We apply equation 2 to the wavelengths of hydrogen to calculate the Rydberg Constant (R_H). The values of n are given by the Balmer series of electron transitions in the Hydrogen atom [2].

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	Colour	n	λ (nm)	$R_{\rm H} (10^5 {\rm cm}^{-1})$		
	Violet	6	399	1.097		
	Violet	5	384	1.097		
	Blue	4	450	1.097		
	Red	3	1490	1.097		

Table 3: Rydberg Constant Calculated for the Four Spectral Lines of Hydrogen.

We use the provided literature values of the wavelengths of hydrogen which have no attached uncertainty. This is a limitation to our uncertainty propagation, and we instead address the uncertainty in the $R_{\rm H}$ calculation by calculating the range uncertainty of the average value calculated.

The mean $R_{\rm H}$ from Table 3 is 1.097×10^5 cm⁻¹, with a range error of ± 0.00018 cm⁻¹. This demonstrates high agreement between the values of $R_{\rm H}$ calculated.

We proceed to calculate the Rydberg energy constant R_{EH} below using formulae 1 and 2. The relationship between R and R is derived as follows.

Given Balmer's formula [1], we have the following formula for energy.

$$E_f = \frac{hc}{\lambda} = hc R_H (\frac{1}{m^2} - \frac{1}{n^2})$$
, where m was taken to be 2 for the Hydrogen atom [1].

The Rydberg equation provides a similar relationship between the difference in energy levels and total energy emitted.

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

Equating the two expressions for E_f we have the following relationship between R_H and R_{EH} .

$$R_{EH}(\frac{1}{m^2} - \frac{1}{n^2}) = hc R_H(\frac{1}{m^2} - \frac{1}{n^2}) \Rightarrow R_{EH} = hc R_H$$

Given a planck's constant of h = 6.626×10^{-34} J·s [1], a speed of light of c = 299 792 458 m/s [11], and an average calculated $R_{\rm H} = 1.097 \times 10^{5}$ cm⁻¹, we calculate $R_{\rm EH}$ below.

$$R_{EH} = hc R_{H} = (6.626 \times 10^{-34} J \cdot s)(299792458 m/s)(1.097 \times 10^{7} m^{-1}) = 2.179 \times 10^{-18} J$$

Converting this value to eV we have:

$$R_{EH} = 2.179 \times 10^{-18} J \times \frac{1[eV]}{1.60218 \times 10^{-19} [f]} = 13.60 \ eV$$

This is nearly identical to the literature value of 13.61 eV.

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

The small separation of the spectral lines of the yellow doublet of sodium has been used in determining the resolving power of diffraction gratings [8]. We provide an observation and calculation of the separation of the doublet using the previous calibration of the system measurements.

	Total Scale (y)	Wavelength (λ) [nm]
Spectral Line #1	9.14	$\lambda_1 = 574 \pm 0.31$
Spectral Line #2 9.06		$\lambda_2 = 579 \pm 0.31$

Table 4. Calculation of wavelength of spectral lines in the yellow doublet of sodium.

The separation of the spectral lines in the yellow doublet of sodium was calculated to be 1.50 ± 0.13 cm⁻¹. The wavelengths of the two yellow spectral lines emitted by sodium were measured to be $\lambda_1 = 574 \pm 0.31$ nm and $\lambda_2 = 579 \pm 0.31$ nm, calculated by inputting the original total scale readings of 9.14 and 9.06, respectively, into eq. (6) . The wavenumber separation ($\Delta \sigma$) is then calculated using the following equation, where the wavelengths in the denominators are converted to [cm] by multiplying by a factor of 10^{-5} :

$$\Delta \sigma = \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{1}{574 \times 10^{-5}} - \frac{1}{579 \times 10^{-5}} = 1.50 \pm 0.13 \ [cm^{-1}].$$

The known wavelengths of the sodium D-line doublet are $\lambda_1 = 589.0$ nm and $\lambda_1 = 589.6$ nm [1], which yields a wavenumber separation of $\Delta \sigma = 7.20$ cm⁻¹ [9]. Our value is much lower than the expected value. The separation value should have been close to the accepted value given a proper calibration of the experimental set-up. However, the significant difference between the accepted value and the value we

measured likely suggests systematic issues in calibration, which will be explored more in detail in the discussion.

7. Discussion

The following section discusses the four key results of this investigation - the calibration process, identification of the unknown gas, calculating the Rydberg constant, and calculating the separation of the spectral lines in the yellow doublet of sodium.

7.1 Discussion - Calibration through the Hartmann Dispersion Relation

The Hartmann dispersion relation was highly representative of the linear relationship between the spectral line separation and the wavelengths of each spectral line. The R^2 value 0.90 represents a very good linear fit. It is worth noting that the error bars on figure 3 are nearly not visible as we took an experimental uncertainty value of \pm 0.005, which is half the smallest analog reading of the vernier sensor. We additionally calculated the root mean squared deviation of the y values (vernier sensor readings) from the linear fit predictions, and calculated an RMSD of 0.80, which is incredibly high given the assumedly low uncertainty value of \pm 0.005 for the y value. This reflects an inconsistency between what we assumed was a reasonable uncertainty due to the high resolution of the sodium doublet lines, and what the RMSD was calculated to be. This suggests that we didn't image the sodium doublet lines at the correct focal length or measure the separation accurately enough.

Additionally, the use of more reference spectral lines would typically increase the accuracy of the spectrometer calibration. However, since only a few helium and hydrogen spectral lines were used, the linear fit (ie. fit for the scale readings as a function of $(\lambda - \lambda_0)^{-1}$) might not have been precise enough, thereby introducing systematic wavelength shifts. For example, we observe greater residuals at the tail ends of the visible light spectrum for the hydrogen and helium lines used in calibration. The Hartmann dispersion relation assumes linear dispersion, however much shorter and much longer wavelengths can possibly demonstrate non linear dispersion that could result in a linear fit with greater errors.

The unknown gas' observed colours aligned with what we calculated the wavelengths to be, with five of the six measured values falling within the expected wavelengths given the observed colours (Table 2). This reflects an accurate line of best fit, regardless of the accuracy of the uncertainties calculated.

7.2 Discussion - Identification of the Unknown Gas

We identified the unknown gas to be Neon based on qualitative matching of the spectral lines to the spectral line reference image provided by the lab manual [1]. The slight deviation in the measured wavelengths compared to the wavelength values on the reference spectra could be due to calibration uncertainties from the scale reading-to-wavelength conversion function we derived from the calibration graph. Instrumental resolution limitations could be another cause for the deviations because this could have affected the accuracy of the cross-hair directly matching on the centre of each spectral line, which would affect the scale reading and therefore, the wavelength. Parallax reading errors and unfocused view of the spectral lines could have both contributed to inaccurate readings and thus inaccurate calibration of the spectrometer readings.

7.3 Discussion - Calculating the Rydberg Constant

The Rydberg constant was calculated using values provided for the spectral lines of Hydrogen. These values had no uncertainties attached to them, and this seemingly infinite uncertainty is reflected in

the extremely low range error demonstrated in the four values calculated for the Rydberg constant (1.097 \times 10⁵ \pm 0.00018 cm⁻¹). This reflects that these values were not determined by our particular experimental set-up, and are instead the result of well studied Hydrogen spectra.

The relationship between the Rydberg constant (R_H) and the Rydberg energy constant (R_{EH}) was derived based on Equations (1), (2), and (4), and calculated to be 13.06 eV. This is an interesting result that reflects the amount of energy required to remove an electron from the n=1 level of the Hydrogen atom, or Hydrogen's ground state energy [10].

7.4 Discussion - Calculating the Separation of Spectral Lines in the Yellow Doublet of Sodium

When looking through the eyepiece, we could clearly distinguish between both of the yellow spectral lines. The uncertainty in our measurements must be less than the separation, and therefore it would depend on the equipment. Since the scale on the spectrometer and the Vernier scale were used to get the total scale reading, and then converted in wavelength, the uncertainty in the scale reading would be equivalent to what is calculated in Eq. (7).

The calculated separation of the spectral lines, $\Delta \sigma = 1.50 \pm 0.13$ cm⁻¹, was lower than the accepted theoretical value of $\Delta \sigma = 7.20$ cm⁻¹ [9]. It is unlikely that much of this difference is caused by the spectrometer's resolution, as the two yellow spectral lines were observed to be clearly distinguishable (ie. minimal blur) when looking through the eyepiece. However, this difference could be caused by human error, as aligning the eyepiece cross-hair from one spectral line to the other could result in inaccurate wavelength measurement, given the very small distance between both spectral lines. This would directly affect the wavelength measurement, and therefore lead to inaccuracies in the separation. Moreover, possible inaccuracies or biases in the fitted slope m and intercept b could cause a consistent underestimation of the converted wavelengths, which could explain the reason why our measured separation is significantly smaller than the expected separation.

7.5 General Improvements for Future Considerations

- 1. *Increasing calibration points*: This will allow for a calibration curve that can be used to create a more accurate function for the scale reading-to-wavelength conversion by minimizing the effect of random errors.
- 2. *Using higher-resolution optical instruments*: This will allow a better distinction between very closely spaced spectral lines, resulting in a more accurate measurement for the wavelengths.

8. Conclusion

This experiment involved the calibration of a prism spectrometer, identification of an unknown gas, calculating of the Rydberg constant, and measurement of spectral lines in the sodium doublet. During calibration, we used known hydrogen and helium spectral lines, and applied the Hartmann dispersion relation to derive a function that converts scale readings into wavelengths. This function was then used to calculate the wavelengths of an unknown gas, which was compared with reference spectral lines it strongly matched with to give us neon. We used wavelength values for hydrogen provided by the lab manual [1] to calculate the Rydberg constant. The Rydberg constant R_H was calculated to be $R_H = 1.097 \times 10^5$ cm⁻¹, and R_{EH} was calculated to be $R_{EH} = 13.60$ eV, with a percent error of -0.07%, demonstrating high accordance with literature values. Finally, the separation of the sodium D-line doublet was measured, providing a wavelength separation of 1.50 ± 0.13 cm⁻¹, which is significantly lower than the known value of 7.20 cm⁻¹. This difference suggests inaccuracies in the calibration function's slope and intercept, which

may have caused an underestimation of wavelength differences, and therefore result in a compressed separation value.

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