

Measuring the Rydberg constant by observing the Balmer spectral series of hydrogen.

Abstract

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The main aim of this experiment was to determine a value for the Rydberg constant for hydrogen R_H , by using a grating monochromator calibrated on Mercury spectral lines to measure the wavelengths of hydrogen spectral lines, as outline in the lab script OP13: The Grating Monochromator^[1]. The value measured was $1.0967 \pm 0.0002 \times 10^7 \text{ m}$, which is within error of our theoretically determined result.

Introduction

In this experiment the goal is to setup a Czerny-Turner monochromator with, calibrate the instrument by measuring the wavelengths of the visible spectral lines of mercury and comparing this to a reference spectrum to produce a calibration curve. Then a hydrogen capillary discharge tube was setup and the hydrogen spectrum observed through the monochromator, and with the wavelengths of the spectral lines measured determine a value for the Rydberg constant using the Rydberg formula.

$$\frac{1}{\lambda_{vac}} = R_X \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1) \quad R_X = \frac{R_\infty}{1 + \frac{m_e}{M}} \quad (2) \quad R_\infty = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{m_e e^4}{4c\pi\hbar^3}. \quad (3)$$

Using the NIST CODATA^[2] values of $R_\infty = 1.09737 \times 10^7 \text{ m}$, $m_e = 9.10938 \times 10^{-31} \text{ kg}$, $m_p = 1.67262 \times 10^{-27} \text{ kg}$, we calculate that $R_H = 1.09677 \times 10^7 \text{ m}$. This is our expected experimental result that we should obtain from our data.

History

In 1885 Balmer^[3] discovered that the wavelengths of the spectral series could be characterized by the formula $\lambda = h \left(\frac{n^2}{n^2 - 2^2} \right)$, where Balmer empirically determined the constant $h = 3645 \times 10^{-7} \text{ mm}$. Balmer did all this work by observing the spectral lines in the corona of the sun, and hence his observed λ was measured in air. Then in 1890 Rydberg^[4] continued work on this and determined the Rydberg. It happens that the Balmer formula is the special case of the Rydberg formula where $n_2 = 2$. The expression of Rydberg's formula in terms of wavenumber instead of wavelength was fundamental to Bohr's development of his model of the atom, where electrons occupy discrete energy levels characterised by their level number n , and hence when electrons transition from level n_1 to n_2 they emit a photon of wavelength λ_{vac} . This work formed the basis of early quantum theory as it showed that electrons must occupy discrete energy levels, and that the energy of these levels was proportional to the inverse square of that energy levels principal quantum number.

Method

The procedure followed for this experiment was close to the one described by the lab script^[1] for this practical. In the morning, the Czerny-Turner monochromator was setup with its surrounding optical system and then calibrated using the blue mercury lamp. A schematic of the monochromator and its internal parameters are shown in Figure 2 and Table 1 below.

The complete apparatus used is shown in Figure 1. On the left-hand side of the image the hydrogen capillary discharge tube is setup in position with the focusing lens in the centre of the image. The blue box is the monochromator which the diagram shows the internals of, with the micrometre on the far side of the box and hence not visible in this image. Finally on the right of the image the eyepiece can is set close to the aperture of the monochromator housing, with the crosshairs housed inside this aperture. The eyepiece used to help magnify the spectral lines and allowed the fainter lines to be seen more easily, and it also allowed the crosshairs to be observed when the eyes were focused at a far distance, reducing the stress on the eyes and making the experiment easier to perform.

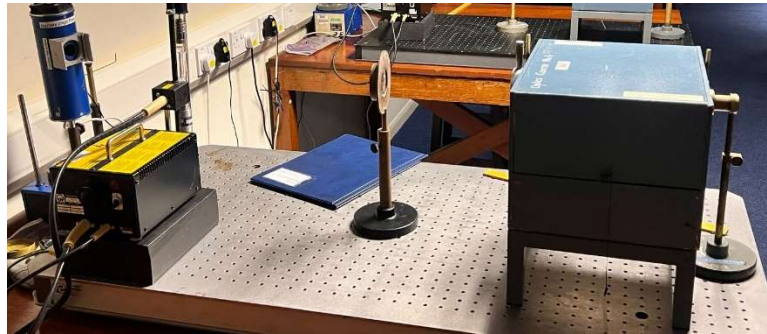


Figure 1: The complete optical setup, with the hydrogen lamp installed.

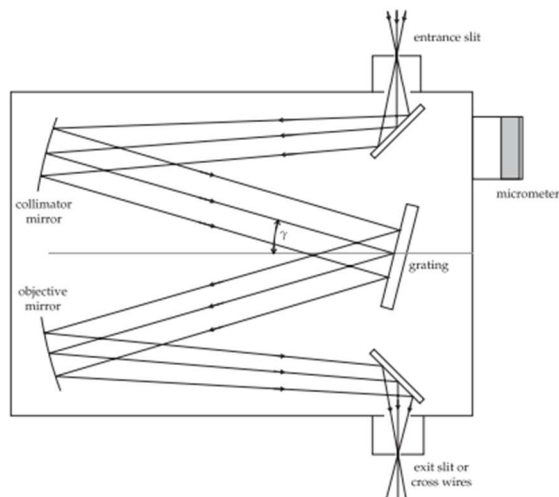


Figure 2, the Czerny-Turner Monochromator.

the red end of the spectrum, we recorded our data and fed it into the python script that accompanies the lab script. The code uses the scipy curve_fit library to fit a quadratic calibration curve to our data. The theory derived in the lab script shows that there should be a linear relationship between z and λ but mechanical imperfections means that this relationship does not hold perfectly. This can be seen by plotting the residuals because of a linear fit, from which a trend will be seen. However, with a quadratic fit there is no clear trend in the residuals, meaning our approximation much better fits our data and we have a much more accurate result.

Once the apparatus was setup accordingly, the mercury lamp was switched on and we took some time to familiarize ourselves with the mercury spectrum, so that when the measurements for the calibration spectra were taken I was familiar with where the spectral lines would be and could identify them easily, and this would hopefully reduce the chance of introducing an accidental error like a backlash error that could happen if I missed a line. After taking 3 complete sweeps of the spectrum, starting from the UV end and working upwards in wavelengths towards

Grating size	48 mm x 48 mm
Ruling frequency ($1/d$)	1200 lines/mm
Mirror diameter	63.5 mm
Mirror radius of curvature	439 mm
Czerny-Turner angle, γ	$25^{\circ}28'$
Length of sine-bar, l	75.24 mm

Table 1: Design parameters of the Czerny-Turner monochromator.

The next part of the experiment involved changing out the Mercury lamp for a fragile Hydrogen discharge tube. This step was difficult for several reasons, as the hydrogen lamp produced a much lower intensity beam than the mercury and was hence harder to see, the beam of light was not always vertical and the lamp had to be carefully adjusted in its holder so that the

focused beam completely illuminated the slit, otherwise it could appear that the slit was lit at an angle, and this causes the spectral lines to look slanted when viewed through the eyepiece, introducing error in the position measurement of the spectral lines that could not have been accounted for during the calibration procedure. Every other piece of the apparatus was left unchanged. If the lines observed from the hydrogen lamp were too dim to be visible it was possible to open up the slit a bit, however this could slightly change the position of our spectral lines and introduce an error into our final reading, so fortunately we were able to avoid this. Having swept down to the purple/UV end of the spectrum, we spent a long time trying to locate the H_δ spectral line as it was a very faint purple colour. I then spent some time just familiarising myself with the spectrum, which was important since not all the spectral lines observed were from the hydrogen spectrum. There were several extra red and green lines in the spectra which were due to H_2 and H_2O . It was also possible to observe a 2nd order diffraction green/aqua peak in the red section, and this is due to the human eye's increased sensitivity to green light. To obtain the data we did 3 sweeps of the spectrum starting at the UV end and working up, taking measurements at the centre of each spectral line and taking care to avoid backlash error. This was then analysed by using the mean of the 3 measurements to obtain a value of the wavelength, with the error in the wavelength being determined by $2a\lambda + b$, and this value being used with the appropriate value of n_2 in (1) to determine several values for the Rydberg constant. Finally, all of these were combined in a weighted mean to find our final value.

Results & Analysis

Figure 3 is a copy of the reference spectra used to calibrate the monochromator in the morning. The wavelengths for the reference spectra values for the spectra could also have been obtained

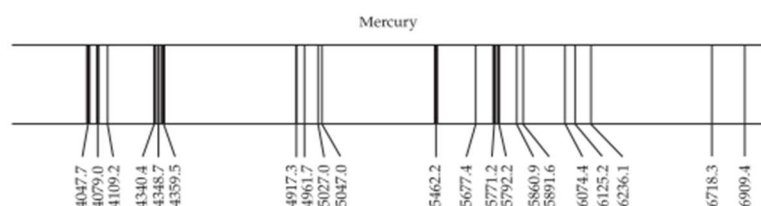


Figure 3: The visible spectral lines of a Mercury discharge tube.^[1]

from NIST^[5], which might have been useful if the experiment was setup more precisely such that the fine detail in the spectral lines as given in the NIST data could be observed.

The residuals from the curve fitting python script with a

linear and quadratic fit are shown below in Figures 4 and 5. It is clear from the linear residual plot that there is a definite pattern in the residuals, and this tells us that our linear model does not accurately represent the system in real life. This is probably due to mechanical

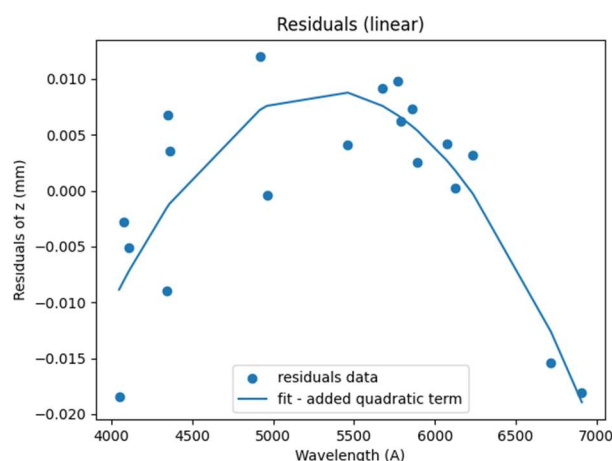


Figure 4: Residuals of a linear calibration curve

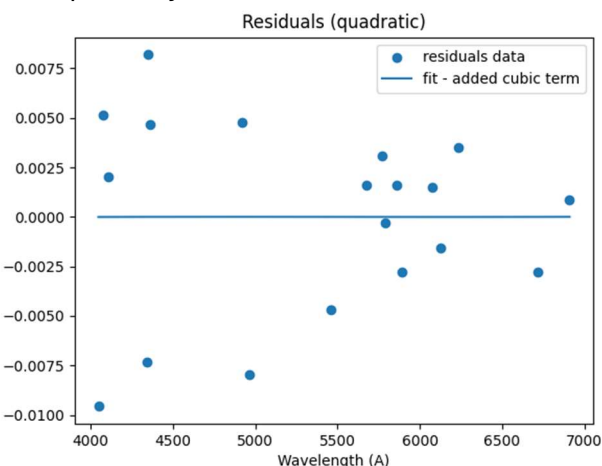


Figure 5: Residuals of a quadratic calibration curve

imperfections in the operation of the sine-bar mechanism. However, we can still obtain a more accurate calibration curve, as by moving to a quadratic fit we see that the residuals are both much smaller but also randomly distributed. This tells us that we have found a better fit for our calibration curve and can proceed with the experiment.

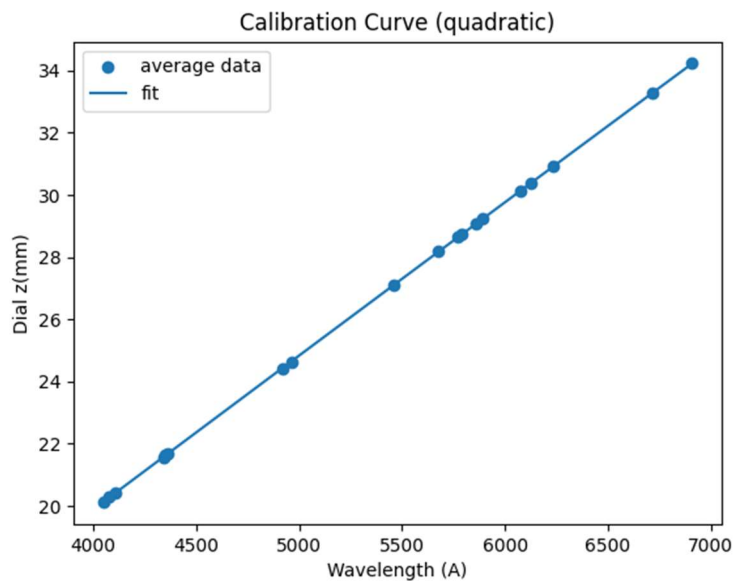


Figure 6: Monochromator calibration curve

Wavenumber/Å	Z1/mm	Z2/mm	Z3/mm
4047.7	20.11	20.11	20.11
4079.0	20.26	20.29	20.29
4109.2	20.43	20.42	20.43
4340.4	21.57	21.57	21.55
4348.7	21.61	21.63	21.62
4359.5	21.67	21.67	21.67
4917.3	24.44	24.42	24.43
4961.7	24.64	24.63	24.64
5462.2	27.11	27.11	27.11
5677.4	28.17	28.18	28.18
5771.2	28.64	28.64	28.64
5792.2	28.75	28.73	28.74
5860.9	29.08	29.07	29.09
5891.6	29.22	29.23	29.23
6074.4	30.14	30.13	30.12
6125.2	30.38	30.38	30.37
6236.1	30.93	30.93	30.92
6718.3	33.29	33.29	33.28
6909.4	34.25	34.21	34.22

Table 2: Morning Calibration Data

Figure 6 shows the final quadratic calibration curve used in the experiment. From the residuals show in Figure 5 no clear outliers were identified and so no data points were excluded from the calibration data.

$$z = a\lambda^2 + b\lambda + c \quad a = -1.105 \times 10^{-8} \quad b = 5.050 \times 10^{-3} \quad c = -1.418 \times 10^{-1}$$

The data taken for the afternoon is shown in Table 3. Although 4 lines were expected, 5 were recorded as I was unable to determine which of the two red lines and 30.55mm and 32.54mm was the H_α line. The incorrect line was easily identified later in analysis as the 30.55mm line. Following this, the readings of z were averaged and these used to calculate a value of the Rydberg constant for hydrogen using equation (1). This is shown in Table 4.

Line	Z1/mm	Z2/mm	Z3/mm
1	20.38	20.37	20.38
2	21.57	21.58	21.57
3	24.16	24.16	24.15
4	30.55	30.54	30.55
5	32.53	32.54	32.54

Table 3: Spectral lines observed from hydrogen lamp.

n	Mean Z / mm	Wavelength / m	Error	%Error	R_H / m^{-1}	R_H Error	Weights	Weighted Value
6	20.387	4101.86	2.02	4.916E-04	1.097064E+07	5.393E+03	3.438E-08	0.3772
5	21.573	4341.26	2.02	4.650E-04	1.096893E+07	5.100E+03	3.844E-08	0.4217
4	24.157	4863.33	2.02	4.160E-04	1.096642E+07	4.562E+03	4.804E-08	0.5269
3	32.537	6565.30	2.04	3.105E-04	1.096675E+07	3.406E+03	8.622E-08	0.9456

Table 4: Final analysis of the Hydrogen spectral lines.

$$\bar{x} = \frac{\sum \frac{x_i}{\sigma_i^2}}{\sum \frac{1}{\sigma_i^2}}, \quad \bar{\sigma} = \sqrt{\frac{1}{\sum \frac{1}{\sigma_i^2}}}$$

These values were then combined in a weighted average to obtain a value of $R_H = 1.0697 \pm 0.0002 \times 10^7 m$. This is an extremely good result as the theoretical value of R_H calculated above using (3) was $1.06977 \times 10^7 m$, and this is within the error of our measurement. This high

accuracy is due to the time taken in setting up the experiment, the addition of the quadratic term in the calibration curve to account for mechanical imperfections in the physical apparatus, and the careful data taking procedure that ensured no back-lash error by always approaching the spectral lines from the same side and making sure to not go beyond the limits of the micrometre. The main factor in the limit of our measurements is the resolution of the micrometre and the error due to our calibration curve, which are both about equal. Reducing the error in the micrometre could mean moving to a large apparatus with a larger sine bar, such that a similar angular displacement in the grating would result in a larger displacement in the position of the micrometre, improving the precision of that reading. Improving the calibration curve is more difficult, as we are limited by the number of visible spectral line that the calibration curve can be based off.

Conclusion

Our experimental value of $1.0967 \pm 0.0002 \times 10^7 \text{ m}$ is consistent with our theoretically calculated value of $1.09677 \times 10^7 \text{ m}$. This shows that our method of using a quadratic calibration curve did reduce error in our measurement of the wavelengths of spectral lines. Checking the wavelengths of the spectral lines against the NIST database^[5], we can see that our values are correct to about 0.5nm or 0.1%. We are now approaching the point where the limiting factor in our error of wavelength is the resolution of the micrometre and the width of the spectral lines observed, as to get a consistent reading of the wavelength of a spectral line we would need a finer line, as when taking measurements for some of the wider spectral lines it was difficult to position the crosshairs accurately in what appeared to be the centre of the line. Additionally, the light intensity of the source was a limiting factor as well, as the H_δ line was difficult to observe, and with a narrower slit to observe sharper spectral lines, not enough light would pass through the slit for the dim spectral lines to be observed.

References

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*It should be noted that all wavelengths stated in this report are measured in vacuum, but those referenced on NIST are measured in air.