

Observing the Quantum States and Spectra of Gases

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1 Introduction

This lab will cover spectral analysis of gases and the transmittance and absorption of light through differently-colored solutions. A spectrum plots the intensity of light as a function of wavelength, where the intensity is a count of the number of photons detected at a given wavelength.

Using our knowledge of quantum mechanics, not all wavelengths are equally likely; in fact, only a select few wavelengths of light will be emitted when excited, corresponding to the energy levels of electrons in the atom. For hydrogen specifically, the energy of emitted photons is given as the Rydberg formula:

$$E = R_{EH} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1)$$

where E is the energy of the emitted photon, R_{EH} is the Rydberg constant with $R_{EH} = 13.605693 \text{ eV}$, and n_1 and n_2 are the initial and final energy levels of the electron respectively. Additionally, using the formulas for the energy of a photon $E = hf$ and the speed of light $c = f\lambda$, we can equivalently express the wavelength of the emitted photon as:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2)$$

where $R_H = \frac{R_{EH}}{hc}$ is the Rydberg constant (in different units) with $R_H = 1.097373 \times 10^7 \text{ m}^{-1}$.

These equations can be further generalized using the Bohr model of the atom, with which we can express the energy levels of the electrons in a hydrogen-like atom as:

$$E_n = -\frac{R_{EH}Z^2}{n^2} \quad (3)$$

Where n is the principal quantum number, and Z is the atomic number of the element. Using this model, we can accurately predict the wavelengths of light emitted by hydrogen and other hydrogen-like atoms.

However, the relative intensities are affected by other factors, one of which are the selection rules. These rules dictate which transitions are allowed and which are forbidden. Such selection rules include $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$, and $\Delta s = 0$. Violations of these rules leads to a quantumly forbidden transition, and thus a lower intensity of light emitted at that wavelength. Other exceptions also exist, but spectral analysis has been well documented, so the expected wavelengths of light emitted by hydrogen and other non-hydrogen-like atoms are well known.

In the first part of the lab we will obtain the experimental values for the mercury spectrum, and compare them to the expected values. We will also obtain a linear fit of both the expected and real wavelength as well as the expected and real energies. This will allow us to calibrate the readings for the spectrometer for the rest of the lab.

The second part of this lab will cover the transmittance and absorption of light through differently-colored solutions. The governing equations for transmittance and absorption are given by:

$$T = \frac{I}{I_0} * 100\% \quad (4)$$

$$A = -\log_{10}(T/100\%) \quad (5)$$

where the transmittance T is expressed as the percentage of incident light I_0 that passes through the solution I and the absorbance A is a measure of the amount of light absorbed by the solution. Knowing the transmittance and absorption at various wavelengths can reveal why we perceive the solution as a certain color under white light.

These can be used to determine various components of the solution, such as the concentration of the solute via the Beer-Lambert Law, or as we will investigate, the band gap of the solute. The absorption edge of a solution is the wavelength where there exists a sharp increase in the absorbance of light, and is related to the band gap of the solute by the energy of the photon at this wavelength:

$$E_g = \frac{hc}{\lambda_{edge}} \quad J = \frac{hc}{1 \times 10^{-9}e} \frac{1}{\lambda_{edge} [nm]} \text{ eV} \quad (6)$$

This energy represents the required energy to excite an electron from the valence band to the conduction band, leading to the absorption of that photon: less energized photons are simply transmitted and do not interact with the solution. A semiconductor should have a band gap of about 4 eV.

2 Method

This lab is broken up into 6 parts, the first four of which deal with the spectral lines of gases, and the last two of which deal with the spectrums of differently dyed solutions.

Figure 1 shows the setup for the gas portion of the lab, with a spectral tube connected to a power supply. The clamp stand is used to hold the probe in place above the tubes, and a diffraction grating is used to observe the spectral lines. These lines are displayed on a computer (not shown), and images of the lines and key values are taken for analysis. When measuring peaks, the value is taken at the peak of the line, and the uncertainty is taken as the full width at half height (FWHH) of the line.

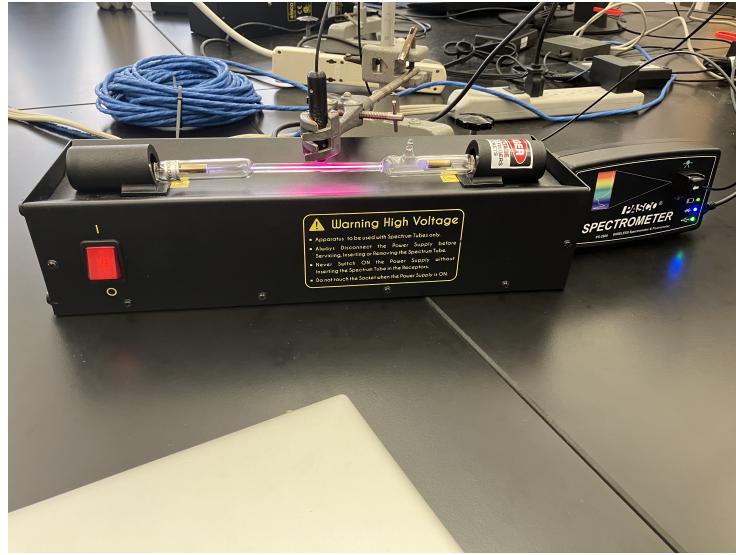


Figure 1: Setup for the gas portion of the lab.

Figure 2 shows the setup for the dyed solutions portion of the lab. The spectrometer is used to measure the absorbance of the solutions by shining a white light through the solution and measuring the intensity of the output light at various wavelengths.

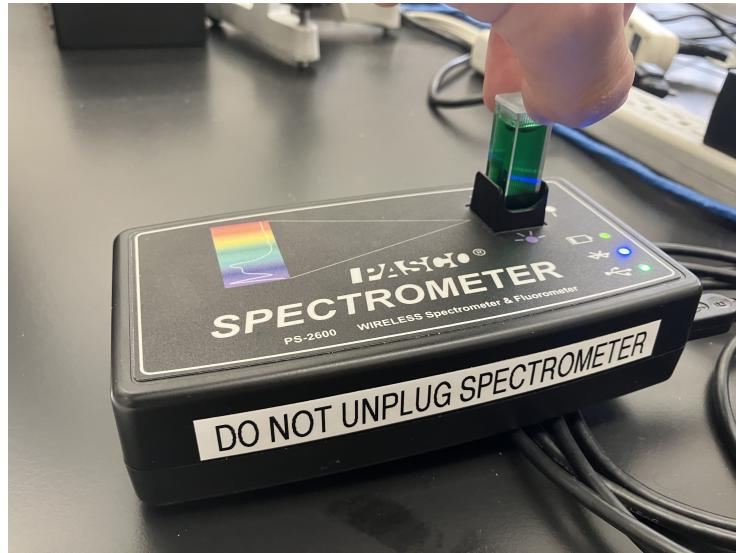


Figure 2: Setup for the dyed solutions portion of the lab.

2.1 Part 1: Mercury

Using known wavelengths of the mercury spectral lines From [4], we measure the experimental locations of the peaks and apply a linear regression against the known values to convert the computer output to true wavelengths. We also repeat this process for the photon energies of the lines.

2.2 Part 2: Hydrogen

For this section, we again measure the experimental locations of the peaks, but compare them with the expected quantum energy of the Balmer series of hydrogen.

2.3 Part 3: Helium

We measure the experimental locations of the peaks.

2.4 Part 4: Unknown Gas

Lastly, we measure the experimental locations of the peaks and convert them to true wavelengths using the results from Part 1. We then compare these wavelengths to known spectral lines to identify the gas.

Color	Violet	Violet	Blue	Green	Yellow	Yellow
Expected λ , nm	404.6565	407.7837	435.8328	546.0735	576.9598	579.0663
Expected energies, eV	3.064	3.040	2.845	2.270	2.149	2.141
Experiment λ , nm	409.40 ± 3.58	412.60 ± 3.58	439.00 ± 3.58	541.40 ± 4.48	570.90 ± 6.27	573.30 ± 6.27
Experiment energy, eV	3.03 ± 0.03	3.00 ± 0.03	2.82 ± 0.02	2.29 ± 0.02	2.17 ± 0.02	2.16 ± 0.02

Table 1: Observed and expected wavelengths and energies of the spectral lines of the hydrogen atom.

2.5 Part 5: Transmittance and Absorbance

We measure the transmittance and absorbance of the blue, green, and red dye solutions at various wavelengths. We then compare the experimental absorbance to the expected absorbance using the formula $A = -\log_{10}(T/100)$ and identify

3 Results

3.1 Part 1

In this part we begin by comparing the expected and observed wavelengths and energies of the spectral lines of the hydrogen atom. The expected wavelengths and energies are calculated using the Rydberg formula (1), and the observed values are obtained from the spectrometer. The results are shown in Table 1 and the plots in Figures 3 and 5. The residuals are shown in Figures 4 and 6 respectively.

The observed wavelengths and energies do not fall within the uncertainty range of the real values, however, most of the values do fit within 2 uncertainty intervals. There seem to be a fixed offset between the real and observed values. This can also be seen in the linear fit equations in figures 3 and 5. This could indicate that the spectrometer is not properly calibrated.

3.1.1 Expected vs observed wavelengths

The best line fit for the expected vs observed wavelengths is given by equation 7, where λ_{exp} is the observed wavelength and λ_{th} is the expected wavelength.

$$\lambda_{\text{exp}} = (0.839 \pm 0.002)\lambda_{\text{th}} + (27.508 \pm 0.9)\text{nm} \quad (7)$$

The residuals plot can be seen in Figure 4. The residuals seem to exhibit a random pattern, which is an indication that the fit is good. At each point, the line of best fit is within the uncertainty range of the observed value. The χ^2 and reduced χ^2 values are given in equation 8. The reduced chi squared of 0.272 indicates that the fit is relatively good, being close to 1.

$$\chi^2 = 1.088 \quad \frac{\chi^2}{v} = 0.272 \quad (8)$$

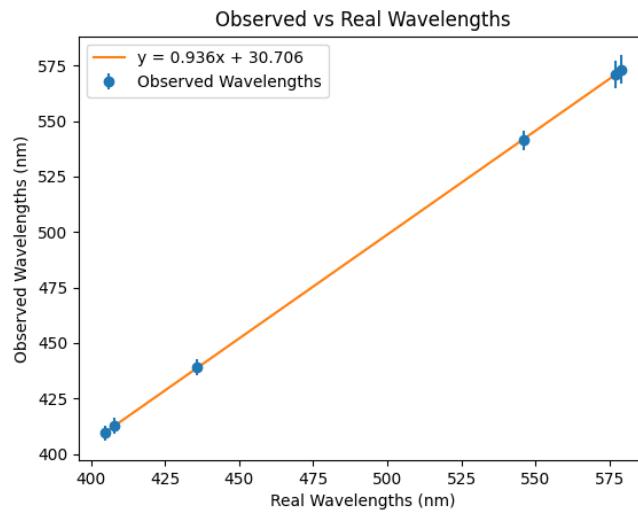


Figure 3: Observed vs expected wavelengths

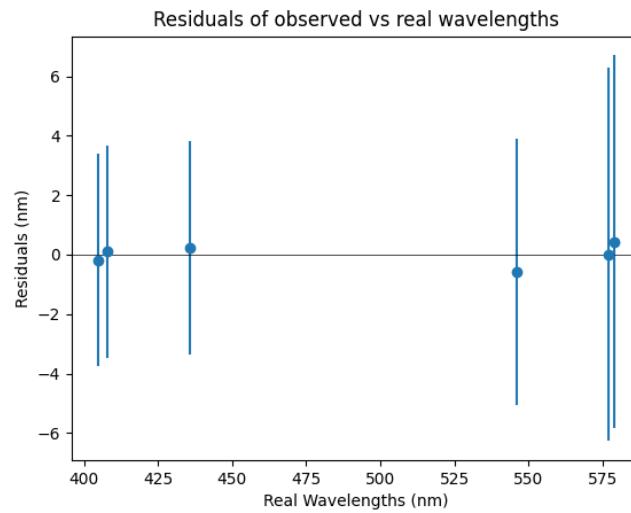


Figure 4: Observed vs expected wavelengths residuals

3.1.2 Expected vs observed energies

The best line fit for the expected vs observed wavelengths is given by equation 9, where E_{exp} is the observed wavelength and E_{th} is the expected wavelength.

$$E_{\text{exp}} = (1.0439 \pm 0.003)E_{\text{th}} + (0.1818 \pm 0.007)\text{eV} \quad (9)$$

The residuals plot can be seen in Figure 4. Again, the residuals seem to exhibit a random pattern, which is an indication that the fit is good. At each point, the line of best fit is within the uncertainty range of the observed value. The χ^2 and reduced χ^2 values are given in equation 10. The reduced chi squared of 0.275 indicates that the fit is relatively good, being close to 1.

$$\chi^2 = 1.103 \quad \frac{\chi^2}{v} = 0.275 \quad (10)$$

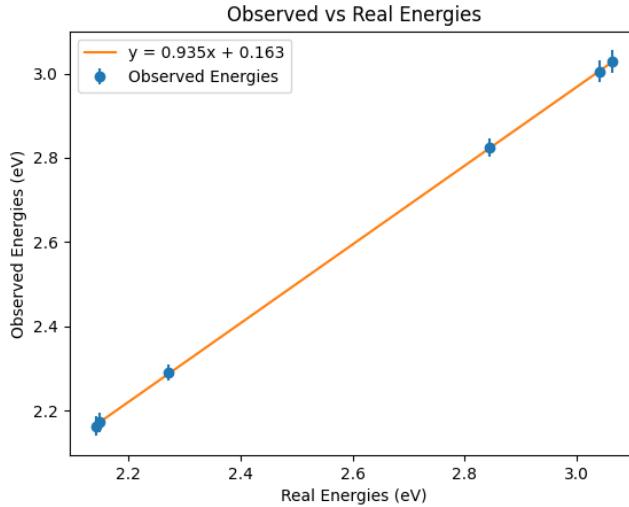


Figure 5: Observed vs expected energies

As a last step, we calculate the relationship between the observed wavelengths as the independent variable, and the expected wavelengths as the dependent variable (Equation 11). This will prove helpful in the next sections, where we will use the observed wavelengths to calculate the expected wavelengths to determine the unknown gas.

$$\lambda_{\text{th}} = (1.068 \pm 0.002)\lambda_{\text{exp}} + (-32.78 \pm 1)\text{nm} \quad (11)$$

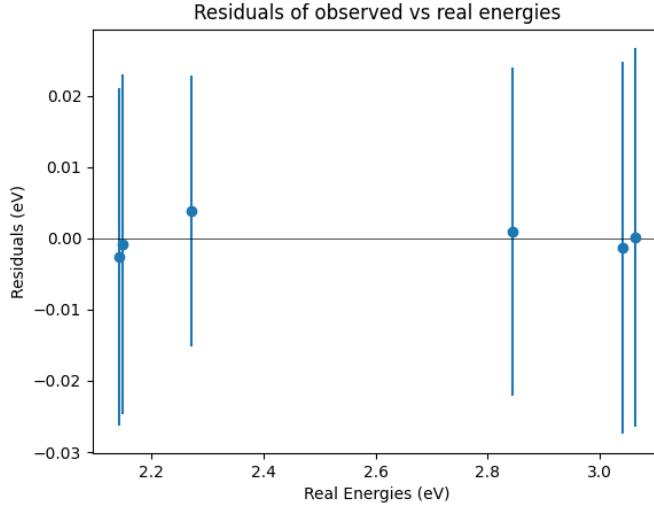


Figure 6: Observed vs expected energies residuals

3.2 Part 2: Hydrogen spectrum

The relative intensities of the lines may vary for the same atoms in the discharge tube from experiment to experiment due to the fact that the atoms are not in the same energy state. The atoms in the discharge tube are excited by the electric field, and the energy levels of the atoms are quantized. This means that the atoms can only have certain energy levels, and the energy levels are not continuous. The atoms can only emit photons when they transition from one energy level to another, and the energy of the emitted photon is equal to the energy difference between the two energy levels. The relative intensities of the lines depend on the probability of the atoms being in a certain energy state, and the probability of the atoms being in a certain energy state depends on the temperature of the discharge tube, the pressure of the discharge tube, and the electric field strength [3, 1]. If the temperature of the discharge tube, the pressure of the discharge tube, or the electric field strength changes, then the relative intensities of the lines will change. This is why the relative intensities of the lines may vary for the same atoms in the discharge tube from experiment to experiment.

The observed and theoretical values of the wavelength for the Balmer series (Referring to the series where the initial state is $n = 2$) of hydrogen can be seen in Table 2. The last column of the table shows the theoretical state energy of the hydrogen atom. The theoretical line energy refers to the energy emitted in a Balmer line with that state as the final state. The observed wavelengths are computed using the calibration regression from Equation 11.

The observed and expected wavelengths match well. All the expected wave-

<i>n</i>	Observed Wavelength (nm)	Theoretical wavelength (nm)	Theoretical line Energy (eV)	Theoretical state energy (eV)
3	660.97 ± 5.66	656.39	1.89	-1.51
4	486.03 ± 4.40	486.21	2.55	-0.85
5	434.76 ± 3.14	434.12	2.86	-0.54

Table 2: Observed and theoretical values for the Balmer series of hydrogen.

Electron configuration of the initial state (upper level)	Electron configuration of the final state (lower level)	Reference intensity in arbitrary units	Reference wavelength of the emission line, λ_r , nm	Measured wavelength of the emission line λ_{exp} +/– uncertainty, nm	Energy of the quantum state E_n , eV	Energy of the quantum state E_m , eV	Selection rule Δn	Selection rule Δl	Selection rule ΔJ
1 s2p(1)	1 s ² (0)	1000	58.43339	—	21.22	-24.57	-1	-1	-1
1 s3 (1)	1 s2p(2)	200	706.5190	713.94 ± 4.91	1.75	-3.60	-1	1	-1
1 s3p(1)	1 s2 s(1)	500	388.8648	388.73 ± 4.30	3.19	-4.75	-1	-1	0
1 s3 d(3)	1 s2p(2)	500	587.5621	588.24 ± 5.52	2.11	-3.60	-1	-1	-1
1 s3 d(2)	1 s2p(1)	100	667.8151	673.25 ± 5.52	1.86	-3.35	-1	-1	-1
1 s3p(1)	1 s2 s(0)	100	501.56783	501.19 ± 3.68	2.47	-3.95	-1	-1	-1
1 s4 d(1)	1 s2p(2)	200	447.14802	447.26 ± 3.07	2.77	-3.60	-2	-1	-1

Table 3: Observed and theoretical values for the Helium atom.

lengths are within one uncertainty of the observed ones.

3.3 Part 3: Calculating energy of quantum states and transmission of helium

The electronic transmission at the highest intensity of the helium spectrum is expected to occur at around 588 nm [2]. Let us first calculate the energy of the quantum states and the energy of the transmission between the states.

For the states $m = 2$ and $n = 3$, we use the formula 1, to obtain its energy:

$$E_2 = -\frac{13.6 \cdot 2^2}{2^2} = -13.6 \text{ eV} \quad \text{and} \quad E_3 = -\frac{13.6 \cdot 2^2}{3^2} = -6.04 \text{ eV} \quad (12)$$

From here,

$$\Delta E = E_3 - E_2 = 7.56 \text{ eV} \quad \text{and} \quad \Delta\lambda = \frac{hc}{\Delta E} = 164.10 \text{ nm} \quad (13)$$

This is clearly not within an acceptable range compared to the value at which the transition does in fact occur. One reason for this is that when more than one electron is present in the atom, we can no longer make use of the single electron approximation which equation 1 relies on. The complex interactions between the electrons create additional repulsion, which increases the real wavelengths of the emission spectra.

In table 3, we can see different parameters like wavelength and energy levels of the Helium atom.

Gas	1	2	3	4	5	6	7	8	9
Neon	540	585	622	640	660	693	703	717	725
Argon	427	435	440	459	473	476	502	696	
Krypton	427	432	557	587	646	759	769	810	826
Xenon	484	529	534	542	597	605	610	681	699
Sodium	588.995	589.592							
Nitrogen	404	444	463	501	568	575	594	648	661
Oxygen	412	423	533	559	605	616	626	637	645

Table 4: Observed wavelengths Different gases.

The 5 transitions corresponding to jumps from $n = 3$ to $m = 2$ are highlighted in blue. These could not be observed for the Hydrogen orbitals since the single electron means that the energy levels are all degenerate, meaning transitioning from 3s to 2s would be equivalent to transitioning from 3p to 2s. For Helium, however, different angular momentum states have different energies due to the different radial distributions of the wavefunctions.

The selection rules show that $\Delta n < 0$, $\Delta l = \pm 1$, and $\Delta J = 0, \pm 1$.

3.4 Part 4: Determining the unknown gas

In this section, an unknown gas will be determined based on its spectral lines. The observed wavelengths of the spectral lines of the unknown gas are shown in Table 5. The observed wavelengths of the spectral lines of different gases are shown in Table 4.

The unknown gas is determined to be Krypton based on the comparison of the observed spectra of the unknown gas and the known spectra of different gases. The wavelength values for the unknown gas range from 551 to 822 nm, which is consistent with the observed wavelengths of Krypton, which range from 427 to 826 nm. The relative intensities also give a strong indication that the observed 822 nm line is significant, as it is more than $\frac{1}{3}$ of the intensity of the strongest spectral line. Other gases presented in the table of known gases only go as high as 725 nm, which is significantly lower than the observed 800 nm line.

3.5 Part 5

This experiment was performed for three different solutions of blue, green, and red, the results of which are given in Tables 6, 7, and 8 respectively. The tables include the experimental T and A values, as well as the expected A value calculated using 5. The experimental and expected A values agree pretty well; however, for some measurements, these numbers are off by many uncertainties, such as the second measurement in the green dye where the expected A value was 1.733 ± 0.00001 , but the experimental A value was 1.848 ± 0.0005 . These errors exist mainly for small T and large experimental A, so there may be light

Wavelength (nm)	Corrected Wavelength (nm)	Relative Intensity
551.20 ± 3.74	555.98 ± 3.74	0.088 ± 0.0005
580.60 ± 5.60	587.38 ± 5.60	0.087 ± 0.0005
748.80 ± 5.60	767.02 ± 5.60	0.696 ± 0.0005
751.50 ± 5.60	769.90 ± 5.60	1.000 ± 0.0005
757.60 ± 3.74	776.42 ± 3.74	0.217 ± 0.0005
760.00 ± 3.74	778.98 ± 3.74	0.248 ± 0.0005
776.60 ± 4.98	796.71 ± 4.98	0.144 ± 0.0005
800.10 ± 7.47	821.81 ± 7.47	0.549 ± 0.0005
803.30 ± 7.47	825.22 ± 7.47	0.719 ± 0.0005
811.20 ± 4.36	833.66 ± 4.36	0.229 ± 0.0005
819.30 ± 6.23	842.31 ± 6.23	0.385 ± 0.0005
822.50 ± 6.23	845.73 ± 6.23	0.340 ± 0.0005

Table 5: Observed wavelengths, corrected wavelengths and relative intensities of the spectra of the unknown gas. A darker shade of red corresponds to a more intense emission.

Experimental T	1.732 ± 0.0005	12.213 ± 0.0005	37.634 ± 0.0005
Experimental A	1.775 ± 0.0005	1.042 ± 0.0005	0.424 ± 0.0005
Expected A	1.761 ± 0.0001	0.91318 ± 0.00002	0.424420 ± 0.000006

Table 6: Transmittance and Absorbance values for various extrema the solution of blue dye

from other sources interfering with the transmittance measurements to cause this error, since that is more prominent if most of the light is absorbed by the solution.

The absorbance and transmittances lines for the red light are given in Figure 7 (the other lines are given in the Appendix). The colors we observe can easily be explained since the red solution transmitted almost no light in the blue-green range, and transmits lots of light in the red range. Thus, the solution appears red, and this reasoning applies to the blue and green solutions, where the dyes transmit mostly blue and green light respectively and absorb the other wavelengths.

Experimental T	1.496 ± 0.0005	1.848 ± 0.0005	3.802 ± 0.0005	10.300 ± 0.0005	10.416 ± 0.0005	34.982 ± 0.0005	70.938 ± 0.0005
Experimental A	1.928 ± 0.0005	1.848 ± 0.0005	1.413 ± 0.0005	0.988 ± 0.0005	0.983 ± 0.0005	0.456 ± 0.0005	0.149 ± 0.0005
Expected A	1.821 ± 0.0001	1.733 ± 0.0001	1.41999 ± 0.00006	0.98716 ± 0.00002	0.98230 ± 0.00002	0.456155 ± 0.00006	0.149121 ± 0.00003

Table 7: Transmittance and Absorbance values for various extrema the solution of green dye

Experimental T	0.080 ± 0.0005	0.196 ± 0.0005	1.638 ± 0.0005	11.793 ± 0.0005	23.230 ± 0.0005
Experimental A	3.036 ± 0.0005	2.670 ± 0.0005	1.793 ± 0.0005	0.929 ± 0.0005	0.634 ± 0.0005
Expected A	3.097 ± 0.003	2.708 ± 0.001	1.7857 ± 0.0001	0.92838 ± 0.00002	0.633951 ± 0.000009

Table 8: Transmittance and Absorbance values for various extrema the solution of red dye

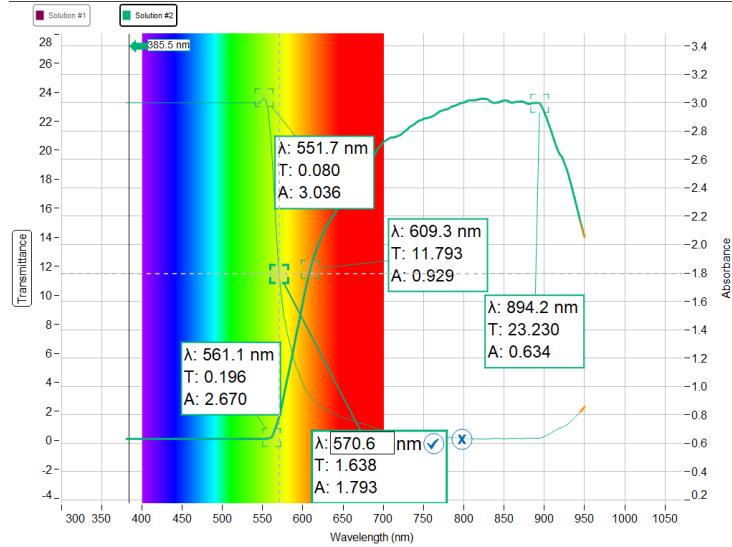


Figure 7: Absorbance and transmittance of red dye

3.6 Part 6

Figures are given in the appendix. For the 405 nm excitation, the absorption edge was at $474.8 \pm 11.4 \text{ nm}$, which corresponds to a band gap energy of $2.61 \pm 0.06 \text{ eV}$. For the 500 nm excitation, the absorption edge was at $473.0 \pm 13.97 \text{ nm}$, which corresponds to a band gap energy of $2.62 \pm 0.07 \text{ eV}$. These two band gap energies are almost identical, which is expected since the band gap energy is a material property and should not depend on the excitation wavelength.

According to Professor Scott Ramsay of MSE160, a semiconductor is any material whose band gap exists and is smaller than 4 eV. Thus, the yellow dye in this experiment is a semiconductor because the band gap is 2.61 eV which is smaller than that.

4 Conclusion

This lab covered the spectral analysis of gases, and looking at transmittance and absorption of light through differently-colored solutions. Using mercury to calibrate the spectrometer, we looked at the spectra of Hydrogen and compared

them to the expected values from the Balmer series. We also looked at Helium to observe the various spectral lines corresponding to the n=3 to the n=2 transition, and how those interact with the various selection rules of transitions. Finally, we looked at the spectrum of an unknown gas, which we identified as Krypton based on matching our observed wavelengths to the known wavelengths of Krypton.

The second part of the lab covered the transmittance and absorption of light through differently-colored solutions. We looked at the absorbance and transmittance of blue, green, and red dyes, and how that resulted in the color we see when looking at the solution under white light. We then looked at the spectrum of the yellow dye under excitation with 405nm and 500nm light, and using that to calculate the bandgap to show that the yellow solution could function as a semiconductor.

Thus, we have successfully completed the objectives of the lab, and have a better understanding of the spectral analysis.

.1 Part 1: Mercury Spectrum

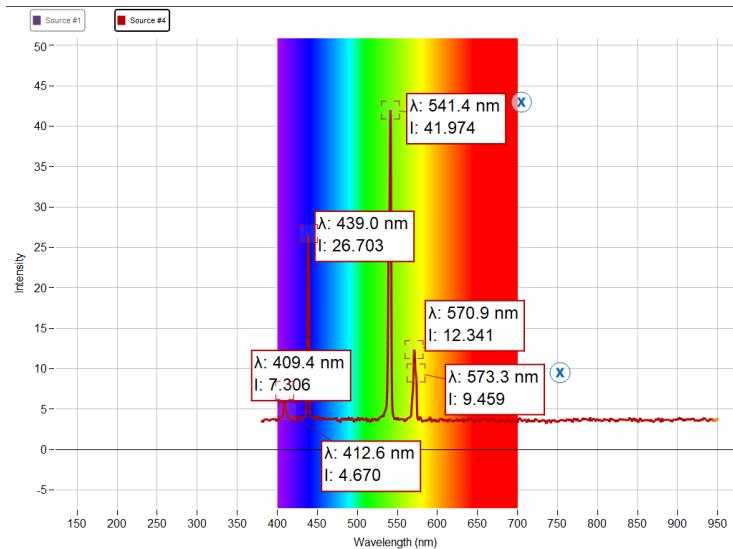


Figure 8: Spectral Lines of Mercury

.2 Part 2: Hydrogen Spectrum

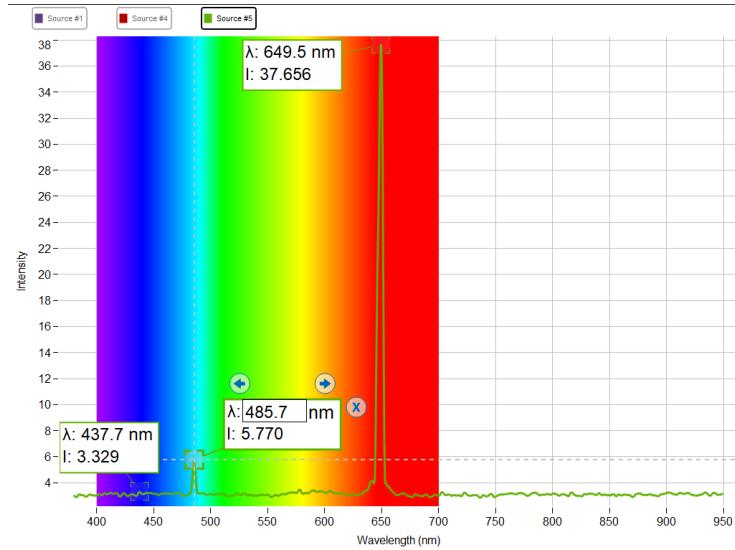


Figure 9: Spectral Lines of Hydrogen

.3 Part 3: Helium Spectrum

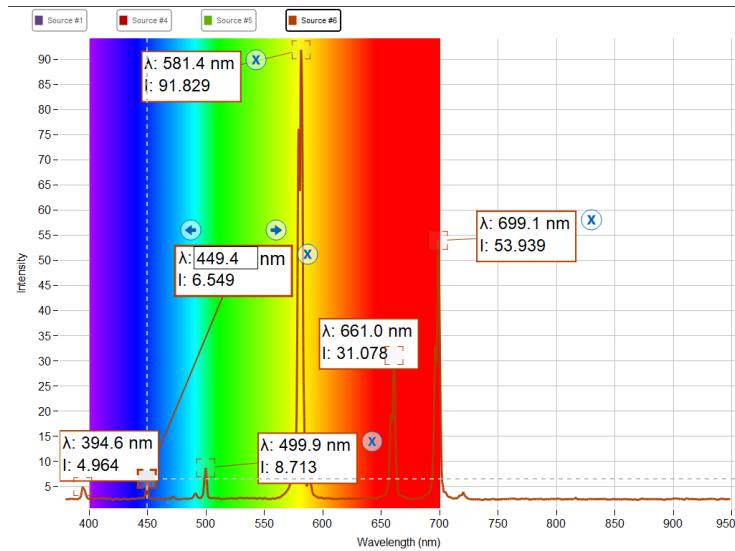


Figure 10: Spectral Lines of Helium

.4 Part 4: Unknown Spectrum

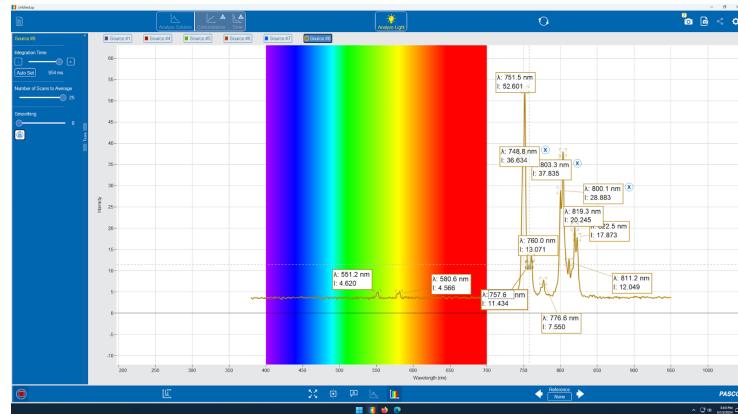


Figure 11: Spectral Lines of Unknown Gas

.5 Part 5: Absorbance of Dyes

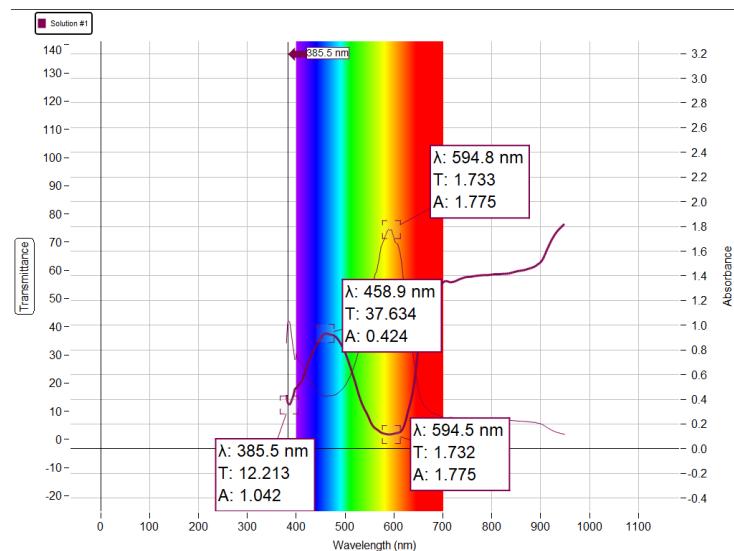


Figure 12: Absorbance and transmittance of blue dye

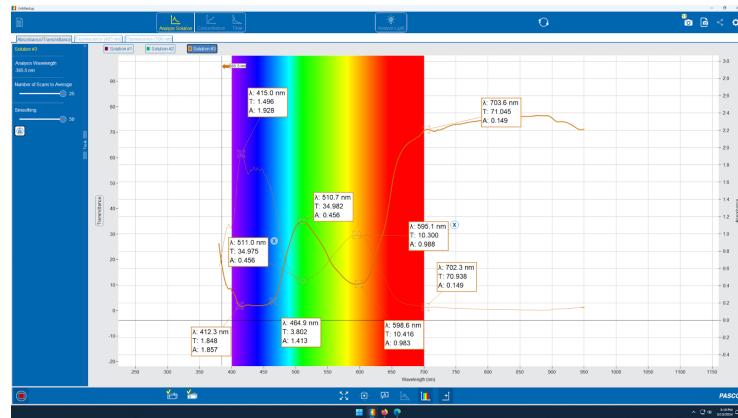


Figure 13: Absorbance and transmittance of green dye

.6 Part 6: Fluorescence Spectrum

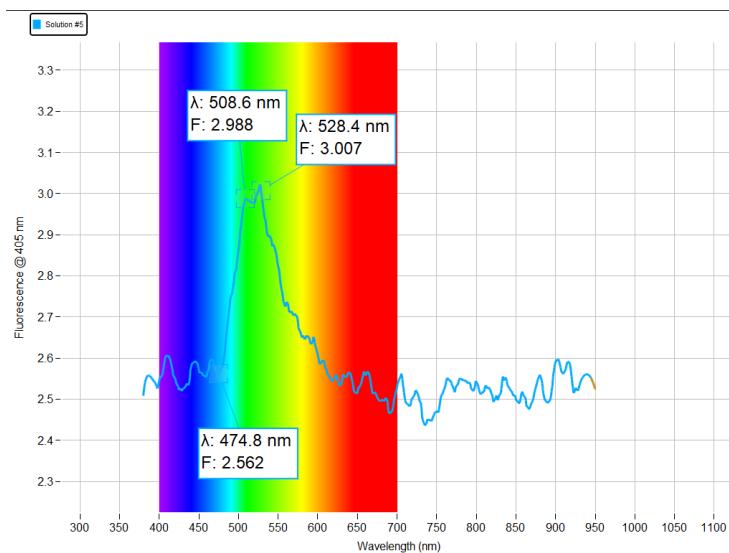


Figure 14: Fluorescence spectrum of yellow dye excited with 405nm light

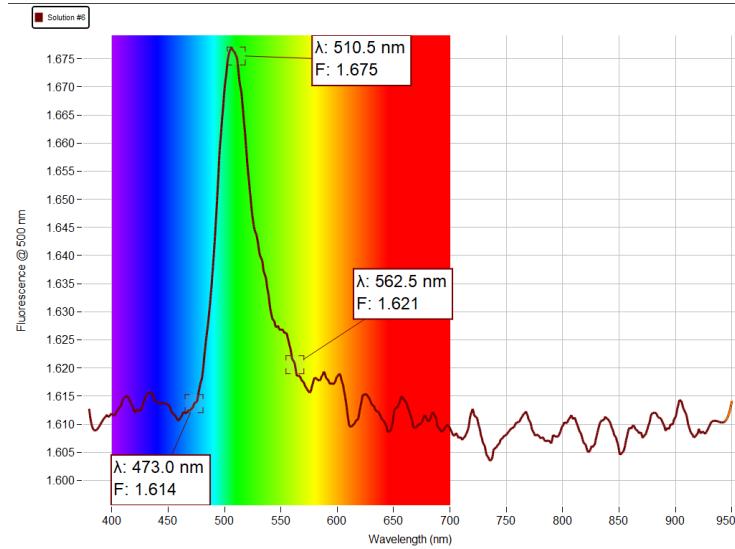


Figure 15: Fluorescence spectrum of yellow dye excited with 500nm light

References

- [1] D. Foguel et al. “Pressure and Low Temperature Effects on the Fluorescence Emission Spectra and Lifetimes of the Photosynthetic Components of Cyanobacteria”. In: *Biophysical Journal* 63.6 (Dec. 1992), pp. 1613–1622. ISSN: 00063495. DOI: 10.1016/S0006-3495(92)81756-3. URL: <https://linkinghub.elsevier.com/retrieve/pii/S0006349592817563%7D> (visited on 03/27/2024).
- [2] PHY293. *Quantum States and Spectra of Gases*. URL: <https://www.physics.utoronto.ca/~phy293lab/experiments/spectra.pdf>.
- [3] PHY293. *Rydberg constant and emission spectra of gases*. URL: <https://www.physics.utoronto.ca/~phy293lab/experiments/rydberg.pdf>.
- [4] *Strong Lines of Mercury (Hg)*. URL: https://physics.nist.gov/PhysRefData/Handbook/Tables/mercurytable2_a.htm (visited on 03/20/2024).