

# Lab #1: Optical Spectroscopy

Kevin O'Brien

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## Abstract

The experiment performed in this lab was performed with the aim of producing and interpreting various atomic and molecular spectra of mercury, neon, hydrogen, helium, sodium, and iodine. From the data acquired, we have arrived at a value of the fundamental vibrational energy of molecular iodine of  $\omega'_e = 110 \pm 1.9 \text{ cm}^{-1}$ , a value of the anharmonicity constant of  $\omega'_e \chi'_e = 0.91 \pm 0.092 \text{ cm}^{-1}$ , a value of the dissociation energy of the first excited state of  $D'_0 = 3324 \text{ cm}^{-1}$ , and finally a value for the dissociation energy of molecular iodine from its ground state of  $D''_0 = 12673 \text{ cm}^{-1}$ .

## 1 Introduction

Optical spectroscopy, a term first coined by Isaac Newton in 1666, is the study of the way that light interacts with various materials, by observing the way that light is absorbed or emitted by these materials. Using the information gathered from this process, one can find out the nature of the material being studied in the form of atomic energy level transitions, or information about the emission spectra of the materials. Spectroscopy has a variety of uses that span across multiple industries, such as the fields of mining, agriculture, chemistry, environmental science, and industry, as it can be used to detect the presence of certain elements [2]. In this experiment, we will be using a spectrometer, photomultiplier tube to observe the optical emission spectra of Mercury, Neon, Hydrogen, Helium, Sodium and molecular Iodine. Using the spectrometer, which in our case is a monochromator, we will pass light along the visible range of wavelengths, and then observe those wavelengths in the form of a voltage produced in the photomultiplier tube to record these spectra. The goal of these measurements will be to receive an accurate measurement of the Rydberg constant from the hydrogen spectrum, the fundamental vibrational energy, the anharmonicity constant, the dissociation of the first excited state, and the dissociation energy of molecular iodine as well as the changes in energy level of the transitions of electrons represented as the dominant spectral lines in hydrogen, helium, and sodium.

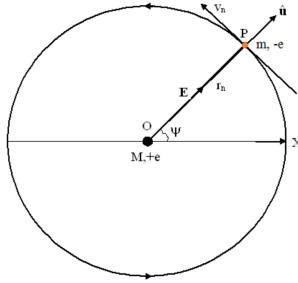
## 2 Theory

Optical spectroscopy relies on measuring the change in energy level of transitioning atomic states. When the energy level changes, this is reflected in a spike in the amplitude through the PMT at the wavelength corresponding to this change. Though heavier atoms like helium, sodium and iodine can not be solved exactly due to their inner complexities, we are able to come up with an exact solution for the hydrogen atom. For the hydrogen atom, the main equation used is the Rydberg equation, or

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

This can be derived through visualizing the hydrogen atom as a proton at the center of an electron orbiting in a circular fashion at a radius  $r_n$  and velocity  $v_n$  around the nucleus.

Figure 1: Visualization of electron revolving around the proton of a hydrogen atom [Taken from 4]



The angular momentum of an electron in this orbit would be given as

$$L = \frac{nh}{2\pi} = mv_n r_n$$

which upon equating the central forces, gives us

$$\frac{mv_n^2}{r_n} = \frac{e^2}{4\pi\epsilon_0 r_n^2}$$

With the left term arriving from the centripetal force and the right term arriving from the coulomb force. From these equations we can find equations for  $v_n$  and  $r_n$  which are

$$v_n = \frac{e^2}{2\epsilon_0 nh}$$

and

$$r_n = \frac{\epsilon_0 n^2 h^2}{\pi m e^2}$$

The total energy of the system given by the hamiltonian  $H$  is the sum of the kinetic and potential energies in the system, with the kinetic energy being  $\frac{1}{2}mv_n^2$  and the potential energy being the coulomb potential, thus our term  $H$  is

$$H = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\epsilon_0 r_n}$$

Subsituting in  $v_n$  and  $r_n$  we arrive at an equation for  $E_n$  that is

$$E_n = -\frac{me^4}{8\epsilon_0^2 n^2 h^2}$$

Finding the change in two arbitrary energy states  $n_1$  and  $n_2$ , we find that

$$\Delta E = \frac{me^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = hf$$

Thus we find

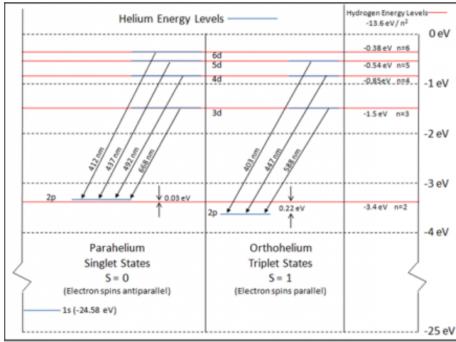
$$\frac{f}{c} = \frac{1}{\lambda} = \frac{me^4}{8ce_0^2 h^3} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

with the constants being grouped together as one value, Rydberg's constant which is  $R_M = \frac{me^4}{8ce_0^2 h^3}$ . This value is equal to 10973731.6 m<sup>-1</sup>. This derivation

is known as Bohr's derivation [4]. The transitions in energy level we will be studying in this experiment all fall in the visible spectrum, and are known as the Balmer series. These transitions all require an end energy level  $n_2$  of 2.

For the next part of the experiment, we will be using helium, which does not have an exact solution like the hydrogen atom. However below is a chart representing the energy transitions of parahelium, the singlet state of helium, and orthohelium, the triplet state. The figure below shows that the binding energy of the helium valence electron is very similar to that of hydrogen, however the  $n_f = 2$  level is shifted 0.22 eV down from hydrogen. The article "A Quantitative Investigation of the Helium Spectrum" mentions that the shielding electron in the helium atom manages to screen the nucleus such that the valence electron on helium only experiences an electrostatic potential from one proton in the nucleus. This results in a split of the 2p level of the helium valence electron that are slightly shifted from those values of the hydrogen n=2 level [5].

Figure 2: Helium energy transitions [Taken from 5]



In the next part of the experiment, we will observe the emission spectrum of sodium. The sodium atom has one valence electron and is thus considered to be a hydrogen like atom. Despite being hydrogen like, the spectrum is vastly different with the spectrum being dominated by a large peak at 588.9950 and 589.5924 nanometers. The line with the smaller wavelength has a peak intensity of about double that of the larger wavelength peak, and the proximity of the two wavelengths occurs due to the transition from the 3p ( $j=3/2$ ) and 3p ( $j=1/2$ ) level to the 3s ( $j=1/2$ ) level. These two peaks interact constructively and produce a peak which makes all of the other peaks look comparatively fainter, and thus the sodium lamp emits its characteristic yellow light. The presence of the doublet depending on the value of the total angular momentum displays an example of the spin-orbit effect [6].

The final spectrum being observed is that of molecular iodine. Though again the iodine molecule can not be solved for an exact solution, the Morse potential is the equation used in this experiment to approximate the energy levels. This potential is given by

$$V(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2$$

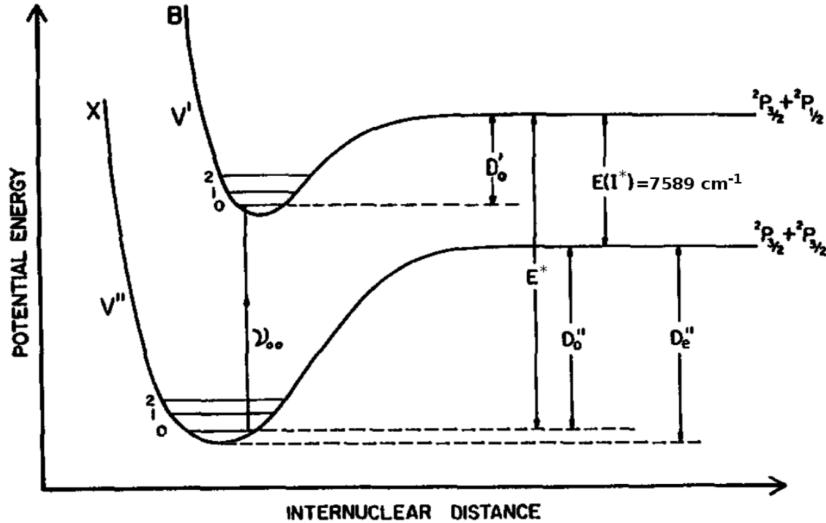
In this potential,  $D_e$  represents the dissociation energy,  $\alpha = \sqrt{\frac{k}{2D_e}}$  and  $r_e$  is the equilibrium bond length. The graph in the lab manual displays the potential

energy of molecular iodine as a function of internuclear distance with the primed quantities pertaining to the first excited state and the double primed quantities pertaining to the ground state. To study the Morse potential with relation to our gathered spectrum, it is important to use convenient units. We find that the value  $G$  of units  $G = \frac{E}{\hbar c}$  can be written such that the Morse potential takes on the form

$$G(\nu) = \omega_e(\nu + 1/2) - \omega_e\chi_e(\nu + 1/2)^2$$

$\omega_e$  is the fundamental vibrational frequency,  $\nu$  is the quantum number of the vibrational energy levels, and  $\omega_e\chi_e$  is the anharmonicity constant which is a factor that separates this potential from that of a simple harmonic oscillator potential, and  $\chi_e = \frac{\hbar^2\omega_e}{4D_e}$ .

Figure 3: Ground and first excited energy levels for molecular iodine [Taken from 1]



This function relates to the derivative spectrum we will gather of the iodine spectrum using the wiggler apparatus  $\frac{dI}{d\lambda}$  as we can say that our ground state level  $\nu''$  equals 0. Thus we receive a linear equation

$$\Delta G(\nu') = \omega'_e - 2(\nu' + 1)\omega'_e\chi'_e$$

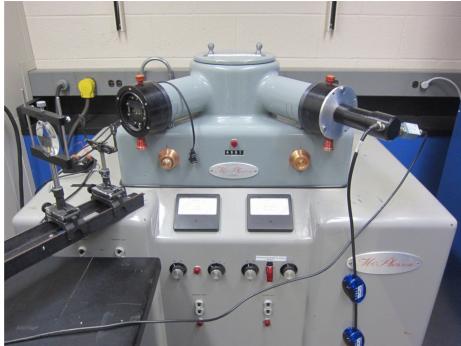
Plotting this data yields a Birge-Sponer plot, which should have a decreasing slope until the potential becomes 0 and the molecule dissociates. This data also helps us to find the fundamental vibrational energy, the anharmonicity constant, the dissociation energy of the first excited state, and the dissociation energy of molecular iodine.

### 3 Experimental Set-Up

The set up for this experiment requires the use of a spectrometer, light sources consisting of Hg, Ne, He and H cold-cathode emission tubes, a sodium lamp, and a tungsten halogen projector lamp, a quartz bulb containing iodine vapor, a photomultiplier tube, a high voltage power supply, a lock in amplifier, an analog to digital converter, a function generator, and the LabView software.

Beginning with the spectrometer pictured below, we used a McPherson spectrometer which is a UV vacuum grating device. The device, whcih is not to be

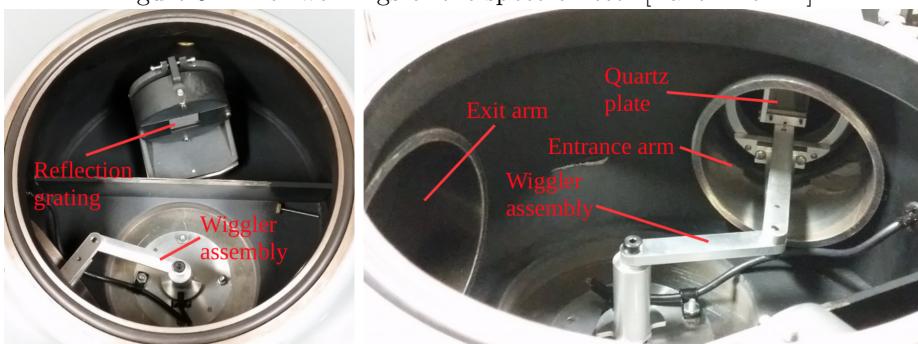
Figure 4: Spectrometer [Taken from 1]



opened without the instructor present, contains a monochromator which serves to project certain wavelengths through the output slits of the spectrometer. The slits themselves are controlled by micrometers, which are set to  $300 \mu\text{m}$  and shutter controls which can be set to O for open or C for closed.

The front face of the spectrometer contained two dials, one which turned the motor either in the forward or reverse direction, and another which controlled the rate at which the motor rotated. In order to avoid backlash from the machine, it is best to start the motor around 10 angstroms before the desired lower limit of measurement.

Figure 5: Inner workings of the spectrometer [Taken from 1]

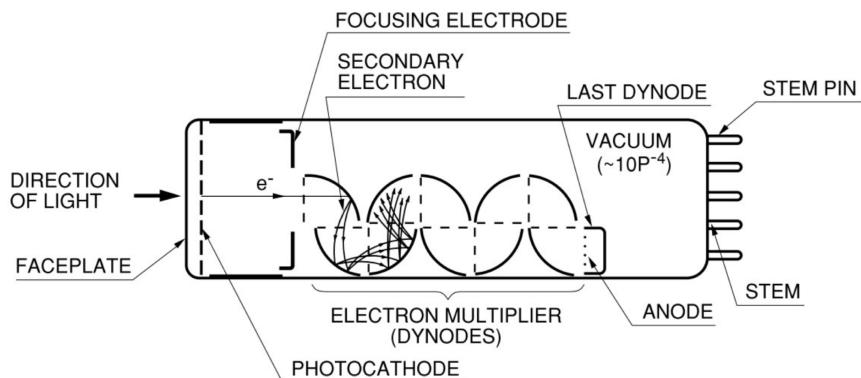


In Figure 2 we are able to see the parts inside of the spectrometer. The left image shows the wiggler assembly which is used to obtain a derivative spectrum

of light as it wiggles, and the reflective grating which is used to act as an individual light source for reflected light. Constructive interference of light causes wavelengths of light to appear in the output slit that are not incident in the input slit. The quartz plate in the spectrometer is wiggled by the assembly at a frequency of about 30 Hz, and is used to obtain the derivative spectrum for the portion of the experiment that uses the Iodine vapor bulb.

Connected to the exit slit of the spectrometer is the photomultiplier tube or PMT. The PMT is connected to the computer using the analog to digital interface, and it is used to detect the intensity of light at the exit slit. It is connected to the analog to digital converter using two BNC sockets, one of which is the high voltage input and the other is the signal output. The tube itself consists of a photocathode and a series of dynodes in a vacuum. Figure 3 shows the interior of the photomultiplier tube which operates according to the photoelectric effect. As photons are sent through the tube, they strip electrons from the cathode which are attracted to the first diode. These "photoelectrons" then eject more electrons from the first dynode, which are sent to the second dynode rapidly, thus producing a current.

Figure 6: Diagram of the interior of the Photomultiplier Tube [Taken from 1]  
pmt.png



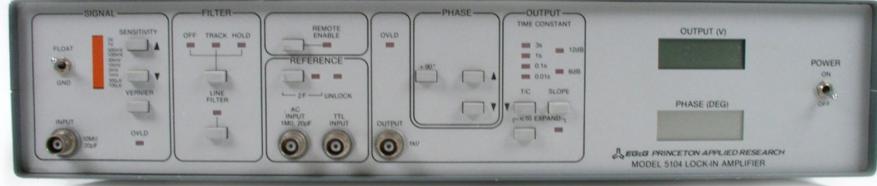
The analog to digital converter being used is a National Instruments NI USB-6008 converter. It is used to process analog signals from the PMT and the lock in amplifier into a digital format which can be recorded by the computer.

The photomultiplier tube used in the experiment is powered by the high voltage (HV) power supply. This power supply is an SRS PS325 which connects via a BNC cable to the PMT. For the purposes of this experiment, we will be turning on the HIGH VOLTAGE switch so that we are receiving 980 V to the PMT.

The lock-in amplifier is another piece of equipment we are using for this lab. The lock-in amplifier is used to amplify the AC signal which is being measured from the wiggler assembly, and reduce noise from other sources in the process. The lock-in amplifier requires an input signal and a reference signal to be adjusted to the proper phase angle. This is done by adjusting the angle buttons in the middle of the device. On the leftmost side of the device there is a toggle setting the controls the sensitivity of the amplifier which has a conversion factor

of 10 V/ 1 mV. This must be adjusted to achieve the proper phase angle such that the system does not become overloaded.

Figure 7: EGG Model 5104 lock-in amplifier [Taken from 1]  
in.png



In addition to these, we will also use a function generator. This function generator can produce a sine, square, or triangle wave and is used to test the lock-in amplifier in order to get a feel for its settings. It contains frequency knobs, and an output level knob which can be used to set the frequency and amplitude of the generated function respectively.

For this experiment, we will be testing the spectra of mercury, neon, helium, hydrogen cold-cathode emission tubes, a sodium lamp, and a tungsten halogen lamp shone through an iodine vapor quartz bulb.

The cold-cathode emission tubes are used in conjunction with a power supply box and are powered by an electric field which moves the electrons, forcing them to collide within the tube and emit a spectrum of light. These tubes are to be handled using Kimwipes because the oils on the hand can cause errors in measurement.

The sodium lamp used is to be aligned on the optical track, and is created by heated sodium forming a vapor which produces the spectrum observed. It takes about two minutes to heat up.

The tungsten halogen projector lamp is used to study the emission spectrum of iodine vapor from the quartz bulb which is mounted on the optical track. The lamp functions through a heated filament which reaches about 3000° C, and thereby emitting a black body spectrum. To avoid damaging the lamp, its power supply should first be turned on, and then adjusted to 30 V, and then turned back down to 0 V before it is turned off. This is to avoid sudden changes in voltage that could damage the bulb.

Lastly, the software used in this experiment is the LabVIEW program, which detects voltages from the PMT and lock-in amplifier. The parameters that we are to adjust throughout the laboratory are the start and end wavelengths, and the scan speed. For a majority of the spectra recording, we will be recording a reading over the full visible spectrum from 3500 Å to 7000 Å at a scan speed of 100 counter numbers per minute. In order to ensure the data recorded is saved to the proper place, we must locate the location in which the file is to be saved and give it an appropriate name, and the program should automatically save the data once the run is completed.

## 4 Procedure

### 4.1 Calibration

The first section of the experiment will be to produce several spectra which can then be used to calibrate each of our recorded spectra moving forward, due to a discrepancy between the counter number of the spectrometer and the actual wavelengths being projected. In order to determine the accuracy and error in our wavelength measurements, we will first be observing the Mercury green line which arises at a wavelength of 5460.74 Å. First we must turn on the high voltage power supply, and enable the HV output so that we can attain a voltage of 980 volts through the PMT tube. It should take around 5 minutes to stabilize. Using the metal alignment rod on the desk, we first must ensure that the height of the middle of the convex lens is level with the entrance slit of the spectrometer. This will allow the emitted light to focus perfectly on the entrance slit, and give us the data that we require. First, using Kimwipe we will grab the Mercury cold-cathode emission tube from the drawer and place it within the power supply box. Next we align it on the optical rack and make sure its emitted light is focused on the entrance slit. From here we are able to enter the "Spectrum.vi" program, and set the starting wavelength to 5440 and the ending wavelength to 5480. The count speed should be at 100 counter numbers per minute. Next, we move to the spectrometer and using the two knobs on the front face, we should move the count number to around 5430 so that we can avoid backlash. After we have made sure that the count speed on the spectrometer is also set to 100 counter numbers per minute, we can turn the motor on in the forward direction, and as it passes over 5440 on the counter, we hit the run button on the LabVIEW software to set the data acquisition process into motion. After the first spectrum is gathered, the name of the file is changed, so as to not overwrite our initial measurement, and 5 more spectra are gathered of the mercury green line. This data can then be reconstructed in a graphing software to determine the accuracy of the spectrometer.

For the next part of the experiment we will determine the  $\tau$  value of the apparatus we are using. This is the response time that it takes for the peak intensity to drop to 1/3 of its highest value. To do this we again scan the mercury green line, and when it reaches its peak we place our hand in front of the entrance slit. The time it takes should be around 0.1 seconds. After this has been done, we can observe the PMT output through the oscilloscope by using the PMT output BNC cable and plugging it in to the CH1 input on the oscilloscope. From here, the mercury green line scan can be repeated again to find the change in signal it creates.

Next, we record full spectra of mercury and neon using their respective cold-cathode emission tubes. The beginning and end wavelengths are 3500, and 7000 angstroms and the count speed is again set to 100 counts per minute. After the spectra have been gathered, they should again be reconstructed in graphing software. Around 15-20 of the peaks should then be chosen across the 3500-7000 angstrom range and those should be plotted on the x axis of a graph, with the y axis being the known values of the peak wavelengths found in the supplied website. This should be a linear value which can be used to calibrate the remaining data in the experiment.

## 4.2 Hydrogen

For the next part of the experiment, we will perform a similar scan for the hydrogen cold-cathode emission tube. This scan will take place over the same range, with the same count speed. From here, as many Balmer lines as possible should be determined, and once a plot of the data is reconstructed, we must make another plot of  $\frac{1}{\lambda}$  vs  $\frac{1}{n_1^2}$ . This will be used to determine the Rydberg constant.

## 4.3 Helium

Again scanning the same region, at the same count rate, the emission spectrum of helium should be measured and reconstructed using graphing software. From here we are to make a table of the wavelengths of prominent spectral lines, and their corresponding transitions in energy level from the same website given.

## 4.4 Sodium

The next portion of the experiment utilizes the sodium vapor lamp. After turning on the lamp and allowing it to settle for about two minutes, and then focusing it on the entrance slit, the same scan is performed. From here we again reconstruct the curve, and create a table of wavelengths of prominent spectral lines and their corresponding energy changes.

## 4.5 Molecular Iodine

The final part of the experiment requires the use of the molecular iodine filled quartz bulb, the tungsten halogen projector lamp, and the lock in amplifier as well as the wiggler assembly within the spectrometer. The tungsten halogen projector lamp is first turned on, and then adjusted to 30 V and placed on the optical track. The first measurement taken will be a reference spectrum of the light emitted by the lamp without the iodine vapor present. The same scan is performed as in the previous steps, over the range of 3500 to 7000 angstroms, with a count rate of 100 counts per minute. After this spectrum has been recording, the quartz bulb is placed on the U shaped mount by the entrance slit. From here another scan is taken of the same range.

After the acquisition of this data, we must next record a derivative spectrum of the iodine vapors emissions by using the wiggler apparatus. To do this we must first understand the workings of the lock-in amplifier using a test signal. The lock-in amplifier is turned on along with the function generator and the oscilloscope. A BNC cable connects the output port of the function cable to CH1 on the oscilloscope. We are using a sine wave with a frequency of 30 Hz for this test signal. The signal amplitude should be set to 100 mV<sub>rms</sub> and the -20 dB attenuation button is pressed to set this amplitude. From here the 100 mV<sub>rms</sub> signal is connected to the signal input port of the lock-in amplifier. The TTL/CMOS port of the function generator is connected to CH1 of the oscilloscope as well. We then observe the reference signal and connect it to the TTL input port on the lock-in amplifier. The time constant on the lock-in must be set to 1s and the phase angle and sensitivity must be properly set such that the rms amplitude is maximized.

After obtaining a reference signal, we will conduct a final scan using the lock-in amplifier and the wiggler assembly. The wiggler motor is first plugged in to the outlet in the wall, and the wiggler reference signal on the front of the spectrometer is switched on. The wiggler reference signal cable is then connected to the oscilloscope to make sure that a square wave is observed, as the lock-in amplifier specializes in AC currents. Once this has been observed, the wiggler reference signal is connected to the TTL input on the lock-in amplifier. The PMT output is connected to the signal input and the To ADC cable is connected to the Output ports of the lock in amplifier. The Time Constant is to be set to 1 second. Repeating the same process from earlier, we are to set the phase angle on the lock-in amplifier such that its output is maximized without overloading the amplifier. This can be done by observing the original iodine spectrum and finding the location of highest positive slope. We then set the spectrometer there and set the angle such that we receive a maximum signal. From here, we perform another scan over the range of 3500 to 7000 angstroms, however this time the scan speed is set to 50 counter numbers per minute, and thus this portion takes double the time. Using the curve that arises from this measurement, we will construct a Birge-Sponer plot by finding where the wiggles of positive slope intersect the x-axis of the plot, and recording the wavelengths at which they occur. This plot will be used to determine the fundamental vibrational energy of molecular iodine, the anharmonicity constant, the dissociation energy of the first excited state, and the dissociation energy of molecular iodine from its ground state with their uncertainties.

## 5 Results

### 5.1 Calibration

First, through using our spectra of mercury and neon, we construct two tables of the known wavelengths of spectral peaks, and the peaks we recorded in our measured spectra. This information is tabulated below, and was used to construct a plot forming a relation between the counter numbers and the wavelength. The plot is linear and has a slope of nearly one, with an intercept of -83.01. As a result, we can calibrate the remaining graphs of this experiment by subtracting 83.01 from the counter number to arrive at a wavelength value in angstroms.

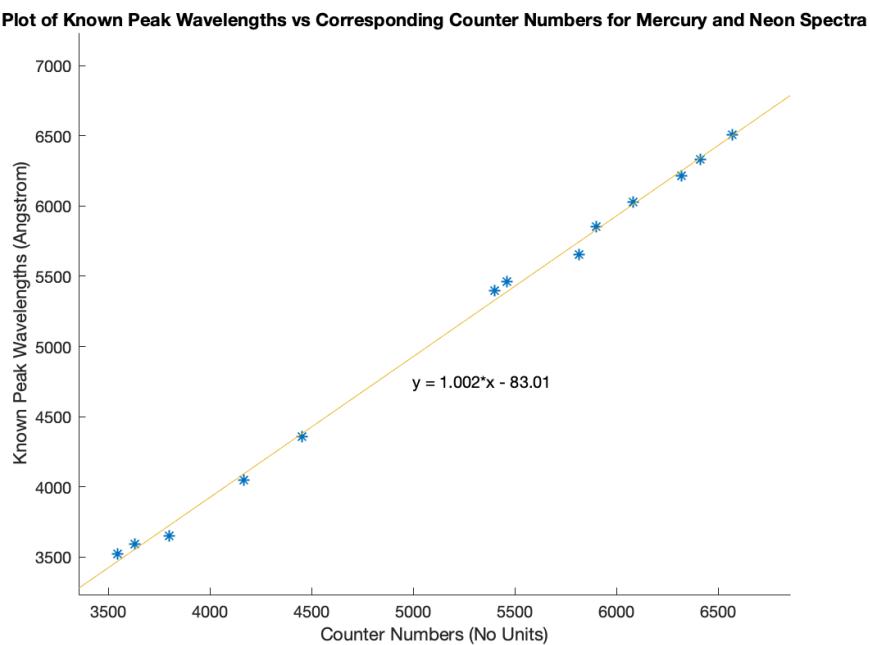
Known Peak Values (Angstrom)	Counter Numbers (No Units)
3650	3801
4046	4166
4358	4452
5460	5461

Table 1: Table of counter numbers and known wavelengths of peaks in Mercury spectrum. Known wavelengths taken from [3]

Known Peak Values (Angstrom)	Counter Numbers (No Units)
3520	3547
3593	3633
5400	5402
5656	5816
5852	5902
6029	6082
6217	6319
6334	6413
6506	6571

Table 2: Table of counter numbers and known wavelengths of peaks in Neon spectrum

Figure 8: Calibration curve of known wavelengths of peaks in mercury and neon spectra and their relation to the measured counter numbers from the spectrometer



Now that this information has been plotted, we can construct calibrated versions of the mercury and neon spectra, which are shown below.

Figure 9: Mercury full spectrum calibrated according to relation found in calibration graph

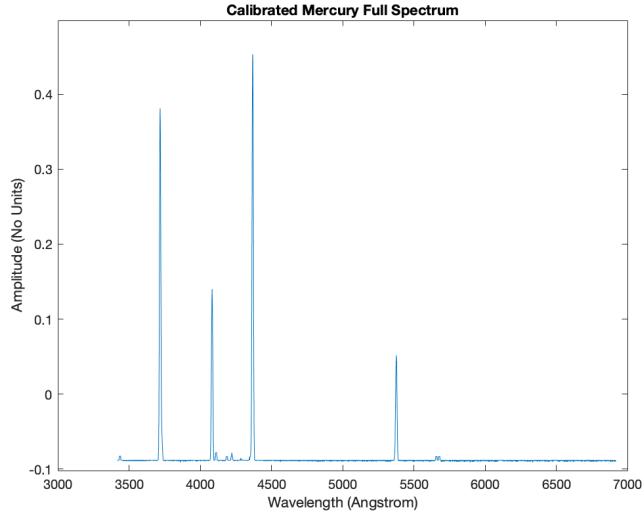
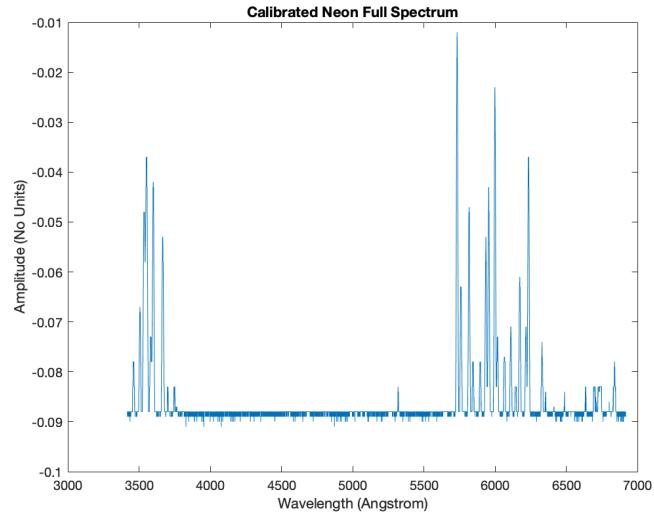


Figure 10: Neon full spectrum calibrated according to relation found in calibration graph



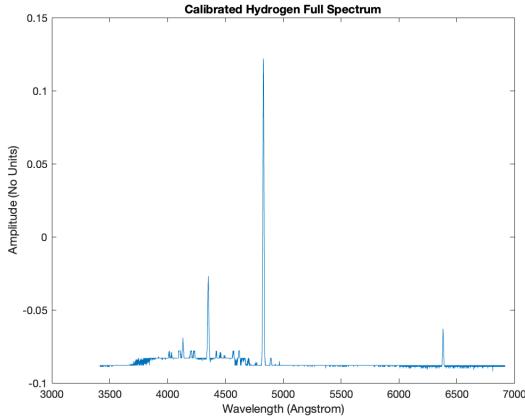
## 5.2 Hydrogen

After reconstructing and calibrating the hydrogen spectrum using our calibration plot, I utilized the information on NIST Atomic Spectra Database Lines Data to tabulate a relation between the wavelengths of peaks and the change in energy level in the hydrogen atom. Once this information was tabulated, I constructed a plot of  $\frac{1}{\lambda}$  vs  $\frac{1}{n_1^2}$ . Using the Rydberg formula

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

We find that this plot will have a slope of  $-R_M$ . The slope gathered from our data is  $-1.02 \times 10^7$ , which implies a value for the Rydberg constant of  $R_M = 1.02 \times 10^7 \text{ m}^{-1}$ . The accepted value of the Rydberg constant is  $R_M = 10973731.6 \text{ m}^{-1}$ .

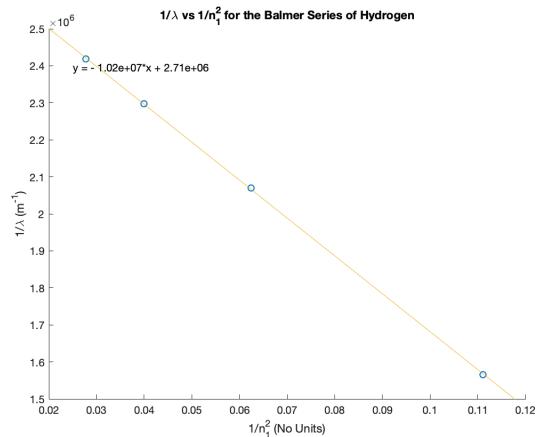
Figure 11: Hydrogen full spectrum calibrated according to relation found in calibration graph



Wavelength (Angstrom)	$n_1$ (No Units)	$n_2$ (No Units)
4134	6	2
4353	5	2
4830	4	2
6384	3	2

Table 3: Table of the measured Balmer lines in hydrogen spectra and corresponding atomic transitions. Atomic transition data recorded from [3]

Figure 12: Plot of measured Balmer lines with best fit line with slope equal to Rydberg constant

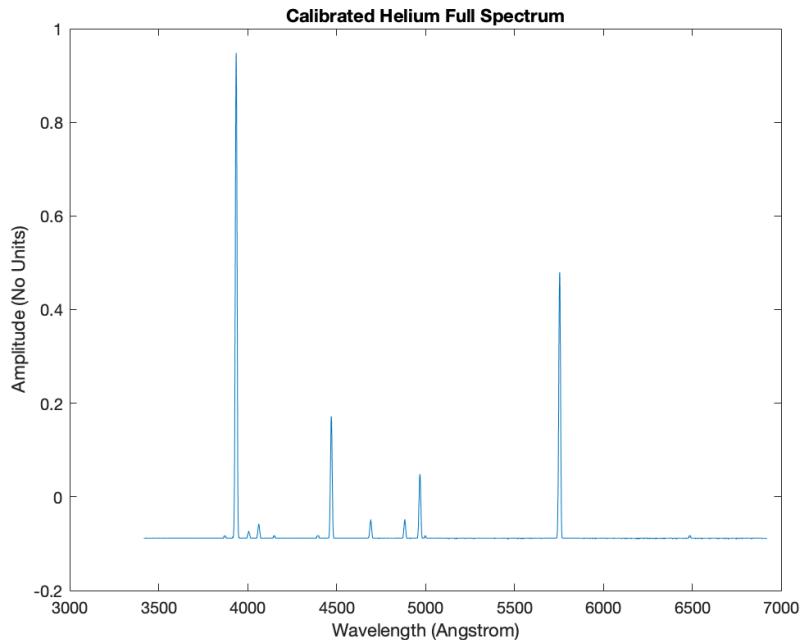


The uncertainty in the slope of this plot of the Balmer lines created is  $6.43 \times 10^4$ , which is equivalent to the uncertainty in our value of the Rydberg constant. This yields a value of the Rydberg constant that can be reported as  $1.02 \times 10^7 \pm 6.43 \times 10^4 \text{ m}^{-1}$ . Though the value is to the correct order of magnitude, the accepted value falls outside of the range of values given our uncertainty.

### 5.3 Helium

After gathering the spectral data from helium and reconstructing the spectrum, there were 4 distinct peaks present. These corresponded to energy level transitions that are tabulated below, with information being taken from NIST Atomic Spectra Database Lines Data.

Figure 13: Helium full spectrum calibrated according to relation found in calibration graph



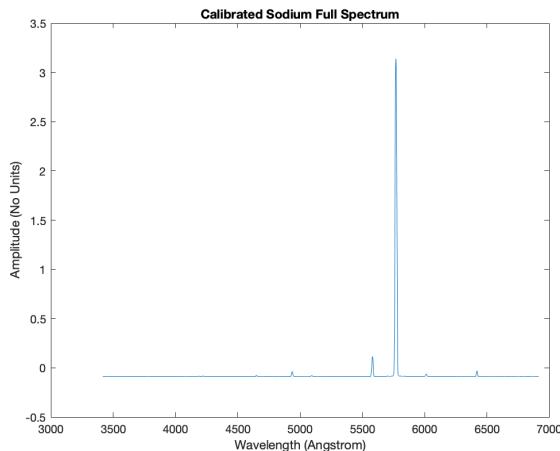
Wavelength (Angstrom)	Energy Level 1 (No Units)	Energy Level 2 (No Units)
3936	1s4p	1s2s
4470	1s4d	1s2p
4971	1s4d	1s2p
5755	1s3d	1s2p

Table 4: Table of the wavelengths of peaks in helium spectrum and corresponding atomic transitions. Atomic transition data recorded from [3]

## 5.4 Sodium

The following is the reconstructed and calibrated spectrum of the Sodium lamp we measured. The next graph is a calibrated view of the sodium doublet taken from scanning from 5600 to 5900 counter numbers with adjusted slit width and then calibrating the graph. The first plot is dominated by what appears to be one large peak, however the second plot shows that the peak is actually a consequence of two overlapping peaks brought about by two transitions from the  $2p^63p$  level to the  $2p^63s$  level, however the higher of the two peaks has a  $j$  value of  $1/2$  and the other has a  $j$  value of  $3/2$ . This information was found using the NIST Atomic Spectra Database Lines Data. There is also a third smaller peak with its transition, as well as the other two transitions tabulated below. Though our data finds that the sodium doublet occurs at 5771 and 5773 angstroms, the accepted value finds the sodium doublet at 5890 and 5896 angstroms. This error could have arisen from errors in our calibration curve.

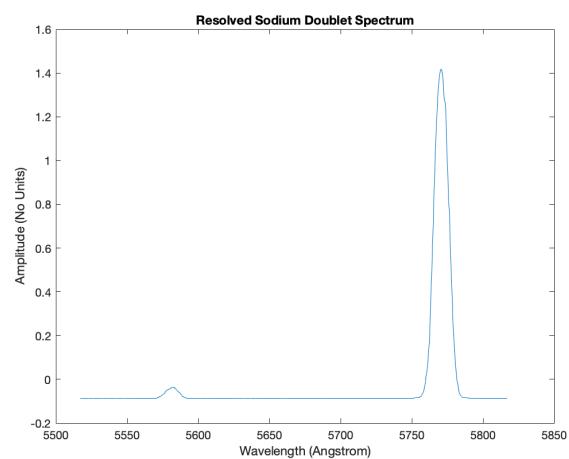
Figure 14: Sodium full spectrum calibrated according to relation found in calibration graph



Wavelength (Angstrom)	Energy Level 1	Energy Level 2
5584	$2p^64d$ ( $j=3/2$ )	$2p^63p$ ( $j=1/2$ )
5771	$2p^63p$ ( $j=3/2$ )	$2p^63s$ ( $j=1/2$ )
5773	$2p^63p$ ( $j=1/2$ )	$2p^63s$ ( $j=1/2$ )

Table 5: Table of the wavelengths of peaks in the sodium spectrum and corresponding atomic transitions. Atomic transition data recorded from [3]

Figure 15: Resolved doublet in the sodium spectrum due to constructive interference of two overlapping changes in energy



## 5.5 Iodine

First, we gathered a reference sample of the tungsten halogen projector lamp which served as the broadband light source. This reference spectrum was calibrated and plotted below. In addition to this we also took reconstructed a calibrated spectrum of the iodine data which is shown below.

Figure 16: Reference spectrum of the tungsten halogen projector lamp calibrated according to relation found in calibration graph

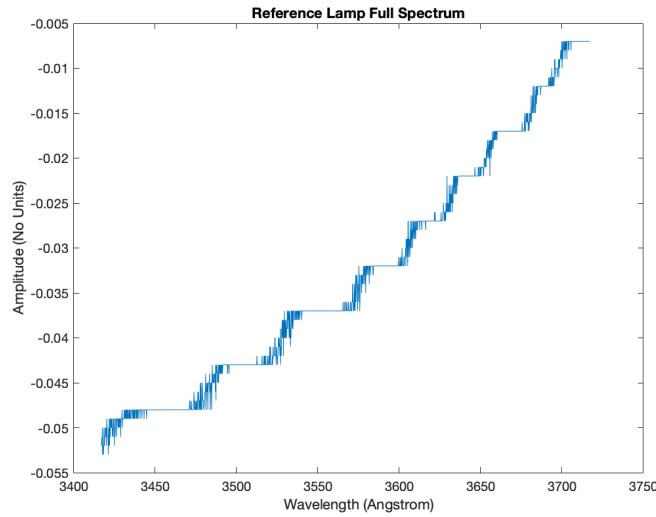
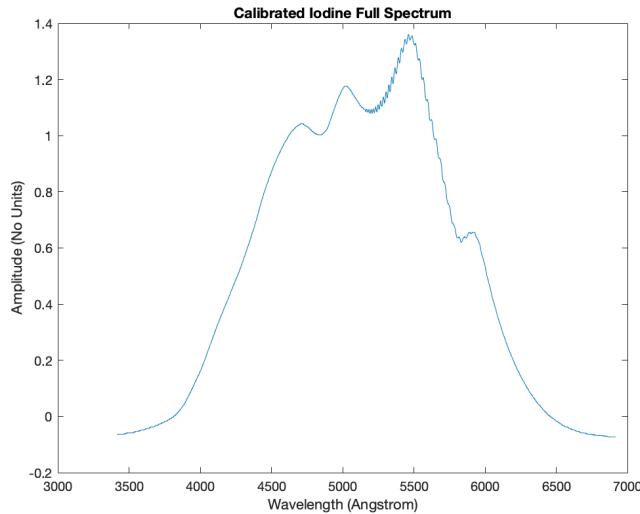


Figure 17: Iodine full spectrum calibrated according to relation found in calibration graph



Once this data was gathered, we constructed a calibrated derivative spectrum of the iodine spectrum. Using the data from this spectrum a table was made of the positive-sloped zero crossings and their uncertainties which are used to create a Birge-Sponer plot.

Figure 18: Derivative spectrum of the iodine spectrum taken using the wiggler apparatus and lock-in amplifier

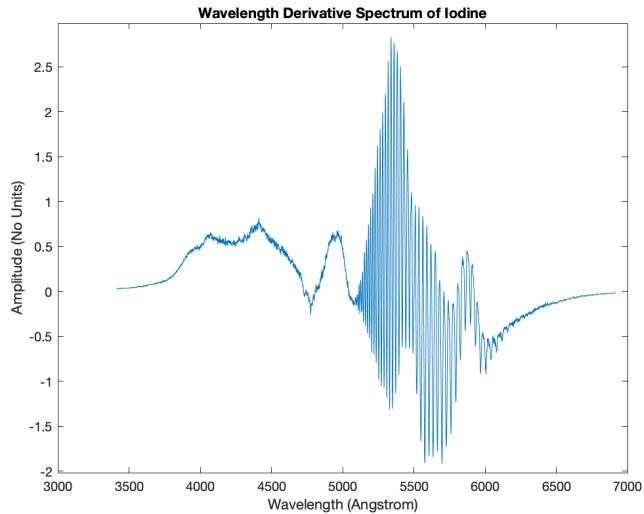
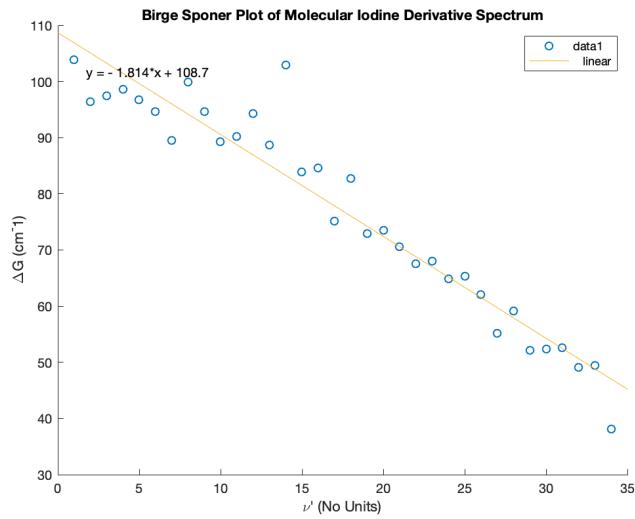


Figure 19: Birge-Sponer plot of Molecular Iodine derivative spectrum data



Using the created Birge-Sponer plot, and the equation from the lab manual

$$\Delta G(\nu') = \omega'_e - 2(\nu' + 1)\omega'_e\chi'_e$$

Wavelength (Angstrom)	Uncertainty (Angstrom)
5114	0.5
5124	0.5
5137	0.5
5150	0.5
5164	0.5
5178	0.5
5192	0.5
5205	0.5
5223	0.5
5240	0.5
5258	0.5
5276	0.5
5295	0.5
5314	0.5
5334	0.5
5355	0.5
5376	0.5
5400	0.5
5422	0.5
5447	0.5
5472	0.5
5503	0.5
5530	0.5
5559	0.5
5587	0.5
5615	0.5
5645	0.5
5677	0.5
5706	1
5737	1
5769	1
5802	1
5835	1
5868	1
5904	1

Table 6: The table shows the wavelengths of positive-sloped zero crossings of the derivative spectrum plot and their uncertainties.

We find that we have plotted a line with slope equal to -2 times the anharmonicity constant, or  $-2\omega'_e\chi'_e$  and an intercept equal to the fundamental vibrational energy of molecular iodine,  $\omega'_e$ . As shown by the equation on the chart, we have a slope of  $s = -1.814$ . Dividing this value by -2, we arrive at an anharmonicity value of  $\omega'_e\chi'_e = 0.907$ . The intercept we have is 108.7, which is equivalent to our  $\omega'_e$  value. Using our uncertainty values in the slope, and intercept taken through MatLab, we can report these values as follows:  $\omega'_e\chi'_e = 0.91 \pm 0.092$  ( $\text{cm}^{-1}$ ) and  $\omega'_e = 110 \pm 1.9$  ( $\text{cm}^{-1}$ ). Though neither of our values are fully accurate, both

lie incredibly close to the accepted values of  $0.834 \text{ cm}^{-1}$  for the anharmonicity constant, and  $128 \text{ cm}^{-1}$  for the fundamental vibrational energy [8].

Next we can find the vibrational quantum number  $v_m$  through the supplied formula  $v_m = (1/2\chi_e) - 1$ . Through our reported value of  $\omega'_e\chi'_e$ , we are able to find a value of  $\chi_e$  of  $8.3 \times 10^{-3}$ . From here through linear extrapolation, at the point in our plot that  $\Delta G = 0$ , we have a value  $\nu_m$  of 60 (No Units). Using the equation

$$G(\nu) = \omega_e(\nu + 1/2) - \omega_e\chi_e(\nu + 1/2)^2$$

We are able to calculate  $D'_0$  in units of  $\text{cm}^{-1}$ . This value comes out to  $D'_0 = 3324 \text{ cm}^{-1}$ . Now that we have calculated the dissociation energy of the first excited state, we can calculate the dissociation energy of the ground state. This comes from the equation  $D''_0 = E^* - E(I^*)$  where  $E(I^*)$  is given as  $7589 \text{ cm}^{-1}$  and  $E^* = D'_0 + v_{00}$  with  $v_{00}$  being the energy of the last observed wiggle in our derivative spectrum. In our case, that value came out to  $16938 \text{ cm}^{-1}$ . Solving this equations, we arrive at a value of  $D''_0$  of  $12673 \text{ cm}^{-1}$ . This experimentally determined value is incredibly close to the accepted value from the literature of  $12440 \text{ cm}^{-1}$ .

## 6 Summary and Conclusions

Through the data gathered in this lab we were able to first produce a calibration spectrum using the known values of the peak wavelengths in the neon and mercury spectra, and plotting them against the counter numbers that we gathered through our data acquisition. This gave us a relationship showing a difference in 83 angstroms between our counter numbers and wavelengths. Using this value, we were able to calibrate each of the spectral plots we gathered in the experiment. For the spectrum of hydrogen, we then made a plot of  $\frac{1}{\lambda}$  vs  $\frac{1}{n_1^2}$ , and found that the Rydberg constant corresponding to our data was  $1.02 \times 10^7 \pm 6.43 \times 10^4 \text{ m}^{-1}$ . The accepted value of the Rydberg constant is  $10973731.6 \text{ m}^{-1}$ . Our value is to the correct order of magnitude, and is relatively close to the value of the Rydberg constant, however the accepted value still falls outside of our measured range.

We then reconstructed the helium spectrum and found various changes in energy level that corresponded to the known energy level changes in the NIST database. The same can be said for sodium, where we found a spectrum that was dominated by the characteristic sodium doublet, however our doublet appears to have been shifted by a value that was not accounted for by our calibration curve. This could have been a result of our calibration curve containing errors in assigning known wavelengths to counter number peaks.

Finally for the iodine spectrum, we constructed a calibrated spectrum of the derivative spectrum, which allowed for the creation of a table of the positive-sloped zero crossing wavelengths and their uncertainty. After this was tabulated, we were able to plot the differences in their energy in units of  $\text{cm}^{-1}$  to form a Birge-Sponer plot of the data. From this data, we arrive at a value of the fundamental vibrational energy of molecular iodine of  $\omega'_e = 110 \pm 1.9 \text{ cm}^{-1}$ , a value of the anharmonicity constant of  $\omega'_e \chi'_e = 0.91 \pm 0.092 \text{ cm}^{-1}$ , a value of the dissociation energy of the first excited state of  $D'_0 = 3324 \text{ cm}^{-1}$ , and finally a value for the dissociation energy of molecular iodine from its ground state of  $D''_0 = 12673 \text{ cm}^{-1}$ . Though none of the data gathered contained the accepted values within their respective ranges of error, they were incredibly close to their accepted values of  $\omega'_e \chi'_e = 0.834 \text{ cm}^{-1}$ ,  $\omega'_e = 128$ , and  $D''_0 = 12440$  [8].

This experiment overall provided a relatively accurate way of interpreting the spectroscopic data of hydrogen, helium, sodium, iodine, neon and mercury. Perhaps in order to improve the experiment, or to reduce sources of error, further calibration readings can be taken so that the calibration for the wavelength is taken to increased accuracy. Additionally, ensuring that the room were kept at a constant temperature between measurements would also ensure that the calibration was kept accurate across multiple days.

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