

Absorption Spectroscopy of Molecular Iodine

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Abstract

This report explores the use of spectroscopy as a powerful tool in our arsenal as scientists in uncovering some of the mysteries that surround the world of atoms and molecules. Spectroscopy is an important weapon in a physicist's arsenal. Some interesting applications of such a tool include non-destructive elemental analysis, measurement of toxic compounds in blood samples, and electronic structure research which is the focus of the following experiment. We analyzed the emission spectrum of iodine, and gained useful insight about the electronic and vibrational states of the diatomic molecule. Our measurements uncovered values for T , ω_e' , $\omega_e x_e'$, ω_e'' , $\omega_e x_e''$, and the dissociation energy D_e'' . To put it briefly, the dissociation energy is the energy level at which a molecule, in this case diatomic iodine, breaks apart. This is one way to measure the strength of the chemical bonds holding molecules together. After considering various sources of error and revisiting some calculations, the final value I calculated for D_e'' was $12329.5 \pm 34 \text{ cm}^{-1}$. This was within three sigma of another posted experimental value and was roughly 110 cm^{-1} less than the actual dissociation energy.

I. INTRODUCTION

Spectroscopy is a very useful tool in understanding the fundamental behavior of atoms and molecules as they gain and lose energy. By taking a closer look at iodine in the form of a diatomic molecule using a spectrometer, the spectral lines absorbed can be recorded and analyzed. To further understand diatomic iodine, it is important to understand the structure of such a molecule.

To be a diatomic molecule means to be two individual atoms bonded together. This structure can be modeled as a macroscopic simple harmonic oscillator. The atoms are considered the masses with a bond that can be thought of as a spring. Similar to a simple harmonic oscillator, diatomic iodine has different vibrational states. By exciting iodine and recording the vibrational spectrum that is absorbed, further insight can be gained about the inter-atomic potential. With careful analysis of the inter-atomic potential, one can then assess whether using the simple harmonic oscillator as a model for a diatomic molecule is an adequate model. By the end of the experiment it will be clear that the simple harmonic oscillator does not supply an acceptable potential for modeling diatomic molecules. Rather, the potential of a diatomic molecule is better described as a Morse potential, which can help determine an important physical parameter, the dissociation energy.

The value for the dissociation energy can be derived from an equation given in the lab manual³. The equation is as follows:

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 \quad (1)$$

This equation describes the vibrational energy in our diatomic iodine in wavenumber. By understanding that the dissociation energy comes from the difference between the vibrational energy ground state and the energy from when the vibrational states of the nuclei become unbound, you get the value for the dissociation energy of a specific molecule. To find the value of the vibration energy ground state, we can set v equal to zero. After plugging in we get the following:

$$G(0) = \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} \quad (2)$$

Next we need to find the value of $G(v)$ when the vibrational energy becomes minimized and the atoms separate. This can be done by setting the first derivative of $G(v)$ equal to

zero. When $G'(v) = 0$, we get a value for the wavenumber as follows:

$$v = \frac{\omega_e}{2\omega_e x_e} - \frac{1}{2} \quad (3)$$

Plugging this back into $G(v)$, we get:

$$G\left(\frac{\omega_e}{2\omega_e x_e} - \frac{1}{2}\right) = \frac{\omega_e^2}{4\omega_e x_e} \quad (4)$$

By finding the difference between the vibrational energy ground state and the minimum vibrational energy when the atoms in the molecule separate, we can find the dissociation energy of the molecule:

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e}{2} + \frac{\omega_e x_e}{4} \quad (5)$$

Furthermore, the model that will be used in the following data analysis comes from the fact that there are both electronic and vibrational transitions in diatomic iodine. The full equation is written out in detail in the lab manual³, but the values that we are interested in determining are T , ω_e' , $\omega_e x_e'$, ω_e'' , $\omega_e x_e''$, and the dissociation energy.

II. EXPERIMENTAL METHODS

The experimental procedure was not modified from the Lab Manual³. I began the experiment by first calibrating the SPEX 1250M spectrometer using a sample of mercury. By getting a broad visual spectrum of the mercury, I could compare the peaks with the documented spectral lines found on the NIST spectral line database². By comparing these values I was able to come up with a value for an offset that will need to be taken account in future data sets. Once the calibration was complete, I then used an iodine sample, heated up to 40 degrees Celsius. Then, doing the same broad visual spectrum as I did with mercury, I again did the same for the iodine to confirm the spectrum was following the correct shape. Once confirming this, I then did a very high resolution spectrum, as high resolution as I could go while staying efficient with lab time I had. It was very important to keep all excess unwanted light from entering the spectrometer, so I shut off the lights in the room as well as covering any other potential light sources. After capturing the fine details of the iodine spectrum, I was able to move into data analysis.

III. RESULTS

The first data taken was a rough large scan of a mercury spectrum to calibrate the spectrometer. The following is the rough scan recorded, followed by a plot of the experimentally recorded peaks versus the actual peaks found in the literature. The actual peak values of iodine were taken from the NIST spectral line database². The confidence interval table displays the correlation between these two, with an approximate slope of 1 expected, the y-intercept will show the wavelength offset that will need to be taken into account when doing the larger iodine spectrum.

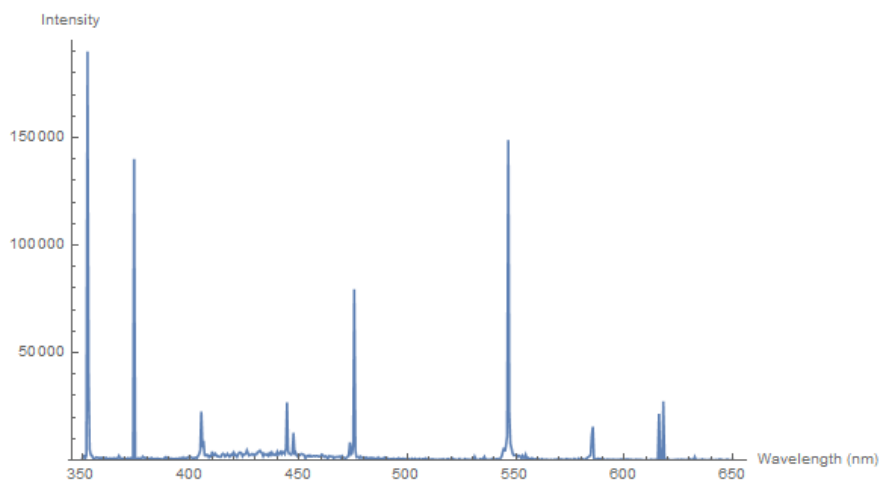


FIG. 1: Mercury Spectrum - the intensity (CPS) of light emitted at certain wavelengths in the visible spectrum for mercury

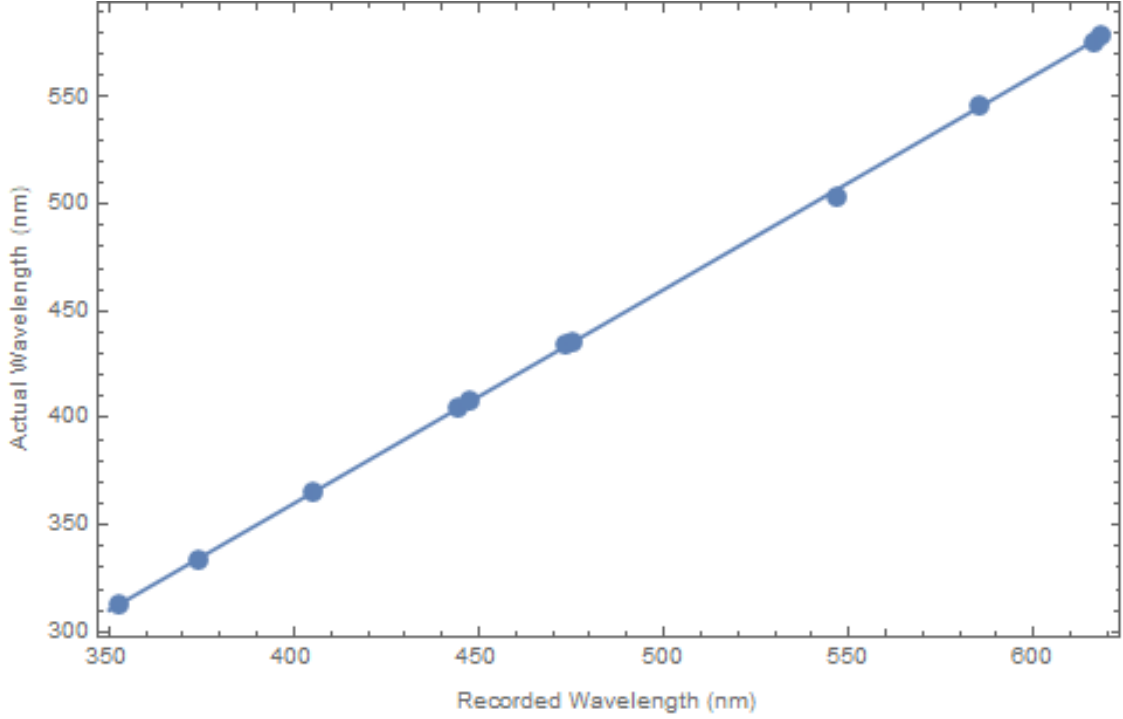


FIG. 2: Spectrometer Calibration - plot of the recorded wavelength peaks for mercury versus the actual peaks

	Estimate	Standard Error
slope	0.999	0.001
y-intercept	-39.799	1.754

TABLE I: Offset Confidence Interval Table

The results from the calibration show the the spectrometer is shifted upwards 39.8 nanometers. The slope of the fit was roughly 0.999 which leads me to believe that the peaks I used to compare the wavelengths were correct. After taking this offset into account, when taking a high resolution iodine spectrum, instead of taking data in a range from 490-610nm, I took data from 530-650-nm.

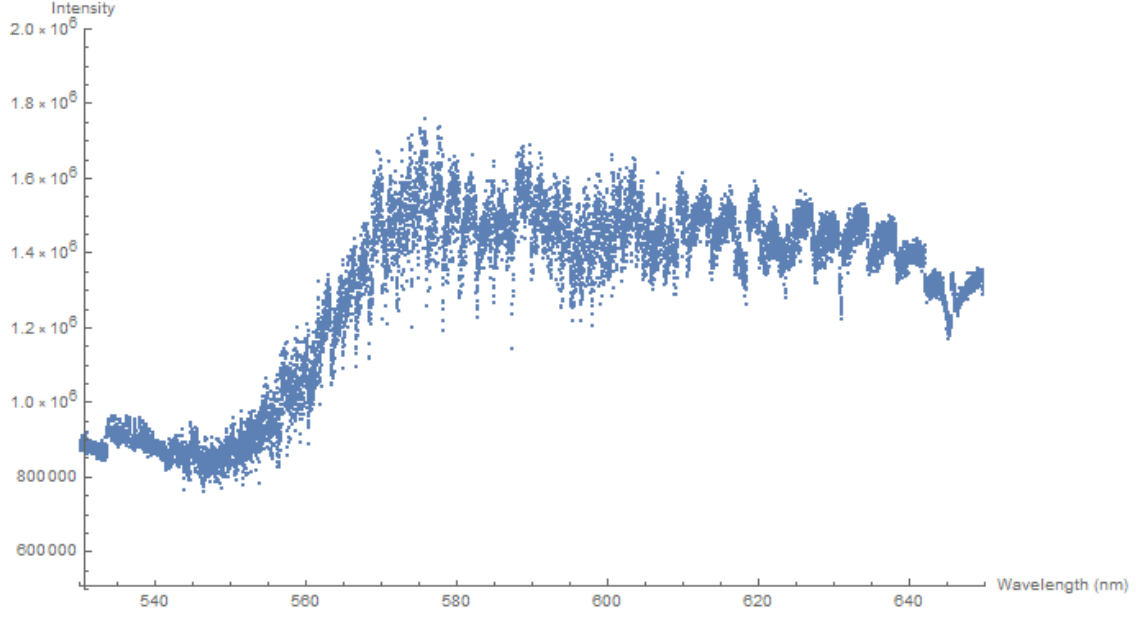


FIG. 3: Iodine Spectrum - the intensity (CPS) of light emitted at certain wavelengths in the visible spectrum for iodine. This is the raw, uncorrected data taken by the spectrometer and the real wavelengths are shifted to the left by 39.8 nanometers.

While difficult to see, there is a data point taken at every 0.01nm to get a high resolution spectrum from the iodine sample. After some analysis with where the transitions occur, the following is a graph of v' versus wavenumber. The three plots correspond to $v''=0$ being the top plot, $v''=1$ is the middle, and $v''=2$ is the bottom.

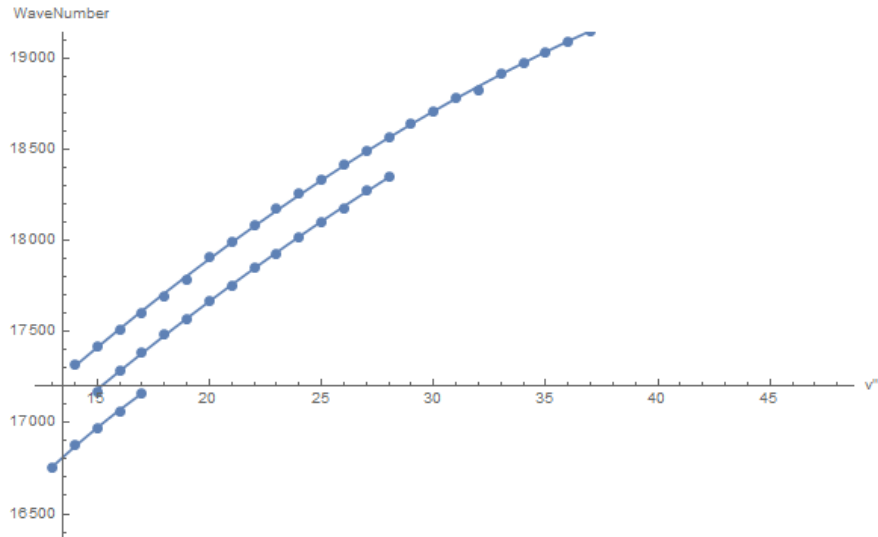


FIG. 4: v' versus Wavenumber (cm^{-1})

The following are the values obtained for the fit parameters discussed in the introduction and their corresponding uncertainties as well as the calculated value for the dissociation energy in units of wavenumbers.

Parameter	Estimate (cm^{-1})	Standard Error (cm^{-1})
T	15681.6	12.9
ω_e'	135.9	0.9
$\omega_e x_e'$	1.0719	0.0141
ω_e''	241.2	8.9
$\omega_e x_e''$	6.525	3.284
D_e'	4236.9	22

TABLE II: Parameter Confidence Interval Table

Finally, when comparing these values to those listed in the literature¹, the value was still about a third of what it should be, or so I thought. the actual dissociation value I was calculating was D_e' when in reality the value posted was D_e'' . In order to find D_e'' it is useful to look at the following graphic:

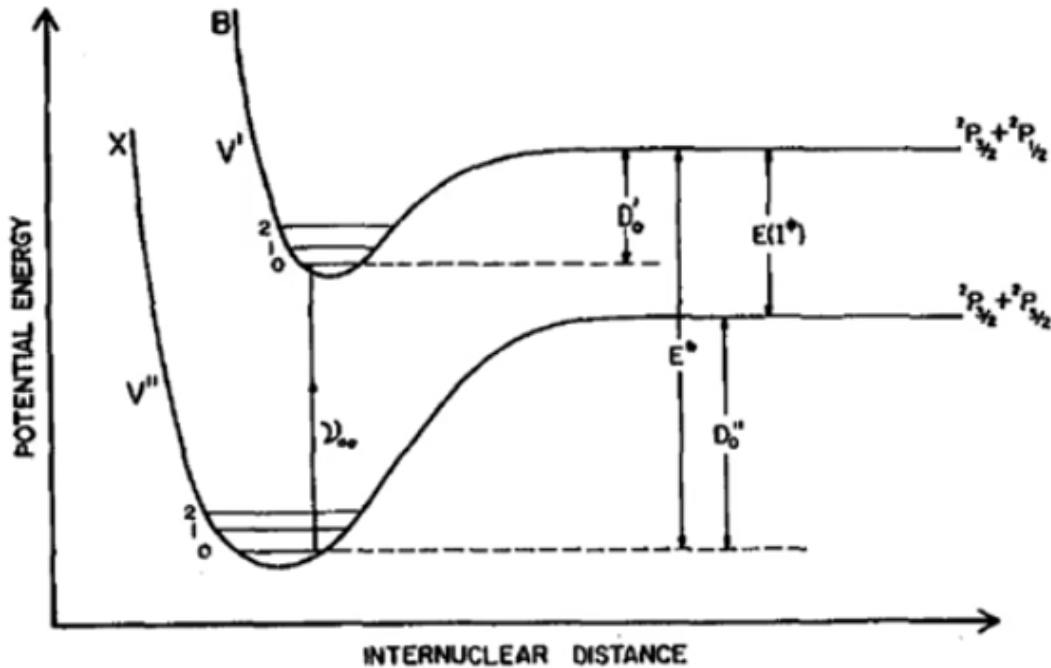


FIG. 5: Potential energy diagram for iodine

In this graphic, the value from the v'' ground state to the v' ground state is our T value. By adding T with D'_e and then subtracting $E(I^*)$, I can find the desired dissociation energy of D''_e . Using the, where $E(I^*)$ is equal to 7589 cm^{-1} , I was able to finally calculate the correct dissociation energy.

$$D''_e = T + D'_e - E(I^*) \quad (6)$$

Parameter	Estimate (cm^{-1})	Standard Error (cm^{-1})
D''_e	12329.5	34

TABLE III: Dissociation Energy

IV. ANALYSIS / DISCUSSION

To begin the experiment, the spectrometer needed to be calibrated. By using the well known spectrum of mercury, I was able to calculate the offset that needed to be taken into account when taking further spectra with the spectrometer. This is important to mention because this offset comes with its own uncertainty and therefore affects and further results where that error may propagate. I chose to mention this at the beginning of this section to assert the claim that this uncertainty in the calibration of the spectrometer is insignificant in the further calculations. I will reason below that the error in any results comes from a different source.

Looking at the overall spectrum gathered for iodine, it looks quite noisy at first glance. The parameters to note for this spectrum is that a data point was taken every 0.01nm with an integration time of 0.02s . I found this combination of wavelength precision and integration time to be the most accommodating. While not presented in this report, in my first attempt at labeling the transition peaks, the $v'' = 1$ line appeared to be slightly different from the other two. There was an upwards shift in the values as they approached lower v' values. I attributed this due to two sources in uncertainty, the first being this noise that is still present in the high resolution spectrum taken. Perhaps knowing the range of these wavelengths, an even higher resolution spectrum could be taken to get a more precise location of the recorded transitions. Fixing the noise and resolution of the spectrum would

help alleviate the second source of error as well, which is human error. A large degree of importance is placed on myself being able to accurately pinpoint the wavelength of specific transitions and a higher resolution scan would help ensure a lower chance of human error. After taking all of these uncertainties into consideration and proceeding to go back to try and resolve the human error in the labeling of the transitions, the results looked much more promising. This supports my claim that human error played a large role in the first set of results and getting a more accurate spectrum would help minimize the correction needed in the data analysis.

Finally, looking at the last dissociation energy calculate, it is relatively close to the expected value. The calculated value of 12329.5 is still lower than the actual value of 12440 presented in the literature¹, but in terms of the experimental results presented in the paper by George and Krishnamurthy, my value falls within three sigma of theirs. This leads me to believe that my results are much more promising after readjusting some labeling errors made after the first trial. Again, perhaps with a higher resolution scan to more precisely pick out the transition peaks, the last discrepancies between my experimental value for the dissociation energy and the actual value could be reconciled.

After all the calculations and corrections were completed, my dissociation energy was not too far off from the value posted in the literature. While a higher resolution scan or better pinpointing of the peaks could help close the gap left in the final values, there are other factors at play that could also be affecting my results. The first factor to consider would be if the offset calculated at the beginning of the experiment shifted at all while running the experiment. This could be alleviated next time by taking another mercury calibration spectrum after taking the high resolution iodine spectrum and comparing the results. The second and more likely factor that is affecting my results is the accuracy of using the Moore potential as a model for this experiment. While using a model that has a second order term is a much better fit than simply estimating the behavior of iodine to be a simple harmonic oscillator, there is nothing saying that only having a second order fit is the best that can be done. Actually, it is quite the contrary. If time had allowed for it, perhaps going back and redoing the experiment with a higher order model would resolve the discrepancies in the experimental dissociation energy I calculated and the actual value posted in the literature.

V. CONCLUSION

Overall, the goal of this lab was to take a look at the emission spectrum of iodine and gain a deeper understanding of the different electronic and vibrational states through spectroscopy. Practicing using spectroscopy is extremely valuable to any physicist as it is extremely useful in many different situations. By exciting a quantity of diatomic iodine, I was able to take a high resolution spectrum and see the different transitions that occurs between these states. After first calibrating the spectrometer and taking into account the nearly 40nm offset needed, a high resolution spectrum of iodine was taken with data points being spaced out by 0.01nm. After careful analysis of the data, I was able to find a dissociation value that looked promising, but still seemed affected by a few sources of error. These sources are most likely a combination of the noise in the spectrum, a shift in the calibration, and the need for a more precise model. The human error that initially faulted some of my results should be minimized after going back and correcting the mislabeled data points. Ultimately, I was able to calculate an experimental value for the dissociation energy of $12329.5 \pm 34 \text{ (cm}^{-1}\text{)}$, which was within three sigma of George and Krishnamurthy's experimental value, and about 110 cm^{-1} less than the actual dissociation energy.

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¹ Simon George and N. Krishnamurthy. Absorption spectrum of iodine vapor—An experiment. *American Journal of Physics*, 57(9):8850–853, 1989.

² NIST. Nist atomic spectra database lines form.

³ Inc. TeachSpin. *Iodine Spectroscopy*. TeachSpin, Inc., 2015.