

# Atomic Spectra

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March 17, 2017

## 1 Goal

The goal of this experiment is to observe the band spectra of Hydrogen and Mercury through the use of an atomic spectrometer. The band spectra of an atom or molecule reveals information about its electronic structure, which can be used to identify or characterize a substance. We also use the observed wavelengths to calculate the ionization energy of Hydrogen and identify specific transitions of the Mercury atom.

## 2 Introduction/Background

As with many quantum mechanical systems, a single electron bound to a proton by the Coulomb force only has access to discrete energy levels [2]. These energy levels are characteristic of the hydrogen atom and the set of possible electronic transitions give rise a unique band structure. In this way, the molecular band structure is a key property for identifying a molecule.

Electrons in a bound state may absorb energy and transition upwards, or release energy to fall. An atom will radiate energy when transitioning downwards, such radiation may be the gamma decay emission of a photon. As in the electron transitions of Hydrogen and Mercury. Then with classical mechanics and the Bohr quantization condition, it is possible to calculate analytically the energy levels of the Hydrogen atom [2]. By requiring the electron angular momentum to be an integral value of  $\hbar$ , one can find the allowed energy levels of the Hydrogen atom and the resulting allowed photon wavelengths. In the Balmer series, electrons fall to the first excited state and release a photon with wavelength:

$$\lambda = \frac{hc/E_r}{1/4 - 1/n^2} = \frac{hc}{E_r}q \quad (1)$$

where  $n^2$  defines the initial energy level and  $E_r$  is the Rydberg energy, which has a theoretical value of  $13.60eV$ .

Even though Mercury has a eighty electrons, Mercury displays a two electron spectra. The Ground state electronic configuration of Mercury has two valence 6s electrons that behave similar to Sodium. After accounting for the spin orbit coupling, the atomic configuration loses degeneracy in the quantum number  $n$  [1]. As a result, Mercury is degenerate and the energy levels are split into an  $S = 0$  singlet and an  $S = 1$  triplet. Singlet and Triplet are so named because when  $S = 1$ ,  $J = L-S, S, L+1$  has three different possibilities, while when  $S = 0$ ,  $J = L + S = L$ , a single option. With the full machinery of the Schroedinger equation and perturbation theory we can make corrections for effects such as relativity, spin-orbit coupling, or spin-spin coupling [1].

The symmetry breaking provides a wealth of new energy levels for electrons to transition between, although transitions are still limited by a set of selection rules. Now to completely describe a system it is necessary to specify  $(n, L, S, J)$ . There is no hope for an analytic solution for the Mercury atom, but a spectrometer can still reveal the energy of each transition by diffracting light according to its wavelength. The well known condition for the angle of constructive interference as seen through a grating spectrometer is:

$$m\lambda = d\sin\theta \quad (2)$$

Where  $m$  is the diffraction order and  $d$  is determined by grating specifications.

### 3 Procedures and Data

In order to observe the band spectra of our samples, we first aligned the spectrometer and found the origin where the viewing tube and ray collimation tube are coaxial. A discharge tube excites the gas molecules to promote atoms to fall back down and release photons. We placed the discharge source about 1cm from a narrow slit at the end of a collimation tube. Then, we aligned the grating face to be normal with the axis shared by the viewing tube and the ray collimation tube.

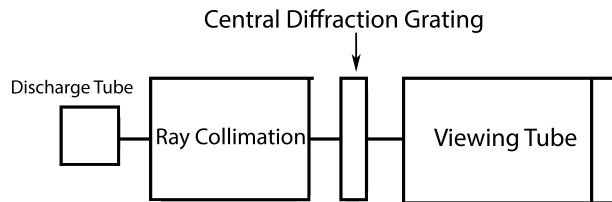


Figure 1: Schematic of the experimental setup. The viewing tube swivels about a vertical axis centered about the diffraction grating.

To observe the spectra, the viewing tube is pivoted about a vertical axis centered about the diffraction grating until a band is visible. Then, the width of the slit is narrowed to the smallest value that still allows the alignment of the cross hair within the viewing tube and an emission band. We used our best judgment to align the cross hair with center of each band and recorded the pivot angle from a built-in vernier scale. We measured these values for the first three transitions of the Balmer series and for five transitions in Mercury. All measurements were recorded of first order diffraction, maximizing the visibility of each line.

Table 1: Measured Diffraction Angles of the Hydrogen Spectrum

|        | Angle $\pm 0.03$ Degrees | CCW Angle $\pm 0.03$ Degrees |
|--------|--------------------------|------------------------------|
| Red    | $11.23 \pm .01$          | $11.20 \pm .02$              |
| Teal   | $8.31 \pm .02$           | $8.29 \pm .02$               |
| Violet | $7.40 \pm .01$           | $7.37 \pm .03$               |

In order to offset systematic error, we took a total of six measurements at each color band for both samples. We alternated directions and took three of the six measurements in the clockwise direction and the remaining three are from the counter-clockwise rotation. Table 1 and 2 display the average value and uncertainty for each band color in both rotation directions.

We identified three contributing factors of uncertainty in our measurements. Our vernier scale was accurate to  $1/60^{th}$  of a degree and the center of each band was difficult to identify beyond precision of  $1/60^{th}$  degree. Thus we estimated the total angular uncertainty to be two minutes. Also, we used a fractional uncertainty of about 0.3% for the grating specifications. We took this value from the Experiments in Modern Physics text by Melissinos [2]. To combine the grating and angular uncertainties we used the relation derived

Table 2: Measured Diffraction Angles of the Mercury Spectrum

|          | Angle $\pm 0.03$ Degrees | CCW Angle $\pm 0.03$ Degrees |
|----------|--------------------------|------------------------------|
| Yellow 1 | 9.83                     | 9.93                         |
| Yellow 2 | 9.81                     | 9.89                         |
| Green    | 9.28                     | 9.37                         |
| Blue     | 8.39                     | 8.42                         |
| Violet   | 7.40                     | 7.43                         |

from Equation 2:

$$\delta\theta = \sin(\theta)\delta d + d\cos(\theta)\delta\theta \quad (3)$$

Where  $\theta$  is the recorded diffraction angle,  $\delta\theta = 2'$  and  $\delta d = 13$  nm.

## 4 Analysis and Discussion

First, we average the data of both the clockwise and counterclockwise measurements for each band. After converting to radians, we use Equation 2 to calculate the resulting wavelength. All measurements were taken of first order diffraction, otherwise the intensity may make measurements inaccurate.

This calculation routine is repeated for Mercury, but as we had insufficient data for Mercury, so Mercury's uncertainties are estimated from the uncertainties for the Hydrogen measurements.

Table 3: Calculated Wavelengths of the Hydrogen Spectrum

|        | Measured Wavelength (nm) | Accepted Value (nm) |
|--------|--------------------------|---------------------|
| Red    | $648 \pm 4$              | 656.3               |
| Teal   | $481 \pm 4$              | 486.1               |
| Violet | $428 \pm 3$              | 434.0               |

Our data for Hydrogen is in reasonable agreement within two standard deviations of the accepted values. Although accepted values lie within the uncertainty of our data, each measured wavelength is of lesser length than the accepted value. This could be a hint there there is some systematic error in our process.

From Equation 1, we can calculate the predicted initial state for each transition. Rearranging for  $n$  and using the measured wavelengths, it is

predicted that we observed the transitions from  $n_o = 3, 4,$  and  $5$ . It is also possible to fit a line to Equation 1 with our data and measure the Rydberg energy. Figure 4 shows a linear fit to our hydrogen data with a resulting slope of  $90.05 \pm .06$  nm, where the slope uncertainty is estimated by the optimization algorithm.

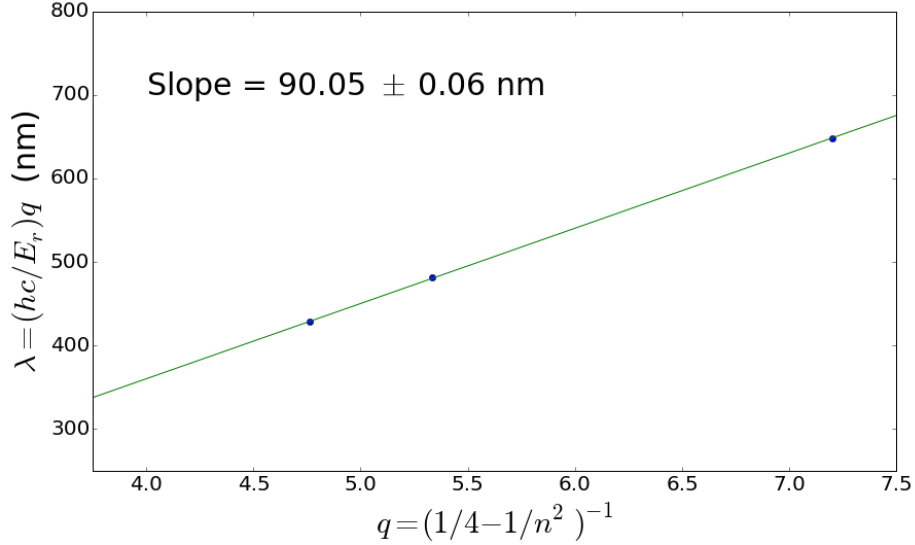


Figure 2: Line fitting results for determining the Rydberg energy.

After inverting the slope and moving a factor of  $hc$ , we find the Rydberg energy to be  $13.8 \pm .1$  eV. Where the uncertainty in this value is calculated from

$$\delta E_r = \frac{hc}{\lambda^2} q \delta \lambda \quad (4)$$

where the  $q$  and  $\lambda$  are chosen to be their average values from Figure 4 and  $\delta \lambda$  is the uncertainty for the red band of Hydrogen.

Mercury cannot be predicted with the same simple natured equations of Hydrogen, instead we show that the energy levels of our observed transitions are consistent with the known transitions and the selection rules for Mercury. The wavelengths of Mercury's spectrum can be used to calculate the energy change of each transition. These energies are then matched to the known transitions of Mercury from the lab manual.

Table 4: Analysis of the Mercury Spectrum

| Mercury  | Measured Wavelength (nm) | Emission Energy (eV) | Transition Terms            |
|----------|--------------------------|----------------------|-----------------------------|
| Yellow 1 | $571 \pm 4$              | 2.169                | $6^1D_2 \rightarrow 6^1P_1$ |
| Yellow 2 | $570 \pm 4$              | 2.175                | $6^3D_1 \rightarrow 6^1P_1$ |
| Green    | $540 \pm 4$              | 2.296                | $7^3S_1 \rightarrow 6^3P_2$ |
| Blue     | $487 \pm 4$              | 2.546                | $8^1S_0 \rightarrow 6^1P_1$ |
| Violet   | $430 \pm 3$              | 2.882                | $7^3S_1 \rightarrow 6^3P_1$ |

As seen in Figure 4, both yellow bands were nearly on top of each other when observed in the spectrometer. This is reflected by their nearly equivalent wavelengths. We also identified the Yellow transitions as ending in the final state, but originating from the single and the triplet state of the  $n = 6$  and  $l = 2$  shell. This fine splitting is due to the electron spin. The second yellow transition is also an example of a special case where the standard selection rule,  $\delta S = 0$ , is disregarded.

## 5 Conclusion

The results of this experiment are scientifically satisfying. We measured a spectrum for Hydrogen that was reasonably close to the accepted values and used the same data to reproduce the Rydberg energy. The results with Mercury were equally desirable as we were able to calculate the transitions energies and find agreement with known measurements. This allowed identification of the transition terms for each energy level, which highlight the important effects of spin related coupling.

The quantization conditions of bound systems let an atom's spectrum be a unique fingerprint that can be observed by atomic spectroscopy. Among the many applications of spectroscopy, is that band structure allows identification of atoms or molecules in a substance. These inherent properties can also be used to detect the constituents of far away gases in other galaxies. Additionally, if an astronomer sees a band that is characteristic of a known element, but all the data is shifted, then it is possible to calculate the red-shift and relative velocities of earth and the object in question.

## References

- [1] David J Griffiths. *Introduction to Quantum Mechanics*, volume 1. 2005. ISBN 0131118927. URL <http://books.google.com/books?id=ipCxQgAACAAJ>.
- [2] Adrian C. Melissinos. *Experiments in modern physics*. Academic Press, 2003.