Measurement of the Mass Ratio of Hydrogen and Deuterium Nuclei and of the Fine Splitting of Sodium Energy Levels

Atomic spectroscopy is a powerful method for studying the fundamental properties of atoms. By studying the spectra of hydrogen and deuterium, we can find the hydrogen Rydberg constant, R_H, and the mass ratio of the hydrogen and deuterium nuclei; we found the Rydberg constant to be $R_H = (1.097073 \pm 0.00016_{\text{stat}} \pm 0.000031_{\text{sys}}) \times 10^7 \text{ m}^{-1}$ and the mass ratio to be $0.494 \pm 0.098_{\text{stat}} \pm 0.041_{\text{sys}}$. We also studied the spectrum of sodium, a similar atom to hydrogen, and calculated the fine splitting of the 3p orbital to be $(0.002127 \pm 0.000023_{\text{stat}} \pm 0.000001_{\text{sys}})$ eV.

I. INTRODUCTION

Spectroscopy, the study of how matter interacts with and emits light, is an extremely powerful experimental technique. Perhaps the most straight-forward atom to study is the hydrogen atom because hydrogen – and other atoms with a single electron, such as deuterium – can be solved exactly using the Schrödinger equation [1].

When an electron transitions from a high energy level to a lower energy level, a photon is emitted with the same energy as the difference between the energy levels. The Rydberg equation accurately gives the wavelength, λ, of these emitted photons for hydrogen to be

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^2 c} \qquad (1)$$

where R_∞ is the Rydberg constant (m_e is the mass of an electron, e the charge of an electron, ϵ_0 the vacuum permittivity, h Planck's constant, and c the speed of light) and n_f and n_i are integers corresponding to the final and initial energy levels, respectively, such that $n_i > n_f$. These wavelengths make up hydrogen spectrum [2].

Equation (1) makes the assumption that the mass ratio of the hydrogen nucleus to the electron is infinite. For a more accurate model, we replace R_∞ with

$$R = \left(\frac{M}{M + m_e} \right) R_\infty \qquad (2)$$

where M is the mass of the nucleus [1]. This suggests that two atoms with different nuclear masses will have different emission spectra with shifted wavelengths. The difference between the wavelength (corresponding to a particular transition) of two atoms with different nuclear masses is known as the isotope shift, $\Delta\lambda$.

We will compare the emission spectra of hydrogen and deuterium, an isotope of hydrogen with an additional neutron in the nucleus. By substituting R_H and R_D, the hydrogen and deuterium Rydberg constants, from equation (2) into equation (1), we find the mass ratio of the hydrogen and deuterium nuclei to be

$$\frac{M_H}{M_D} = 1 - (\Delta\lambda)R_\infty \left(\frac{M_H}{m_e} \right) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad (3)$$

where M_H and M_D are the nuclear masses of hydrogen and deuterium, respectively. We will use known values for the mass of the proton (M_H) and electron.

Finally, we will delve into more complex spectroscopy by studying the fine splitting of the sodium atom. An electron moving in an orbital creates a magnetic field, which interacts with its own magnetic moment. [1] The fine splitting of hydrogen energy levels is caused by this effect, known as spin-orbit coupling, and it can be derived in the hydrogen atom using a quantum mechanical approximation technique known as perturbation theory. We find that orbitals with non-zero angular momentum will split into two levels based on the combined angular momentum of the orbital and electron spin [3]. Because the fine splitting of hydrogen is too small to study with our apparatus, we will study the splitting of the sodium atom, which is large enough for us to observe [2].
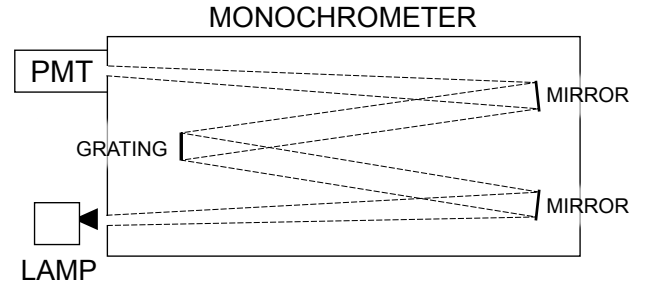
II. EXPERIMENTAL SET-UP

FIG. 1. This is a diagram of the monochrometer. The grating diffracts different wavelengths of light in different directions so that only one wavelength at a time is measured by the PMT. By rotating the grating, we can scan across many different wavelengths.

The set-up for measuring the spectra of hydrogen, deuterium, and sodium is shown in Figure 1. Our sources for the spectra were glass cylinders filled with our atoms of interest in gaseous form. By applying a high voltage to the cylinder, we induced lots of electron energy level transitions, and the gas cylinder emitted bright light [2].

The hydrogen and sodium spectra were taken from gas cylinders with pure hydrogen and sodium. The deuterium spectrum was taken using a gas cylinder which contained a mixture of hydrogen and deuterium.

We used a Jobin Yvon 1250M monochromer to measure the spectra. Light from our source would enter through a 10 μm slit, bounce off a mirror, and land on a grating. The grating is made up of many small groves which diffract light at an angle dependent on the wavelength. As a result, the grating spatially separates the light into individual wavelengths [2]. Our grating had 1800 groves/mm.

The wavelength-separated light from the grating is reflected off of another mirror and finally passes through another 10 μm slit into a photomultiplier tube (PMT), which measures the intensity of the light. For a given grating position, a single wavelength will pass through this slit into the PMT. As the grating is slowly rotated, different wavelengths will pass through the slit, allowing for a range of wavelengths to be measured individually.

The monochromer was controlled using a LabVIEW program, which allowed us to control the step size, i.e. how much the grating was rotated between PMT measurements, and the range of wavelengths measured. For all our scans, we used a step size that changed the measured wavelength by 0.01 A between PMT measurements.

The monochromer software reports a wavelength for every data point, but is not accurate. In order to calibrate the monochromer, we measured the spectrum of mercury. Mercury has well-known spectral lines, so by comparing our reported wavelengths to the known wavelengths, we can find a conversion between the two. Performing this calibration is perhaps most important step in the analysis.

III. ANALYSIS

Before exploring the properties of the atomic spectra, we must calibrate the monochromer with our mercury spectrum. The first challenge is in determining the center of each peak. Figure 2 shows one peak from our mercury spectrum. The peak is wide due to a combination of spectroscopy physics and geometry.

We fit a Gaussian curve to the peak and determined its center to be the center of the Gaussian. We see from Figure 2 that a Gaussian is not a perfect fit for the peak, but it appears a reasonable way to find the center of the peak. We also tried fitting the peaks to a Lorentzian function, but this did not change the values significantly.

After determining the center of all the mercury spectral lines, we compare our data to the known mercury spectrum found in [4]. Figure 3 shows the wavelengths as reported by the monochromer plotted against their distance to the wavelengths we expected to see.

It is not immediately clear what the relationship between the reported and real wavelengths should be. One guess is that they are linearly related; however, a linear
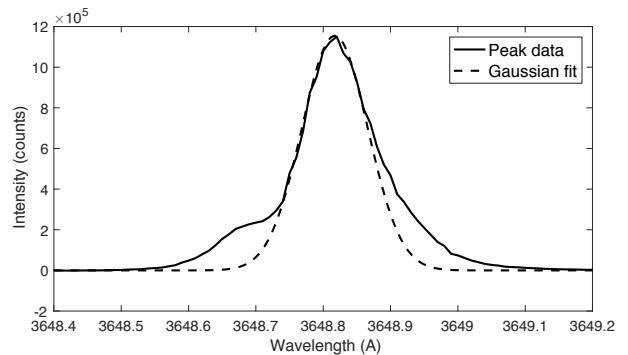

FIG. 2. This is the (uncalibrated) 3650.15 A peak from the mercury spectrum. For all our peaks in all our spectra, we used a Gaussian fit to determine the center of the peak.
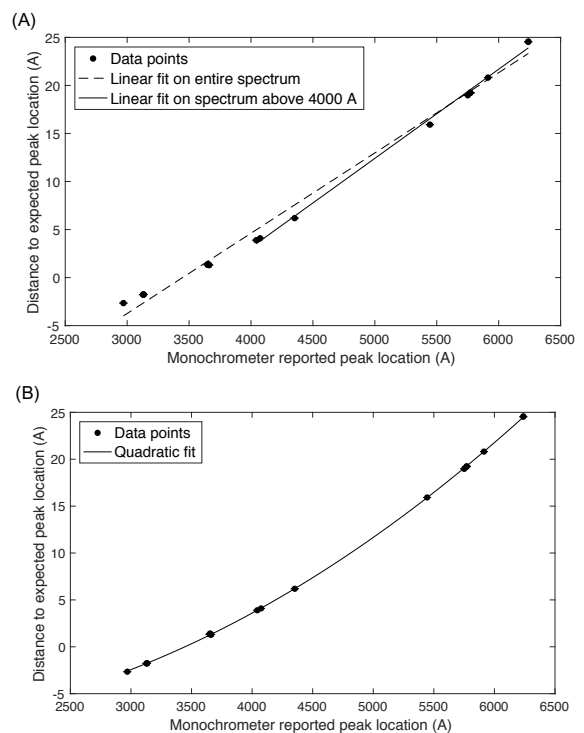

FIG. 3. Here we plot the reported wavelengths of mercury spectral lines against the difference between that value and the wavelength we expect to see. (A) The linear fit of the entire spectrum has a χ_ν^2 value of 80.7, and the fit of the spectrum above 4000 A has a χ_ν^2 value of 11.7. (B) The quadratic fit is much better, with a χ_ν^2 value of 0.388.

fit has a χ_ν^2 value of 80.7. Next, we try restricting the fit to points above 4000 A, since that is the range we care most about for the spectra we will measure. This second fit is better, but still not excellent, with a χ_ν^2 value of 11.7. Finally, we fit a quadratic curve to the data. This resulted in a very low χ_ν^2 value of 0.388, suggesting that this is the best way to model the calibration curve.

TABLE I. This table compares the knowns wavelengths with the hydrogen spectrum ("Expected") with the wavelengths calculated using the linear and quadratic calibration methods.

Expected (A)	Linear (A)	Quadratic (A)
6562.785 (doublet)	6561.057	6562.429
4861.33	4862.087	4861.392
4340.47	4340.656	4340.488
4101.74	4101.697	4101.952
3970.072	3969.667	3970.205
3889.049	3888.499	3889.229
3835.384	3834.708	3835.573

TABLE II. Here are the sodium doublets with their corresponding orbital transition. Shown in the last column is the splitting of the 3d orbital as calculated from each transition.

Doublet (A)	Transition	Splitting (eV)
6154.06 and 6160.62	$3p - 5s$	0.002144
5889.84 and 5895.83	$3s - 3p$	0.002140
5682.36 and 5687.94	$3p - 4d$	0.002140
4747.88 and 4751.74	$3p - 7s$	0.002122
4494.27 and 4497.67	$3p - 7d$	0.002088

To test which calibration method is most accurate, we used all three methods to determine the wavelengths of our hydrogen spectrum. The results, displayed in Table 1, show that for every peak except one, the quadratic calibration was significantly closer than the linear calibrations, with an average error of 0.16 A. (Note that both linear calibration methods gave the same values to three decimal places, and thus are displayed in one column of the table.) We will proceed using the quadratic calibration in our calculations, and our uncertainty in which method to use will be accounted for in systematic error.

III.1. Isotope Shift in Deuterium

Using the calibration developed in the previous section, we arrive at accurate spectral lines for hydrogen and deuterium. Since the deuterium spectrum was taken from a cylinder of mixed deuterium and hydrogen, we ended up measuring the hydrogen spectrum twice. For purposes of accurate comparison with deuterium, we will use only the spectrum taken alongside deuterium for our calculations. However, we will examine the difference between the two hydrogen spectra when assessing systematic error.

For each wavelength we measured in the hydrogen spectrum, we can use equations (1) and (2) to calculate the Rydberg constant for hydrogen, R_H. The resulting values are averaged to arrive at $R_H = (1.097073 \pm 0.00016_{\text{stat}} \pm 0.000031_{\text{sys}}) \times 10^7$ m^{-1}. This was repeated for deuterium to find $R_D = (1.097375 \pm 0.00016_{\text{stat}} \pm 0.000031_{\text{sys}}) \times 10^7$ m^{-1}.

Using our values for R_H at every wavelength, we find R_∞ by using equation (2). We can find the isotope shift, $\Delta\lambda$, by examining the distance between peaks in the two spectra. Finally we use equation (3) to find the ratio of the hydrogen nucleus to the deuterium nucleus, M_H/M_D, from each peak. This is averaged to get an overall value for the ratio: $M_H/M_D = 0.494 \pm 0.098_{\text{stat}} \pm 0.041_{\text{sys}}$. In the literature, this ratio has been measured to be 0.4963, so our measured value is quite close [7].

III.2. Sodium Spectrum

We followed the same procedure as before to find the wavelengths in our sodium spectrum. The spectrum is a series of doublets, i.e. peaks that are very close together. By comparing our results to the transitions listed in [5], we find that all the transitions we measured either come from or go to the 3p orbital. The doublets and their transitions are show in Table 2.

As mentioned earlier, perturbation theory tells us that orbitals with non-zero angular momentum (p, d, f, etc.) will split into two energy levels. This matches our data, as the doublets transitioning from and to 3p suggest that we are observing the splitting of 3p into two energy levels.

We convert the wavelengths into energies using the formula $E = h/\lambda$. The energy splitting of the 3p orbital is the difference between the energies of a doublet, since the energies of the doublet are simply the energies of the 3p orbital relative to a different orbital. These values were calculated for every doublet, as shown in the third column of Table 2. Averaging these values, we arrive at a final value for the 3p sodium orbital splitting of $(0.002127 \pm 0.000023_{\text{stat}} \pm 0.000001_{\text{sys}})$ eV.

It should be noted that it is possible that a transition from a d orbital to 3p could be a doublet because of splitting in the d orbital instead of the 3p orbital, since d orbitals also have non-zero angular momentum. However, this is likely not the case for both the 3p – 7d and the 3p – 4d transitions that we see. Because the formulae for spin-orbit coupling tell us that the energy level splitting decreases with n and ℓ, splitting for the 4d and 7d orbitals would be much smaller than than for the 3p orbital. We do not observe such small splitting energies.

III.3. Sources of Systematic Error

The main sources of systematic error in the calculation of R_H, R_D, the mass ratio of the hydrogen and deuterium nuclei, and the energy splitting of the sodium 3p orbital are listed in Table 3.

The largest source of error in calculating all these values was the uncertainty in what calibration method to use.

TABLE III. Here are all the sources of systematic error accounted for in the calculation of R_H, R_D, and the mass ratio of the hydrogen and deuterium nuclei. Sources of error are listed along with the size of the error they contributed, expressed as a percent of the final value.

Source of error	Percent
R_H:	
Uncertainty in correct calibration method	0.0026%
Ability of monochrometer to reproduce results	0.00018%
Mass ratio:	
Uncertainty in correct calibration method	5.4%
Proton and electron mass uncertainty	$\ll 1\%$%
Sodium orbital splitting:	
Uncertainty in correct calibration method	0.035%
Planck's constant uncertainty	$\ll 1\%$

We recalculated everything using the three calibration techniques discussed at the beginning of Section III and observed how the results changed. The systematic error was taken to be one half of the range of results.

Another source of error in the calculation of R_H and R_D was the ability of the monochrometer to reproduce results. As mentioned earlier, we measured the spectrum of hydrogen twice – once using the gas cylinder of pure hydrogen, and once using the gas cylinder of hydrogen mixed with deuterium. The two measurements of the spectrum were off from each other by an average of 0.015 A. This was added as a systematic error to the wavelengths of all our spectra to account for the monochrometer's inability to reproduce results perfectly. Note that this error was not applied to the mass ratio or orbital splitting, as they only depended on the distance between peaks taken in the same monochrometer scan.

IV. RESULTS

By studying the spectra of hydrogen and deuterium, we have found the Rydberg constant for hydrogen to be $R_H = (1.097073 \pm 0.00016_{\text{stat}} \pm 0.000031_{\text{sys}}) \times 10^7$ m^{-1}. The accepted values is $R_H = 1.096776 \times 10^7$ m^{-1}, which is extremely close to what we found; the percent error on our value for R_H is 0.027%.

The mass ratio of hydrogen and deuterium nuclei was measured to be $0.494 \pm 0.098_{\text{stat}} \pm 0.041_{\text{sys}}$. This mass ratio has been previously measured to be 0.4963, so our value is quite close, with a 0.47% error [7]. However, the error on our value is quite large, and future experiments should aim to reduce this error. It should be noted that the ratio we measured is not equal to the ratio of $m_p/(m_p + m_n) = 0.49966$, where m_p and m_n are the masses of a proton and neutron, because of bonding energies within the nucleus.

Finally, we found the splitting of the sodium 3d orbital to be $0.002127 \pm 0.000023_{\text{stat}} \pm 0.000001_{\text{sys}}$ eV. This matches the accepted value of 0.0021 eV [8].

Overall, our results match the currently agreed-upon values quite precisely. We were able to calculate these fundamental constants and properties of hydrogenic atoms by the simple, but powerful, technique of spectroscopy.

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