SPECTROSCOPY AND THE HYDROGEN ISOTOPE SHIFT

Spectroscopy is of great importance in many branches of physics and chemistry. From the wavelengths of light that are emitted or absorbed by a source one can determine the chemical composition of that source. In astrophysics, spectroscopy is used to figure out what stars are made of. In nuclear physics, spectroscopy is used to determine things like the nuclear magnetic and quadrupole moments. In condensed matter physics, spectra give information about different states of matter and physical conditions like temperature. Spectroscopy stands on its own as a field in physics, as is demonstrated by the vast number of texts on the subject. It is important for all physics students to learn the basics of spectroscopy, if not for their own work, then for the ability to understand the work of others.

Introduction: Bohr Model of Hydrogen

Neils Bohr modeled the hydrogen atom as a single electron in orbit about a nucleus comprising a single proton. He assumed the only force acting on the particles was the Coulomb attractive force. As you may recall, the force, F, on an electron due to a hydrogen nucleus is given by

$$F = \left| \frac{k(q_e)(q_p)}{r^2} \right| = \frac{ke^2}{r^2} \tag{1}$$

where e is the electron charge, which equals 1.60×10^{-19} C, k is a constant that equals $1/(4\pi\epsilon_0) = 8.99 \times 10^9$ N·m²/C², and r is the distance of separation between the proton and the electron. Bohr assumed that the electron orbits in a circular fashion around a fixed nucleus. Since the mass of the proton is roughly 2000 times greater than that of the electron, the assumption of a fixed nucleus (called the Born-Oppenheimer approximation in some texts) is reasonable. The implication is that

$$F = \frac{m_e v^2}{r} \tag{2}$$

where m_e is the mass of an electron, which equals 9.11×10^{-31} kg, and v is the velocity of the electron as it orbits the nucleus.

The startling assumption that Bohr made was that this entirely classical situation was quantized. The notion of quanta had already been introduced by Planck, but the application to atoms was novel and extremely counterintuitive.

The Wilson-Sommerfeld quantization condition states that

$$\oint p_a da = nh \tag{3}$$

where *n* is an integer, $h = \text{Planck's constant} = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$, *a* is some generalized coordinate in a Lagrangian, *L*, and p_a is the conjugate momentum given by

$$P_a = \frac{\partial L}{\partial a} \tag{4}$$

For a particle moving in a circle, the generalized coordinate is θ , and the quantization condition may be rewritten as

$$\oint p_{\theta} d\theta = nh , \qquad (5)$$

which is the same thing as saying that angular momentum is quantized.

Calling the potential energy U and the kinetic energy T, the Lagrangian is written as

$$L = T - U = \frac{1}{2} m_e v^2 + \frac{k e^2}{r} = \frac{1}{2} m_e (r \dot{\theta})^2 + \frac{k e^2}{r}$$
 (6)

which makes the angular momentum

$$P_{\theta} = \frac{\partial L}{\partial \theta} = m_e r^2 \stackrel{\bullet}{\theta} \tag{7}$$

Since θ and $\dot{\theta}$ are independent,

$$\oint P_{\theta} d\theta = 2\pi (m_e r^2 \dot{\theta}) = 2\pi (m_e r v) = nh \tag{8}$$

From equations (1), (2) and (8) it is possible to show that r is quantized (dependent on n). One can take this a step further and show that the total energy is quantized as well. The total energy, E, is given by

$$E = T + U = \frac{1}{2} m_e v^2 - \frac{ke^2}{r}$$
 (9)

Of course, the Bohr model is not perfect. It doesn't give any insight into why a classical electron orbit should have quantized angular momentum. It is puzzling in that the electron is presumed to obey classical electromagnetic theory and yet does not radiate because of the acceleration associated with its angular motion. Although the Bohr model succeeds in predicting the hierarchy of atomic energy levels in the hydrogen atom, it lacks a fundamental basis.

Bohr theory is also incomplete. Since the Wilson-Sommerfeld quantization rule can be applied only to periodic systems, this theory has no way of approaching non-periodic quantum-mechanical phenomena like scattering. Also, Bohr theory predicts energy levels, but cannot predict transition rates between levels. Most obviously, the theory, even limited to single-electron atoms, occasionally fails to fit observations (*e.g.*, ionized helium). A completely quantum-mechanical treatment of atomic structure with the Schrödinger equation corrects these faults. You can refer to any standard quantum mechanics textbook for further discussion (for example, Eisberg and Resnick p. 111).

Exercise 1a: Derive the expression for *r* in terms of n, $\hbar = h/2\pi$, m_e , k, and e.

Exercise 1b: Derive the expression for *E* in terms of n, $\hbar = h/2\pi$, m_e , k, and e.

Exercise 1c: Write your answer for Exercise 1b in the form $E = -hc\frac{Ry}{n^2}$

where c is the speed of light in vacuum. Ry is called the Rydberg

constant. What are the units on Rv?

Exercise 1d: Give a numerical result for E as a function of n in both J and eV.

The latter number should be familiar to you.

Introduction: Transitions Between States

If an electron is in a high energy (high n) state, it may be possible for it to undergo a transition to a lower energy state. When it does so, the extra energy may be released in the form of a photon. For light of wavelength λ we know $E = hc/\lambda$, so that

$$\frac{1}{\lambda} = \frac{\left| E_f - E_i \right|}{hc} = Ry \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \tag{10}$$

Eq. 10 is known as the Rydberg equation. It can be used to calculate the wavelength of light given off for a transition between arbitrary initial and final states.

Different names are assigned to certain sets of lines in the hydrogen spectrum, as you can see by the following list.

- Lyman series: $n_f = 1$ and $n_i = 2, 3, 4, ...$
- Balmer series: $n_f = 2$ and $n_i = 3, 4, 5, ...$
- Paschen series: $n_f = 3$ and $n_i = 4, 5, 6, ...$
- Brackett series: $n_f = 4$ and $n_i = 5, 6, 7, ...$
- Pfund series: $n_f = 5$ and $n_i = 6, 7, 8, ...$

The Balmer series is the most famous, since Balmer was the first to stumble upon equation (10). The Balmer series is the set of wavelengths you will be studying in this lab.

Exercise 2: Derive equation (10) from Exercise 1c and $E = hc/\lambda$.

The above equations were all derived under the assumption that the nucleus was fixed (Born-Oppenheimer approximation). To account for the motion of the nucleus it is easiest to consider the motion of the electron *relative* to the nucleus (since the Coulomb force is a central force). Doing this means the electron's *relative* acceleration is proportional to the force (see Figure 1). The constant of proportionality between the force, F, and relative acceleration, a, is $F = \mu a$ where μ is the *reduced mass* given by

$$\mu = \frac{m_e M}{m_e + M} \,, \tag{11}$$

where *M* is the mass of the nucleus.

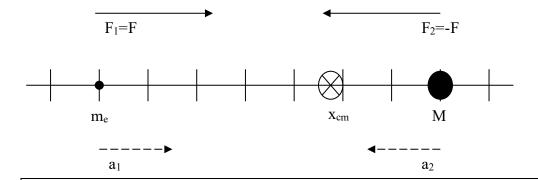


Figure 1. The figure above looks at the electron-nucleus system from the center of $mass(x_{cm})$ frame. The relative acceleration of the electron is given by

$$a = a_1 - a_2 = \left(\frac{F}{m_e}\right) - \left(\frac{-F}{M}\right) = F\left(\frac{1}{m_e} + \frac{1}{M}\right)$$

This can be rewritten as $F = \mu a$, where μ is the reduced mass given by

$$\mu = \frac{m_e M}{m_e + M}.$$

With the electron mass m_e changed to the reduced mass μ , the Rydberg equation becomes

$$\frac{1}{\lambda} = Ry \frac{\mu}{m_e} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \tag{12}$$

For different isotopes of hydrogen, M and thus μ will differ. This will give rise to slightly different spectra for different isotopes, a phenomenon called the *isotope shift*. In this lab you will look at the isotope shift between hydrogen (whose nucleus is a single proton) and deuterium (whose nucleus contains a proton and a neutron).

Exercise 3: Calculate the first six wavelengths of the Balmer series to five-place accuracy for both hydrogen (H) and deuterium (D). The accepted value of Ry is $Ry=1.097373x10^7$ m⁻¹.

Exercise 4: What minimum resolution (in Å) will be required to distinguish the sixth wavelength of H from that of D?

Exercise 5: In doing this lab you will need to do a calibration measurement. Calibration is done by looking at two spectral lines of Hg that are closely spaced (called a *doublet*). Would it be better to use a doublet with short or long wavelength?? (Hint: the doublet spacing decreases with shorter wavelengths) Explain.

Materials and Methods:

Early spectral observation was done by means of shining a light source on a prism. Since the prism's index of refraction depends on the wavelength of light (see Hecht pp. 163-164), after it passes through the prism the light will show different colored bands. The list of detected wavelengths and their relative intensities comprise the spectrum of the light source.

Diffraction gratings have the same effect as a prism, but with fewer losses and greater accuracy. Rather than separating light via a wavelength-dependent index of refraction, gratings take advantage of the phenomenon of interference. Our diffraction gratings look like many small angled mirrors lying next to each other (see Figures 2 and 3). Since the path length difference between adjacent mirrors is slightly different, interference occurs between their reflected light rays. As more and more mirrors are

put together there will be more and more path length differences. These path length differences will always be multiples of the first path length difference. As infinitely many mirrors are added, only one wavelength will then fit the constructive interference condition. In practice, a very large number of mirrors is used, and only wavelengths within a narrow band constructively interfere. The constructive interference condition is given by

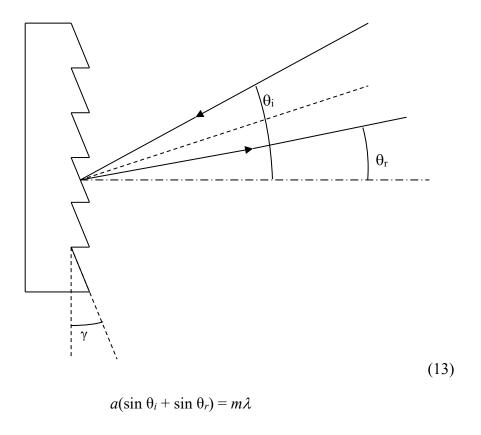


Figure 2. Here the grating reflects incident light. The angle γ is known as the blaze angle. Notice that the angles θ_i and θ_r are measured relative to horizontal and not the normal to the mirror faces. Typically, a grating is placed perpendicular to a light beam. This implies that light is incident from along the horizontal axis $(\theta_i = 0)$.

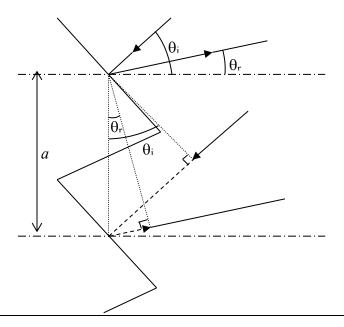


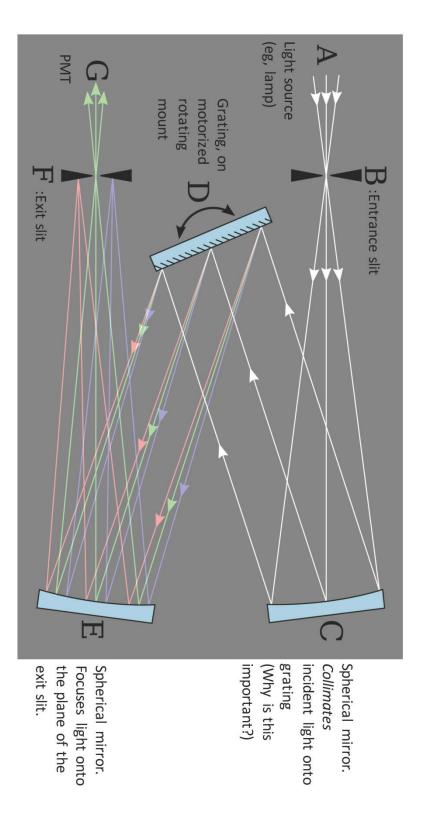
Figure 3. The path length difference, δ , is shown as a dashed line (both segments together). By using trigonometry we find $\delta = x_i + x_r = a(\sin \theta_i + \sin \theta_r)$ where a is the grating spacing. This leads to a constructive interference criterion of $a(\sin \theta_i + \sin \theta_r) = m\lambda$ where m is an integer and λ is the wavelength of light. Notice that if θ_r is negative, the second term in δ is also negative. Adding more mirrors will allow fewer and fewer wavelengths to meet simultaneously all possible interference conditions.

Materials and Methods: Devices

Spectrometer

In practice, a mechanism is used to turn a diffraction grating slowly while the spectrum is recorded. This machine is called a *spectrometer*. A small amount of light passes into the spectrometer through a thin slit (about 30 microns wide) and strikes a motorized grating. A speed control allows you to determine how quickly the machine sweeps through the spectrum (PULL and turn). At slower speeds it is easier to get fine details, while faster speeds are best for getting a rough idea of where you are in the spectrum. A counter provides a rough estimate of the wavelength being detected, but you will need to use a known source to calibrate the spectrometer (you will use a Hg arc lamp). The motorized drive is reversible so you can scan up or down in wavelength (but take note of Exercise 6 on page 10). The figure on the next page shows the layout of the optical elements inside the spectrometer you are using. Page 9 lists the strong emission lines from the mercury lamp.

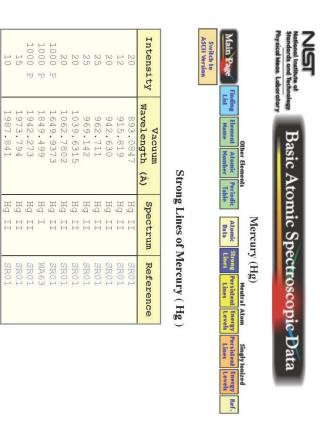
Czerny-Turner type Monochromator: what's on the inside



Only the 1^{st} order rays from the grating are depicted here. Of course, the n=2, 3...order light is also focused on the plane of the exit slit.

Table of the emission lines from a mercury arc lamp

http://physics.nist.gov/PhysRefData/Handbook/Tables/mercurytable2.htm



Exercise 6:

While it is possible to sweep the spectrum up or down, it is considered better experimental practice always to scan in the same direction (and to scan from before the starting wavelength). Why is this???? Also, is the spectrometer accurate all the way through the spectrum from top to bottom? Think about the internal mechanism of the spectrometer. This is related to why you are instructed in the Procedures/Calibration section to scan through the second order of the Balmer series. Why??

DO NOT CHANGE THE SWEEP SPEED WHILE THE MOTOR IS RUNNING!! DO NOT QUICKLY REVERSE THE DRIVE DIRECTION; KEEP THE SWITCH IN THE "OFF" POSITION FOR A FEW SECONDS!! DO NOT ATTEMPT TO LOOK INSIDE THE SPECTROMETER!!

Photomultiplier Tube

To get accurate spectra by means of a grating, it is important to have a very thin slit (\sim 10-30 microns) between the light source and the grating.

Exercise 7: Why is it necessary to have a very thin slit between the light source and grating?

Since only a thin strip of light is hitting the grating, however, the lines will be very faint. In order to determine the intensity of light at each wavelength, we must use a very sensitive light detector.

A photomultiplier tube (PMT) can detect very faint light signals by taking advantage of the photoelectric effect, with gain on the order of 10⁷. Light strikes a metallic or semiconducting material, which then emits electrons, called photoelectrons. The photoelectrons are accelerated towards a positively charged plate called a dynode. When an electron strikes a dynode, the dynode emits secondary electrons. Inside a PMT there is a series of dynodes, each at a higher positive voltage than the previous one. By guiding the electrons into collisions with several successive dynodes, a typical PMT ends up producing about 10⁷-10⁹ electrons from a single photon. Though this process of amplification takes some time (0.1-20 ns), that time is negligible for many experiments. A simple calculation of currents (see **Exercise 8**) shows that the output of a PMT is actually measurable by the devices in this lab.

Even when no photons strike the metal or semiconductor, some electrons will be ejected because of thermal excitations. The thermal electrons cascade from dynode to dynode just as the photoelectrons do, producing a current. Since this current is produced without any photons it is called a *dark current*.

To achieve its tremendous gain in signal the PMT requires a high voltage power supply. For optimum performance the PMT power supply should be left on and

should not be adjusted by the student. If it has been turned off, the PMT will require a long time to warm up again. IF THE PMT IS EXPOSED TO HIGH LIGHT LEVELS IT WILL BE PERMANENTLY DAMAGED. NEVER OPEN THE SPECTROMETER UNDER ANY CONDITIONS!

Exercise 8a: Assume that a 100-Watt source disperses spherically. The

spectrometer slit is 10 μm by 1 cm and is 10 cm away. How much

power is radiated through the slit?

Exercise 8b: Assume this light then travels for about 1 m inside the

spectrometer before hitting the PMT slit (same dimensions). What

is the power radiated into the PMT?

Exercise 8c: Assuming a wavelength of 5000Å, how many photons per second

will arrive at the PMT? Hint: $P \sim E/t$ and $E = hc/\lambda$.

Exercise 8d: Use $I = \Delta Q/\Delta t$ to determine the current produced by a typical

PMT (assume each photon hitting the PMT produces 10⁷ electrons). Notice the insanely large current that would melt the PMT if it were exposed to a 100-Watt bulb by opening the

spectrometer with the shutter open!

Exercise 8e: What is the required resolution of the current measuring device to

get at least 5-digit accuracy in measuring the photocurrent?

Picoammeter & Chart Recorder

To measure the very minute currents, similar to the ones you calculated in **Exercise 8**, from the PMT, you will use a picoammeter. As its name suggests, a picoammeter can measure currents accurately into the picoampere range or better. It has provisions for nulling the dark current of the PMT. In this experiment setup, information from the picoammeter is sent to a computer. The level of the trace rendered on the screen is proportional to the PMT current output read by the picoammeter (see **Exercise 9**).

Exercise 9: By reading the manual for the picoammeter, figure out how

the input current (from the PMT) determines the signal to the computer. What is the maximum level of this signal (give

units)?

Exercise 10a: Assume that you set the maximum of the Y-axis at 2 V,

the minimum at zero, and the picoammeter is on the 2 nA scale. At what value on the Y-axis will the trace be with

PMT currents of 0, 0.5, 1, 2, 2.5 nA?

Exercise 10b: What happens if the Y-axis maximum is set to 1 V (with

the minimum at zero)? What if the picoammeter scale is changed to 20 nA with the Y-axis maximum still at 2 V?

Exercise 10c: Give the optimum scale settings for both the recorder and

picoammeter to measure the following currents: 1, 5, 9, &

20 nA.

Materials and Methods: Procedures

Calibration

The shift you are to measure is of the order of 1 Å. The data for the H and D spectra will be recorded on the computer via a program called "DataLogger." You will need to correlate distances along the X-axis (time) with wavelength differences. You can do this by recording a known spectrum, in this case that of elemental Hg, which has two bright lines spaced by a known amount. Once this is recorded, you will know what time difference corresponds to the difference in wavelength of the two Hg peaks, at least for the computer data rate and spectrometer scan settings you used. If you use different spectrometer speeds, you will need to calibrate the recorded spectrum for each one.

- 1. Set the spectrometer slit and PMT slit to 30 microns. You can find a list of slit sizes for the spectrometer below and to the right of the PMT. If you need assistance, ask your TA!
 - o To set PMT slit width: Turn the knob just underneath the PMT from the zero mark to your desired slit width. Each line on the knob of the micrometer head corresponds to 10 microns. The setting shown below adjusts the slit width to 30 microns.



O To set spectrometer slit width: On the spectrometer, rotate the knob to '3'. You know you've reached it when you feel a click. (The click will probably not be sharp, but you will feel the knob settle into position. The desired number should face you as you look from the front of the table.) You will probably need to rotate the knob multiple turns to line up the desired slit. *Important: Make sure that the slit is actually lined up in front of the entrance to the spectrometer. The photographs below illustrate this.*



- 2. The mirrors of the spectrometer are set in the appropriate positions. (Two, inside the instrument, are inaccessible. Two are for optional placements of the entrance and exit slits.) Do <u>not</u> change these settings. The light should enter the slit in the port opposite the PMT (the one nearer the wall).
- 3. Place the Hg lamp between 1 and 10 inches from the spectrometer slit.
- 4. Once the lamp is in place, be sure the PMT shutter and the spectrometer slit shutter are open.
- 5. Follow the turn-on procedure for the picoammeter, located on the cover of the spectrometer. Disengage the autorange feature and select a range appropriate to the current reaching the picoammeter. (Autorange might cause problems when you are recording spectra.)
- 6. Sweep the spectrometer to the second-order diffraction peak located at about 6263 Å (called the 6263.0 Å/6263.6 Å doublet). The picoammeter reading should increase. Try to get the spectrometer on the peak by finding the maximum current on the picoammeter. You may have to change ranges on the picoammeter.
- 7. Run the chart recording program (DataLogger; see Appendix A on page 16).

- 8. Try moving the Hg lamp and try to maximize the current. You may have to change the range of the picoammeter.
- 9. Try to record the doublet while running the spectrometer at 5 Å/minute. (PULL and turn the knob to set this.) You may get only a single peak, but you will probably at least partially resolve the doublet (the peak will at least show a slight dip in the middle).
- 10. Try adjusting the slit sizes for the spectrometer and the PMT and repeating steps 6-8 until you can resolve the doublet as clearly as possible. This requires some patience, but will pay off later.
- 11. Once you have adjusted the resolution, make several chart recordings of the doublet and the peak located at 6251.4 Å. Use this information to calibrate the X-scale. {Hint: You know the distance between the doublet peaks. Find the time difference and determine (Å/second).}

Measuring the Isotope Shift

CAUTION: The HD lamp emits UV light. PLACE THE UV SCREEN BETWEEN THE LAMP AND EVERYONE NEAR THE SPECTROMETER BEFORE YOU TURN THE LAMP ON.

- 1. Place the Hydrogen-Deuterium tube near the slit spectrometer slit.
- 2. Sweep the spectrometer onto a known peak of the Hydrogen spectrum (see **Exercises 5 and 6**). It is probably advantageous to start with the longest wavelength and work your way down. Try to record the spectrum at 5 Å/sec. You may need to adjust the resolution as you did in the calibration phase.
- 3. When the resolution is adjusted, record the first six Balmer lines. You should record each line several times to get an average.
- 4. Measure the separations and determine the average value of the isotope shift for each spectral line.

Spectral Shift Analysis:

1. The Bohr model assumes a single hydrogen atom (or deuterium atom) with a single electron orbiting it. The lamp uses H₂ and D₂ molecules. How will this affect the spectra? (Hint: How highly excited are those molecules? Exactly what species are emitting the spectra you observed?) Is there any

- way to excite the molecules other than bumping an electron to a higher energy level? (Hint: There is more than one.)
- 2. Compare the relative peak heights of the H and D spectra for each of the six Balmer lines studied. Is there a pattern? What does it mean?
- 3. Why are the spectrometer slits vertical instead of horizontal?
- 4. Describe and explain the relative heights of the six Balmer lines. Describe several possible factors that may affect the peak heights.
- 5. Estimate the error and identify the main sources of error for the experiment. Calculate the expected error in your measurement of the shift. Compare your experimental values to those determined in **Exercise 3** in terms of percent difference. Are your experimental values acceptable? Explain any discrepancies or possible sources of error that you didn't account for, which may have affected the experimental values.

Include the following in your lab book:

- Exercises 1 through 10
- Measuring the Isotope Shift Questions
- Spectral Shift Analysis Questions
- Printout of your Spectrum (both Hg and Hydrogen-Deuterium spectra)
 - calibration calculation and appropriate wavelength labels
- Procedure and Conclusion

Appendix A: Using the Signal Recording Software

The Signal Recorder program, along with an analog-to-digital (A/D) converter, allows you to monitor and record the output of the picoammeter. Before opening the program, turn on the picoammeter and follow the initialization instructions located on the front of the monochromator. Be sure to disable autorange. The XXX.0000 nA scale is appropriate for the mercury source calibration stage. You will have to experiment to find out the proper range for subsequent parts of the lab.

Before recording you should create a new folder to save your work. Please create this folder inside the "data" folder on the Desktop. Label this folder with your name; make sure you place all of your recordings here! It is also recommended that you copy all of your data onto a flash drive to make sure they don't get overwritten. You can now start the program by double clicking the "DataLogger" icon shown below. When you open it you should see something similar to Figure 1.



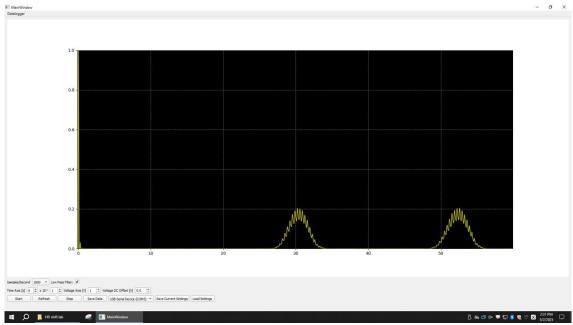


Figure 1.

Below is an enlargement of the control and settings panel at lower left.



The "Samples/Second" menu allows you to select the rate at which the computer takes samples. 1000 samples per second should be fine. Because you will be looking at a slowly changing voltage, you should make sure that the "Low Pass Filter" box is checked. Use the seconds and power of ten settings under "Time Axis [s]" to set the acquisition time. For example, the setting shown sets the window at one minute; changing the power of 10 to "2" would set it to 10 minutes.

When you click "Start," the trace begins at the left edge of the plot window and runs across the screen. When it reaches the right edge, data continue to be added at the right end of the trace, while earlier data are pushed off to the left. *Any data that go off the left edge are lost.* Because of this, you must be careful to set the scan rate and the time axis so that all the peaks you need to observe in a single scan will fit within the time of the plot window.

Use the "Voltage Axis [V]" and "Voltage DC Offset [V]" settings to adjust the scale and offset so that the whole trace appears in the window, and takes up as much of the window as possible without going offscale.

Once you have recorded a spectrum click the "Save Data" button. A window will open, where you can choose the file name and the location where you wish to save it. The data will be saved in a comma-delimited text file (.csv). Be sure to label your files appropriately, and also to write down in your lab book the slit widths, picoammeter scale and spectrometer scan speed for every recording/file name. At the end of this experiment you should have multiple data files; each Balmer line should have its own file!

Once you have acquired your data you are ready for analysis. You can open your data files with Excel or any other spreadsheet or graphing and fitting program that you desire. The file contains two headers with information about the data acquisition, a line with column labels, then two columns that contain the time in seconds and the picoammeter output voltage. At a data collection rate of 1000 Hz, an X-Y pair is recorded every 0.001 seconds, which you can see by examining the first column of data.

It is recommended to use a smoothing function to help smooth the data, especially on the low intensity signals where the data jump around a lot.

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