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 moment. 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 any physics student 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 comprised of 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

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

where e is the electron charge $= 1.60 \times 10^{-19}$ C, k is a constant $= 1/4\pi\varepsilon_0 = 8.99 \times 10^9$ $\mathrm{Nm^2/C^2}$, 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

$$F = \frac{m_e v^2}{r} \qquad (2)$$

where m_e is the mass of an electron $= 9.11 \times 10^{-31}$ kg and v is the velocity of the electron as it orbits the nucleus.

The startling assumption which 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

$$\oint p_a\, da = nh \qquad\qquad (3)$$

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

$$P_a = \frac{\partial L}{\partial \dot{a}} \qquad\qquad (4)$$

For a particle moving in a circle, the generalized coordinate is $\boldsymbol{q}$ and the quantization condition may be rewritten as

$$\oint p_q\, d\boldsymbol{q} = nh, \qquad\qquad (5)$$

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

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

$$L = T - U = \frac{1}{2} m_e \boldsymbol{n}^2 + \frac{k\,e^2}{r} = \frac{1}{2} m_e (r\,\dot{\boldsymbol{q}})^2 + \frac{ke^2}{r} \qquad\qquad (6)$$

which makes the angular momentum

$$P_q = \frac{\partial L}{\partial \dot{\boldsymbol{q}}} = m_e r^2 \dot{\boldsymbol{q}} \qquad\qquad (7)$$

Since $\boldsymbol{q}$ and $\dot{\boldsymbol{q}}$ are independent,

$$\oint P_q\, d\boldsymbol{q} = 2\boldsymbol{p}\,(m_e r^2\,\dot{\boldsymbol{q}}) = 2\boldsymbol{p}\,(m_e r\boldsymbol{n}) = nh \qquad\qquad (8)$$

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

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Senior Lab, Physics Department

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

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 due to 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 only be applied 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 using the Schrödinger equation corrects these faults. You can refer to any standard quantum mechanics textbooks for further discussion (for example, Eisberg and Resnick p. 111).

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

Exercise 1b: Derive the expression for E in terms of n, $\hbar$, m_e, k, and e.

Exercise 1c: Write your answer for **Excercise 1b** in the form $E = -hc \dfrac{Ry}{n^2}$ where c is the speed of light in vacuum. Ry is called the Rydberg constant. What are the units on Ry?

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. In doing so, the extra energy may be released in the form of a photon. For light of wavelength $\boldsymbol{l}$ we know $E = hc/\boldsymbol{l}$, so that

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

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 attributed to certain members of the hydrogen spectrum as can be seen by the following list.

- Lyman series: $n_f=1$ and $n_i=2, 3, 4, \ldots$

- Balmer series: $n_f=2$ and $n_i=3,4,5, \ldots$

- Paschen series: $n_f=3$ and $n_i=4, 5, 6, \ldots$

- Brackett series: $n_f=4$ and $n_i=5, 6, 7, \ldots$

- Pfund series: $n_f=5$ and $n_i=6, 7, 8, \ldots$

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

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

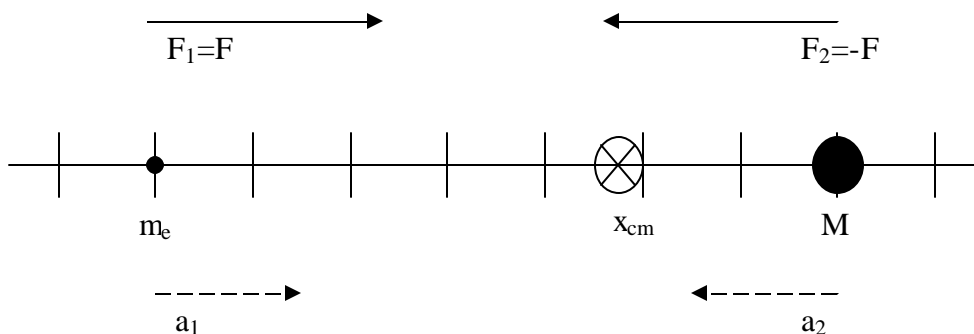where M is the mass of the nucleus.

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 $F = \boldsymbol{m}a$ where $\boldsymbol{m}$ is the reduced mass given by

$$\boldsymbol{m} = \frac{m_e M}{m_e + M} \; .$$

With the electron mass m_e changed to the reduced mass $\boldsymbol{m}$, the Rydberg equation is modified to read

$$\frac{1}{\boldsymbol{l}} = Ry \frac{\boldsymbol{m}}{m_e} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \qquad (12)$$

For different isotopes of hydrogen M and thus $\boldsymbol{m}$ 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_2) and deuterium (D_2). The accepted value of Ry is $Ry = 1.097373 \times 10^7 \, m^{-1}$.

Exercise 4:   What minimum resolution (in Å) will be required to distinguish the sixth wavelength of H_2 from that of D_2?

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 spectra observation was done by shining a light source on a prism. Since the prism's index of refraction depends on the wavelength of light (see Hecht pg. 163-164), looking at the light after it passes through a prism will show different colored bands of light. The list of detected wavelengths and their relative intensity 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 there will be interference occurring. As more and more mirrors are put together there will be

more and more path length differences. These path length differences will always be a multiple 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 gratings are used and a narrow band of wavelengths constructively interfere. The constructive interference condition is given by
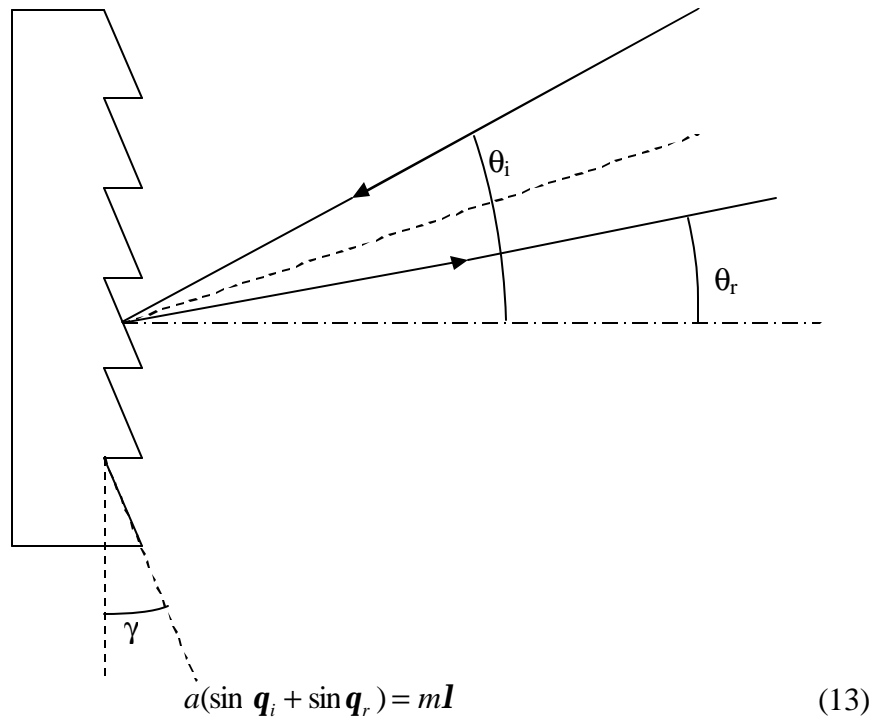

$$a(\sin \boldsymbol{q}_i + \sin \boldsymbol{q}_r) = m\boldsymbol{l} \qquad \qquad (13)$$

Figure 2.   Here the grating reflects incident light. The angle $\boldsymbol{g}$ is known as the *blaze angle*. Notice that the angles $\boldsymbol{q}_i$ and $\boldsymbol{q}_r$ are measured relative to horizontal and not the normal to the mirror faces. Typically a grating would be placed perpendicular to a light beam. This implies light would be incident from along the horizontal axis ($\boldsymbol{q}_i$=0).
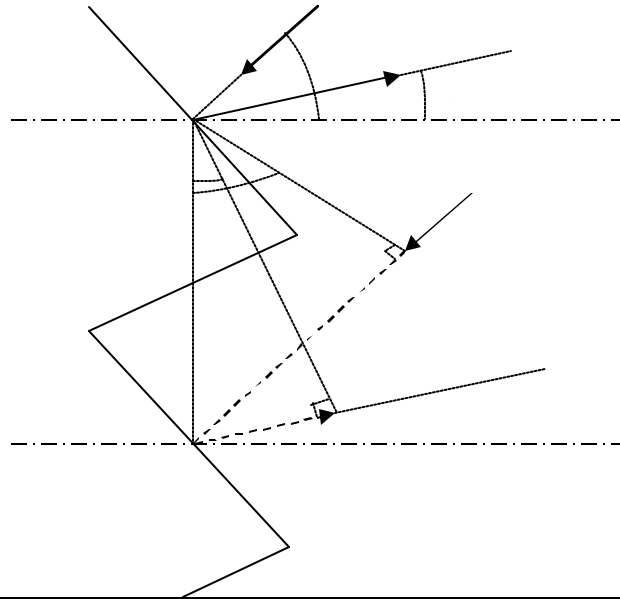
Figure 3. The path length difference, d, is shown as a dashed line. Using trigonometry we find $d = x_i + x_r = a(\sin q_i + \sin q_r)$ where a is the grating spacing. This leads to a constructive interference criteria of $a(\sin q_i + \sin q_r) = ml$ where m is an integer and l is the wavelength of light. Notice that if q_r is negative the second term in d is also negative. Adding more mirrors will allow fewer and fewer wavelengths to simultaneously meet all possible interference conditions.

Materials and Methods: Devices

Spectrometer

In practice a mechanism is used to slowly turn a diffraction grating while the spectra is recorded. This machine is called a *spectrometer*. A small amount of light is passed into the spectrometer through a thin slit (about 30 microns wide) and strikes a motorized grating. There are speed controls to determine how quickly to sweep through the spectra. 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 calibrate the spectrometer using a known source (you will use a Hg arc lamp). The motorized drive is reversible so you an scan up or down in wavelength.

Exercise 6: While it is possible to sweep the spectrum up or down it is considered better experimental practice to allways scan the same direction. 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 sction to scan through the second order of the Balmer series. Why ??

DO NOT REVERSE THE DRVIE DIRECTION WHILE THE MOTOR IS RUNNING! DO NOT ATTEMPT TO LOOK INSIDE THE SPECTROMETER UNLESS THE PMT SHUTTER IS CLOSED! See the next section to find out more about what a PMT is.

Photomultiplier Tube

To get accurate spectra using a grating it is important to have a very thin slit (~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?

However, since only a thin strip of light is hitting the grating the spectra will be very faint. In order to determine the intensity of light at each wavelength a very sensitive light detector must be used.

A *photomultiplier tube*(PMT) can detect very faint light signals based on the photoelectric effect, with gain on the order of 10^7. Light strikes a metallic or semiconducting material and 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 10^7-10^9 electrons from a single photon. Though this process of amplification takes some time (0.1-20 ns), that time constant is negligible for many experiments. A simple calculation of currents (see **Exercise 5**) 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 due to thermal excitations. The thermal electrons cascade from dynode to dynode just like the photoelectrons, producing a current. Since this current was 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. DO NOT OPEN THE SPECTROMETER UNLESS THE PMT IS CLOSED!**

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 1m 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: Using $I = \Delta Q / \Delta t$ determine the current produced by a typical PMT (assume each photon hitting the PMT produces 10^7 electrons). Notice the insanely large current that would melt the PMT if it was 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 3,** from the PMT you will use a picoammeter. As it's name suggests, a picoammeter can measure currents accurately into the picoamp range or better. It has provisions for nulling the dark current of the PMT. In this experimental setup, information from the picoammeter is sent to a computer. The signal rendered on the screen is proportional to the current output read by the picoammeter (see **Exercise 4**).

Exercise 9: By reading the manual for the picoammeter determine what type of signal governs the signal. What is the maximum level of this signal (give units)?

Exercise 10a: Assume that the computerized signal recorder is set at 2 V sensitivity and the picoammeter is on 2 nA sensitivity. How far across the paper will the pen move with PMT currents of 0, 0.5, 1, 2, 2.5 nA?

Exercise 10b: What happens if the recorder sensitivity is set to 1V? What if the picoammeter sensitivity is changed to 20 nA with the chart recorder still at 2 V?

Exercise 10c: Give the optimum sensitivity scales for both the recorder and picoammeter to measure the following currents: 1, 5, 9, & 20 nA.

Materials and Methods: Procedures

Calibration

The shift to be measured is of the order of 1 Å. The data for the H_2-D_2 spectra will be recorded on the computer chart recorder. You will need to correlate distances on the paper with wavelength differences. This is achieved 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 distance on the paper corresponds to the difference in wavelength of the two Hg peaks, at least for the computerized chartrecorder and picoammeter 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. A listing of slit sizes for the spectrometer can be found below and to the right of the PMT. If you need assistance ask your TA!

    o   To set PMT slit width : Turn knob just underneath PMT from the zero'd out mark to your desired slit width. Each line measures 10 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.

2. The four mirrors of the spectrometer are set in the appropriate position. . Do <u>not</u> change these settings. The light should enter slit 1 and exit slit 4.

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. <u>Disengage the autorange feature</u> and select a range appropriate to the current reaching the picoammeter (autorange might cause problems when 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.

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/sec. You will probably only get a single peak.

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 or better than shown in Figure 2 in old lab manual. This requires some patience, but will pay off later.

11. Once the resolution is adjusted, make several chart recordings of the doublet and the peak located at 6251.4 Å. Calibrate the chart paper using this information. {Hint: You know the distance between the doublet peaks. Count the boxes and determine (Å/box). }

Measuring the Isotope Shift

1. Place the Hydrogen-Deuterium tube near the slit spectrometer slit.

2. Sweep the spectrometer onto a known peak of the Hydrogen spectrum(see **Exercise 8**). 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 was done 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 H_2 and D_2 *molecules*. How will this affect the spectra? 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_2 and D_2 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 which 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 8a** using percent difference. Are your experimental values acceptable? Explain any discrepancies or possible sources of error which 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
- Print out 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 a data acquisition card, allow us 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 USB drive to make sure it doesn't get overwritten. You can now start the program by double clicking the Signal Recorder icon. When you open it you should see something similar to Figure 1.
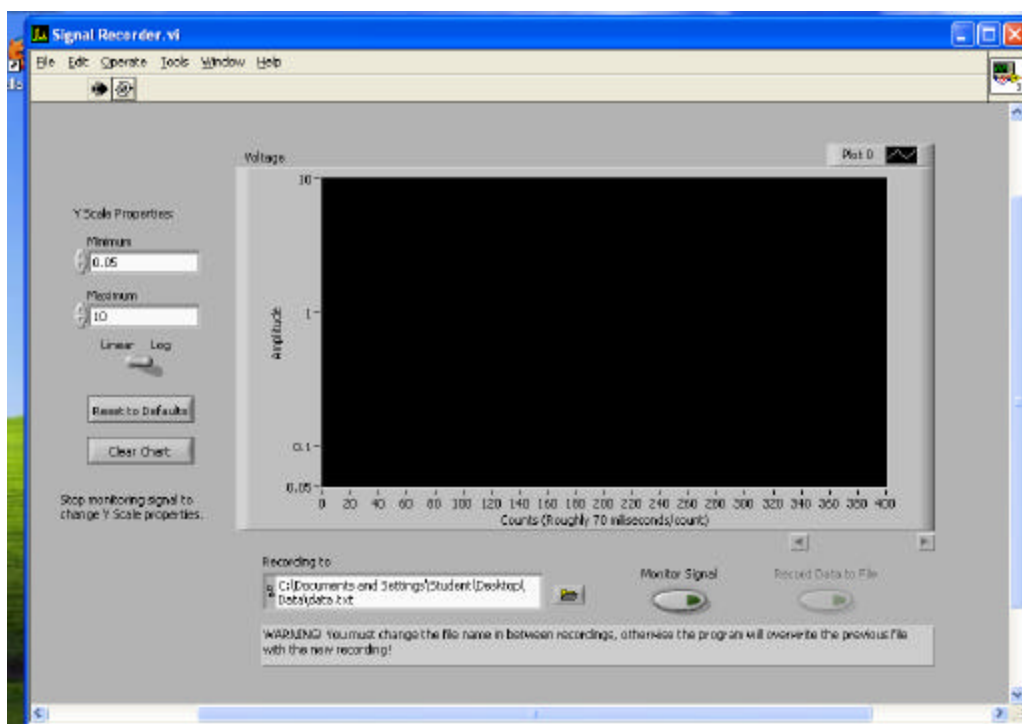

Figure 1.

The main functions for the program are operated through the Monitor Signal and Record Data to File buttons. When the program is first opened the Monitor Signal button is not activated. At this time you can change the Y scale properties of the chart. For now it is recommended to leave these at their defaults, but when you are more familiar with the amplitude of data being acquired you can change these.

Once you are comfortable with your Y scale settings you can start monitoring the signal. This will start a continuous acquisition and charting of data. The program takes a sample approximately every 70 milliseconds. The numbers at the bottom of the chart DO NOT correspond to milliseconds, but rather counts (1 count per sample, ~70 milliseconds per count). While you are monitoring the signal, the Record Data to File button becomes available. Before you begin recording be sure to change the "Recording to" path to a file in the folder you created earlier. Press the Record Data to File button to begin recording, press it again to stop. Data will be recorded as a tab delimited text file to the path specified. The first column in the file is time, measured in seconds, the second column is the amplitude. This file can be imported into Igor Pro for analysis (See below for instructions on how to do this).

IMPORTANT: The data file will be overwritten every time you start a new recording! If you do not want your data overwritten specify a different filename before recording. Be sure to label your files appropriately, and also write down in your lab manual the slit widths, picoammeter scale, and spectrometer sweeping speed for every recording/filename. 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. Directions for doing this in Igor Pro are below.

1) Open Igor Pro
2) In the top menu bar click Data→Load Waves→Load Delimited Text
3) Select the file you want to load from your data folder.
4) Insert appropriate names for each column of your data. Also make sure Make Table is checked and click Load.
5) A table of your data should appear. It is recommended to use the smooth function under Igor's Analysis menu to help smooth the data, especially on the low intensity signals where the data jumps around a lot.
6) To make a graph, from the menu bar select Windows→New Graph. Specify which waves you want on each axis.
7) Once you have a graph you can use Igor's info option to measure the peak separation. From the menu bar select Graph→Show Info. In the bottom of the graph window it now displays info about your plot. You can click and drag the circle and square crosshairs to your graph, they will automatically lock onto the trace and Igor will display their separation in the bottom of the window.

Overview of Program functions:

Y Scale Properties, Minimum: Sets the minimum number displayed in the y axis of the chart. Lowest value is 0. The y scale properties can only be changed when the program is not monitoring a signal.

Y Scale Properties, Maximum: Sets the maximum number displayed in the y axis of the chart. Highest value is 10. The y scale properties can only be changed when the program is not monitoring a signal.

Linear/Log: Adjusts the y scale to Linear or Logarithmic. The y scale properties can only be changed when the program is not monitoring a signal.

Reset to Defaults: Resets all controls to their default settings.

Clear Chart: Clears the chart history. This has no effect on recording; the chart is only there for visual feedback.

Recording to: Sets the path to which the recorded data will be saved. This file is overwritten on subsequent recordings.

Monitor Signal: Starts a continuous acquisition and charting of data. You must start monitoring the signal before the Record Data to File button becomes available.

Record Data to File: Starts/Stops recording acquired data to the file specified in the Record to path.

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