

Experiment 25A

BALMER LINES OF HYDROGEN

Introduction	1
Theory	1
The Monochromator	3
Prelab Problems	8
Procedure	10
Data Analysis	14

INTRODUCTION

In this experiment you will determine whether the visible-light emission spectrum of hydrogen, the simplest of atomic systems, is consistent with an elementary theory derived from the quantum *Uncertainty Principle* with a minimum of additional assumptions. You will use a research-grade spectrographic instrument called a *monochromator*, because it transmits only a narrow band (~ 0.1 nm) whose center wavelength can be tuned through the visible spectrum.

Werner Heisenberg, Erwin Schrödinger, and others provided the first formal mathematical treatment of the modern theory of quantum mechanics during 1925–1926. The old quantum theory proposed by Niels Bohr in 1913, although able to account for the main features of the hydrogen spectrum, was proving to be ever more inadequate to explain the wealth of experimental data being gathered, and it was becoming clear that a new (and revolutionary) approach to the physics of microscopic systems would be necessary. The most fundamental postulate of the new theory — the so-called *quantum condition* — is, in essence, captured in the idea that any two *canonically conjugate variables*, such as the components of the position and momentum vectors along a common coordinate axis, cannot simultaneously be measured with arbitrary precision but are connected by an uncertainty relation of the form

$$\Delta x \Delta p_x \geq \hbar \quad (1)$$

where, for this example, we have chosen the x components of position and momentum, and Δx , Δp_x are the precisions within which their values can be repeatably determined (Heisenberg, 1927). That same year E. H. Kennard showed that the new quantum theory required that the standard deviations of measurements of the positions and also of the momentums of an *ensemble* of identical systems would obey the relation

$$\sigma_x \sigma_{p_x} \geq \hbar / 2 \quad (2)$$

THEORY

Let us start with the relation (1) and see if it can be used to estimate the energies of various bound states of a particle in an inverse-square field such as the Coulomb field. If the center of the field is the origin of our coordinate system, then we expect the average position and momentum of a particle bound to the field to be 0, since on average the particle stays in the vicinity of the origin, forever. Equations (1) and (2) then say something about the expected magnitude of the distance of the particle from the origin and its expected speed at any particular instant. When the particle is in its lowest possible energy state, the *ground state*, we expect the uncertainty relation (1) to become very nearly an equality, so that $(\Delta x \Delta p_x)_{\text{ground}} = \hbar$.

Since the particle is in a spherically-symmetric potential, it must be true that $\Delta x = \Delta y = \Delta z \sim \bar{r}$, where \bar{r} is the average distance of the particle from the origin. Similarly, $\Delta p_x = \Delta p_y = \Delta p_z \sim \bar{p}$, the average magnitude of the momentum of the particle as it moves in the field. The values of \bar{r} and \bar{p} then determine the average potential and kinetic energies of the particle (the zero of

potential energy is at $\bar{r} \rightarrow \infty$). For the Coulomb potential, $V = -e^2 / r$ (Gaussian units) and, of course, $T = p^2 / (2m)$. For an inverse-square law the **Virial Theorem** requires the following relationship between the total energy, E , and the average values of the potential and kinetic energies for a bound particle:

$$E = \bar{V} / 2 = -\bar{T} \quad (3)$$

Therefore, for the ground state of the hydrogen atom we can estimate the binding energy as follows:

$$\begin{aligned} \bar{r} \bar{p} &\sim \Delta x \Delta p_x = \hbar \\ \left(\frac{e^2}{-\bar{V}} \right) \sqrt{2m\bar{T}} &\sim \hbar \rightarrow \frac{2m e^4 \bar{T}}{(\bar{V})^2} = -\frac{m e^4 E}{2E^2} \sim \hbar^2 \\ \boxed{-E_{\text{ground}} \sim \frac{m e^4}{2\hbar^2} = 13.598 \text{eV}} & \quad (4) \end{aligned}$$

which turns out to be just the right value, if m is the *reduced mass* of the proton–electron system!¹

The excited states (bound, but with energies higher than the ground state) must have more extended volumes of position and momentum than the ground state, so that the inequality (1) becomes ever larger as the system is excited to ever higher states. In the case of a 1-dimensional square-well potential, we know that Δx is the same for each excited state, but that the number of half-wavelengths of the particle's wave-function goes up by 1 for each successive state above the ground state. Since the momentum of a particle is inversely proportional to its wavelength (the *de Broglie hypothesis*), we have that $\Delta x \Delta p_x \propto n\hbar$ for the state n ($n = 1$ is the ground state).

Now we make a theoretical leap and postulate that this relation between the excited states of the 1-D square well potential **holds more generally**, including the case of the hydrogen atom, so that

$$\begin{aligned} (\bar{r} \bar{p})_n &= n(\bar{r} \bar{p})_1 \sim n\hbar \\ \therefore \boxed{E_n = \frac{1}{n^2} E_1} & \quad (5) \end{aligned}$$

where E_1 is the ground-state energy given by (4). Your task in this experiment is to test the validity of the relation (5). Assume that an excited hydrogen atom may decay to a less excited state by emitting a photon with energy equal to that lost by the atom, so that a transition from the state m to the state n would be accompanied by an emission with energy and wavelength (next page)

¹ Note that our argument should have resulted in only an order-of-magnitude estimate of the hydrogen ground state energy. In particular, $\bar{r} \bar{p} \sim \hbar$ should at best be a rough estimate. In this case, though, happy circumstance results in an accurate expression.

$$E_{mn} = \left(\frac{1}{n^2} - \frac{1}{m^2} \right) |E_1|; \quad m > n; \quad m, n \in \mathbb{N} \quad (6)$$

$$E_{mn} = h\nu_{mn} = hc / \lambda_{mn}; \quad E_1 = hc / \lambda_1$$

$$\lambda_1 = hc / E_1 = 91.176 \text{ nm}$$

$$\boxed{\frac{1}{\lambda_{mn}} = \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \frac{1}{\lambda_1}; \quad m > n; \quad m, n \in \mathbb{N}} \quad (7)$$

With $\lambda_1 \approx 91\text{nm}$, emission in the range of the visible spectrum (approximately 350–700 nm) requires that $n = 2$ in equation (7).

THE MONOCHROMATOR

The monochromator is a Spectral Products model DK-480. It uses a diffraction grating ruled onto the surface of a flat mirror to disperse light from the source. A schematic diagram of the optical arrangement of the DK-480 is shown in figure 1, which is known as a *Czerny-Turner* arrangement.

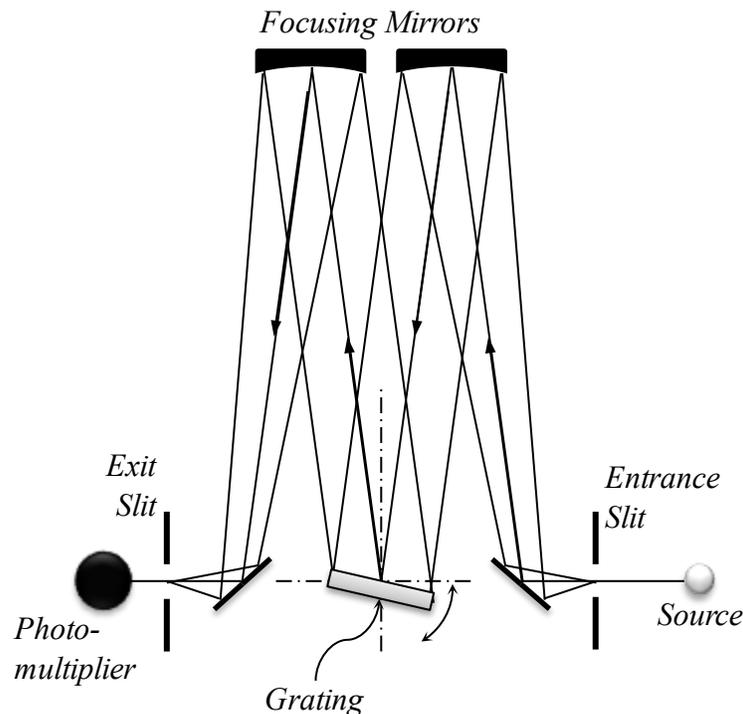


Figure 1: The optical arrangement of the DK-480 monochromator, a *Czerny-Turner* design. All optical elements are at a fixed position except for the grating, which is rotated to select the wavelength of the source which reaches the exit slit. The entrance and exit slits have adjustable widths to control the wavelength resolution. The focusing mirrors each have a focal length of 0.48 meter. The grating has 1200 grooves/mm and is approximately 6.8 cm square.

How does the angle of the grating control the output wavelength of the monochromator? To answer this question we must consider the interference of the waves scattered by the grooves on the grating. Consider the close-up diagram of the waves and the grooves shown in figure 2.

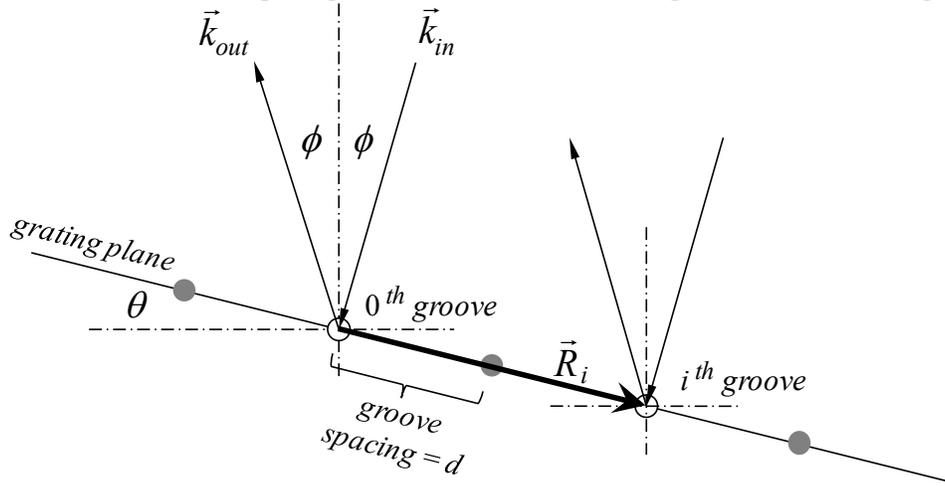


Figure 2: The plane wave from the source (wave vector \vec{k}_{in}) shines on the grating with grooves spaced by distance d (the grooves are oriented perpendicular to the plane of the figure). Each groove scatters the incoming wave, emitting a cylindrical wavefront. We are interested in that part of each scattered wave with wave vector \vec{k}_{out} , which is in the direction of the output focusing mirror. The grating and the wave vectors are oriented with the angles θ and ϕ , as shown.

The first focusing mirror takes the image of the input slit and projects it to a virtual image at infinity, so that the light from the source is a plane wave as it illuminates the grating. If the incoming wave has wave vector \vec{k}_{in} and the i^{th} groove is at position \vec{R}_i , then the relative phase of the incoming wave at the groove is

$$(\phi_i)_{in} = \vec{R}_i \cdot \vec{k}_{in} \quad (8)$$

For an outgoing wave in the direction of \vec{k}_{out} , on the other hand, the relative phase of the wave emitted by the i^{th} groove is

$$(\phi_i)_{out} = -\vec{R}_i \cdot \vec{k}_{out} \quad (9)$$

The total relative phase of the i^{th} groove's contribution to the outgoing wave \vec{k}_{out} is just the sum of the phases (8) and (9). For a maximum intensity in this output direction, the contributions of each of the grooves should be in phase, so the relative phase of each groove must be an integer multiple of 2π . Since the grooves are evenly spaced along a line with separation d (figure 2), it must be true that $\vec{R}_i = i \vec{R}_1$ (i is an integer), and therefore

$$\begin{aligned} \forall i \in \mathbb{Z}, \phi_i &= (\phi_i)_{in} + (\phi_i)_{out} = \vec{R}_i \cdot (\vec{k}_{in} - \vec{k}_{out}) = i \vec{R}_1 \cdot (\vec{k}_{in} - \vec{k}_{out}) = 2\pi n_i; \quad n_i \in \mathbb{Z} \\ \therefore \boxed{\vec{R}_1 \cdot (\vec{k}_{in} - \vec{k}_{out})} &= 2\pi m; \quad m \in \mathbb{Z} \end{aligned} \quad (10)$$

Clearly, $|\vec{k}_{in}| = |\vec{k}_{out}| = 2\pi / \lambda$, so given the geometry of figure 2,

$$\boxed{\lambda(\theta) = \frac{2d \cos \phi \sin \theta}{m} = \frac{2 \cos \phi \sin \theta}{mN} ; \quad N \equiv 1/d} \quad (11)$$

N is the groove density, which is 1200 grooves/mm for the DK-480 you will be using, and ϕ is approximately 9° . θ is adjustable through the range $0^\circ - 70^\circ$ in steps of 2.5×10^{-4} degrees. The integer m is called the **order** of the diffraction; $m=0$ corresponds to simple plane-mirror reflection; the wavelength calculated by the instrument for a given grating angle assumes that $m=1$ (first order).

Now to estimate the wavelength resolution of the monochromator: the two major effects which limit the resolution are (1) diffraction because of the finite sizes of the optical elements and (2) the angular sizes of the slit openings (slit widths) as seen by the grating.

Let's consider the diffraction limit to resolution caused by the finite size of the grating. At a given grating angle θ , then for the wavelength $\lambda(\theta)$ each groove of the grating contributes a bit that is in phase with all the others, a fact we used to derive equation (11). At a slightly different wavelength, however, there will be a phase error from each groove that varies linearly across the grating because the n_i in the first line of (10) is no longer exactly equal to an integer. Assume that the total number of grooves is M , so that the groove index i ranges from 0 to $M-1$, with, of course, $M \gg 1$. When the wavelength $\lambda' = \lambda(\theta) \pm \Delta\lambda$ is such that there is either an extra 2π or a missing 2π of phase variation across the grating, then the signal from the groove $i+M/2$ will be out of phase with the signal from groove i for each $0 \leq i < M/2$, and the output intensity should be very much less than it is at $\lambda(\theta)$. This condition on $\Delta\lambda$ implies that

$$M \vec{R}_1 \cdot (\vec{k}_{in} - \vec{k}_{out}) = 2\pi m M \pm 2\pi = 2\pi m M (1 \pm 1/m M) \Rightarrow \vec{R}_1 \cdot (\vec{k}_{in} - \vec{k}_{out}) = 2\pi m (1 \pm 1/m M)$$

$$\frac{2d \cos \phi \sin \theta}{\lambda(\theta) \mp \Delta\lambda} = m \left(1 \pm \frac{1}{m M} \right) = \frac{2d \cos \phi \sin \theta}{\lambda(\theta)} \left(1 \pm \frac{1}{m M} \right)$$

$$\therefore \frac{\lambda(\theta)}{\lambda(\theta) \mp \Delta\lambda} = 1 \pm \frac{1}{m M} \approx 1 \pm \frac{\Delta\lambda}{\lambda(\theta)}$$

$$\boxed{\text{Ideal grating diffraction limit to resolution:}} \quad (12)$$

$$\frac{\Delta\lambda}{\lambda} \approx \frac{1}{m (\text{total number of grooves})} = \frac{1}{m w N}$$

where m is the order, w is the width of the grating, and N is the groove density, as in equation (11). Because of the not-quite-perfect surfaces and alignment of the grating and additional optics, the actual resolution of the monochromator is significantly poorer than this. In first order ($m=1$) its best resolution is $\Delta\lambda \sim 0.06$ nm, but the resolution improves with order, so high-resolution measurements should be done using second or even third order.

Next consider the effect of slit opening width (refer to figure 1). A finite source slit width w_s illuminates the first focusing mirror with light coming through a small range of angles

$\Delta\varphi_s = (w_s / f) \ll 1$, where f is the focal length of the mirror. Refer to figure 2 and consider the effect of rotating \vec{k}_{in} counterclockwise by $\Delta\varphi_s$, while leaving \vec{k}_{out} fixed (since the direction to the exit slit hasn't been changed). To restore the symmetry of the figure, we rotate the axes by $\Delta\varphi_s / 2$; this transformation changes the angles θ and ϕ to $\theta + \Delta\varphi_s / 2$ and $\phi - \Delta\varphi_s / 2$, so the new wavelength of the monochromator becomes

$$\lambda(\theta) + \Delta\lambda = \frac{2 \cos(\phi - \Delta\varphi_s / 2) \sin(\theta + \Delta\varphi_s / 2)}{m N}$$

$$\sin(\theta + \Delta\varphi_s / 2) = \sin\theta \cos(\Delta\varphi_s / 2) + \cos\theta \sin(\Delta\varphi_s / 2) \approx \sin\theta + (\Delta\varphi_s / 2) \cos\theta$$

$$\cos(\phi - \Delta\varphi_s / 2) = \cos\phi \cos(\Delta\varphi_s / 2) + \sin\phi \sin(\Delta\varphi_s / 2) \approx \cos\phi + (\Delta\varphi_s / 2) \sin\phi$$

$$\therefore \lambda(\theta) + \Delta\lambda \approx \frac{2(\cos\phi \sin\theta + (\Delta\varphi_s / 2)(\cos\phi \cos\theta + \sin\phi \sin\theta))}{m N} = \lambda(\theta) + \frac{\cos(\theta - \phi)}{m N} \Delta\varphi_s$$

where terms of order $(\Delta\varphi_s / 2)^2$ and higher have been dropped. Similarly, a finite exit slit width w_e will accommodate a range of angles for light diffracted from the grating $\Delta\varphi_e = (w_e / f) \ll 1$, and a calculation similar to the above will result in a similar expression for its effect on the resolution. The contribution of the finite slit widths to the resolution is thus

slit width limit to resolution: $\Delta\lambda \approx \frac{ \cos(\theta - \phi) }{m N} \left(\frac{w_s + w_e}{f} \right) \lesssim \frac{1}{m N} \left(\frac{w_s + w_e}{f} \right)$	(13)
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Again, m is the diffraction order and N is the groove density, as in equation (11). The slits are adjustable in the range 10 – 3000 μm . Wide slit settings let in more light, increasing sensitivity to faint lines. Wide slit settings are also very useful to reduce the spectrum resolution so that larger $\Delta\lambda$ steps may be used during wide-wavelength scans. This speeds up the scan while still detecting all lines in the spectrum.

The monochromator's light output is detected by a photomultiplier which emits a current proportional to the signal intensity. The experimenter can adjust the photomultiplier's high-voltage bias to control its sensitivity. An amplifier (with adjustable gain and low-pass filtering) converts the output current to a voltage, which is displayed on a meter on the amplifier and is also connected to a computer's data acquisition system (DAQ) analog input port AI0.

The monochromator is normally computer-controlled using an RS-232 serial connection. The program that provides the overall data acquisition and control of the experiment is ***Monochromator.exe***. The program's user interface is straightforward and includes prompts and help information. The DK-480 monochromator also includes a local, manual control panel, which allows the experimenter the opportunity to override computer control and input commands directly to the instrument.

Lenses and filters are positioned between the light source and the entrance slit to optimize the intensity at the slit and to select a particular wavelength range (so that you may determine whether a spectral line you detect is in 1st or 2nd order from the grating ($m = 1$ or $m = 2$)). Most lens and filter glass is opaque to ultraviolet light, so a special *fused-silica* lens is also available to obtain good ultraviolet spectra (down to a wavelength of ~ 230 nm).

PRELAB PROBLEMS

1. Derive equation (5), repeated below, from the assumption that $(\bar{r} \bar{p})_n = n(\bar{r} \bar{p})_1 \sim n \hbar$.
Hint: consider the equations leading up to equation (4).

$$E_n = \frac{1}{n^2} E_1$$

2. Use equation (7) to calculate the wavelength of the longest wavelength line of hydrogen which falls in the visible range (350 – 700 nm). Recall that $\lambda_1 = 91.176 \text{ nm}$. What are the index integers n and m for this line, which is commonly called *Hydrogen α* ?
3. Refer to figure 2 and equation (11). What grating angle θ would give $\lambda(\theta) = 546 \text{ nm}$, near the wavelength of a prominent line in the spectrum of mercury? Other parameter values you need:

$$\phi = 9^\circ$$

$$N = 1200 \text{ lines/millimeter}$$

$$m = 1 \text{ (first order)}$$

According to the ideal grating diffraction resolution limit expression, what should be the spectrometer resolution $\Delta\lambda$ at this wavelength if the width of the grating is 6 cm?

If the source and exit slits are both set to 20 μm and the monochromator focal length is 0.48 m, then what is the slit width resolution limit to $\Delta\lambda$?

4. To what width should the source and exit slits be set to reduce the resolution to $\sim 1 \text{ nm}$? Assume both slits are set to the same width and that the characteristics of the monochromator are those listed in problem 3.
5. The index of refraction of air reduces the wavelength of light slightly below its value in vacuum, because light travels slightly more slowly in air. If the index of refraction is n , then wavelengths are reduced by the factor $1/n$. At a temperature of 0°C and a pressure of 760 mm mercury the index of refraction of air (at $\lambda = 589 \text{ nm}$) is 1.0002926. The quantity $(n-1)$ is proportional to the density of air. What is the index of refraction at 25°C and 740 mm mercury?

6. **National Institute of Standards and Technology (NIST) Atomic Spectra Database.** Go to this website: <http://www.nist.gov/pml/data/asd.cfm> and familiarize yourself with how to access the database (push the “**Lines**” button). Use the lines form page (link and illustration below) to retrieve a list of the unionized mercury lines (Hg I) for wavelengths between 300 and 800 nm. What is the wavelength of the most intense Hg I line wavelength in the 500 – 600 nm range?

Make the following selections in the “Additional Criteria” section of the Lines Form:

1. Lines: Only with observed wavelengths
2. Wavelength Data: Observed (deselect Ritz)
3. Wavelengths in: Vacuum (all wavelengths)

Lines Form page http://physics.nist.gov/PhysRefData/ASD/lines_form.html

The screenshot shows the NIST Atomic Spectra Database Lines Form web page. The page is titled "NIST Atomic Spectra Database Lines Form" and is displayed in a Windows Internet Explorer browser window. The form includes several sections:

- Dynamic Plots:** Includes options for "Line Identification Plot" and "Saha-LTE Spectrum", both of which are currently unselected.
- Grotrian Diagram:** Includes a "Java subwindow size" selection (640 x 640, 800 x 640, 1024 x 768, 1280 x 1024) and checkboxes for "Group by configurations", "Term multiplicity", and "Show only radiatively linked levels". A "Make Grotrian Diagram" button is present, with a note "(requires Java2)".
- Output Options:** Includes a "Format output" dropdown (HTML formatted), a "No JavaScript" checkbox, "Energy Level Units" (cm⁻¹), "Display output" (in its entirety), "Page size" (15), and "Output ordering" (Wavelength, Multiplet).
- Additional Criteria:** This section is highlighted and contains the following selections:
 - Lines:** Only with observed wavelengths (selected).
 - Bibliographic Information:** TP references, Line references (checked).
 - Wavelength Data:** Observed (checked), Ritz (unchecked), Observed - Ritz (difference) (unchecked), Wavenumber (in cm⁻¹) (unchecked).

PROCEDURE

NEVER EXCEED 1000V bias to the photomultiplier!

Don't touch the surfaces of the lenses and filters, because your skin oils will damage the surfaces. Don't blow on them, either.

1. Note the room temperature and pressure. Familiarize yourself with the instrument and controls. Turn on the mercury lamp. Set the photomultiplier high-voltage bias to $\sim 500\text{V}$ and set the amplifier to its lowest gain setting with the low-pass filter disabled. Ensure that the amplifier signal output is connected to the computer DAQ analog input AI0. Ensure that the monochromator is in *Remote* using its control panel. Start the *Monochromator* control program on the computer.

If you are using the DK-480 manual control panel, and you inadvertently enter a command or a mode that you want to exit, try using the ← key. If this doesn't seem to help, get assistance from your TA.

Don't push the ENTER/STOP key unless you understand what it will do!

The mercury and hydrogen lamps emit ultraviolet light which can be harmful if you stare at them for prolonged periods with unprotected eyes. Eyeglasses will block the most damaging UV (shorter than 320nm), as will protective glasses available in the lab.

Observe the mercury lamp's spectrum using a handheld spectroscope. Note the approximate wavelengths of prominent spectral lines. Look at the spectra of the room lighting and sunlight reflecting from a cloud or building wall.

Call up a listing of mercury (Hg I) spectral lines using the web-based NIST data base (Prelab problem 6). The mercury lamp has an especially strong line at $\sim 254\text{ nm}$ (check this using the database); this line is used to excite the white material in a fluorescent bulb and is also used in tanning salons.

2. Install the large, visible-light (glass) lens in front of the monochromator entrance slit and rotate the filter wheel so that no filter is in the optic path. Using the control program, set the slit widths to 50 microns. Align the Hg lamp in front of the lens and focus the lamp's image

on the slit. The lamp should be positioned at about twice the lens focal length from the lens (focal length = 75mm).

Now try to detect the 546.2 nm Hg line using the control program's *manual* dialog to set the wavelength. Step the wavelength using the arrow buttons until the signal indicator is maximized. If you can't find the line after a few minutes, exit the *manual* dialog and open the *scan* dialog. Perform a 2 nm scan centered at 546.2 nm with about 100 steps. The scan should find the line, and you can use the plot cursor to find the observed wavelength of the line. Reopen the *manual* dialog and set the monochromator to the line wavelength. If all else fails, ask your TA! Once you've found the line, adjust the amplifier gain and the photomultiplier bias and note their effects on the signal strength. While watching a signal meter, either the program's or the one on the amplifier, carefully adjust the position of the Hg lamp until the signal is maximized. Lower the gain settings if necessary so that the output signal is not saturated.

3. Exit the *manual* dialog and open the *scan* dialog. Perform a 2 nm scan centered on the 546.2 nm line with about 100 steps. Adjust the slit widths to 20 μm and scan again. Note the effects on resolution and signal peak value. Open the slits to the width you calculated in prelab problem 4. Adjust the high-voltage bias so that the line signal is not saturated and scan again. Is the line width now approximately 1 nm? Change the displayed graph's vertical axis mapping mode to linear instead of logarithmic and rescale the plot (ask your TA how to do this, if necessary). Consider the shape of this broad, 1nm wide line. Can you figure out why it has this roughly trapezoidal line shape? How wide is the line where its intensity drops to half its peak value (full width at half maximum)?
4. Now you can increase the high voltage to 600 – 700V and perform a scan that covers the entire visible and near-ultraviolet spectrum range (300nm – 800nm). The higher voltage will cause bright lines to be saturated, but will increase the sensitivity so that even weak lines will be detected. Choose the number of points so that the wavelength increment between points is slightly less than 1 nm (~700 points?). The result will be a "catalog" of Hg lines, which you can identify using the NIST database.

5. CALIBRATING THE MONOCHROMATOR WAVELENGTH SCALE

You will use the mercury lines to calibrate the monochromator by fitting the observed wavelength values to the values in the NIST spectral line database for the various lines you have found. You must scan each line with a much narrower slit width so that you can get an accurate line position. Make sure you record the expected line wavelengths (from the database) for each line you scan (you can use the comment line in the file headers of saved scans for this, if you wish). Here is a list of a few of the prominent lines:

Useful Hg Calibration Lines (Vacuum Wavelengths, nm)

302.238 (strong)	546.227 (strong)
312.658 (strong)	577.121
365.120 (strong)	579.228
404.771 (strong)	580.539 (faint)
407.900	671.819 (faint)
434.872	690.937 (faint)
435.956 (strong)	708.385 (faint)

6. OBSERVING THE HYDROGEN LINES

Replace the Hg lamp with the hydrogen lamp. Ask your TA how to hook it up if required. Note that there are two tubes: one containing hydrogen only, the other containing a mixture of hydrogen and deuterium. Use the hydrogen-only tube. Position the tube so that you see the slit illuminated. Find the H β line (vacuum 486.269 nm), since it is near the Hg 546 line wavelength. Optimize the lamp position.

Open the slit widths and perform a full-spectrum scan. Identify the brightest hydrogen lines, which should decrease in intensity with decreasing wavelength and get closer together (equation (7), according to the theory). This series of hydrogen lines is the famous *Balmer Series*. Note that there seem to be many other weak lines in the spectrum as well. Interesting...

Find and do individual precision scans of as many of the *Balmer* lines as you can find. See if you can get lines all the way up to $n = 9 \rightarrow 2$ at 383.6472 nm (vacuum, according to the theory).

7. Another element in the hydrogen lamp: the hydrogen lamp generates atomic hydrogen by disassociating water vapor. Can you identify additional emission lines from oxygen in the hydrogen lamp? ***Remember that observation of only one line does not make a conclusive identification.***

8. OPTIONAL OBSERVATIONS

You should have time to do one or more of these other observations:

When you first turn on the Hg lamp, it has a definite purple hue which changes to pale blue as the lamp warms up. This purple color could be due to the presence of some strong violet line or due to a mixture of blue and red lines. Identify another element in the Hg lamp (a noble gas element). Look in the region between 700 and 900 nm. Use the amber filter to decide if the observed lines are 700–900 nm in 1st order or 350–450 nm in 2nd order. The amber filter cutoff is at 550 nm. Use the NIST database to identify the lines. If you can identify them, you may use them along with the mercury lines in your monochromator calibration.

To observe lines with higher resolution or to observe near-ultraviolet lines, you must use the 2nd or higher-order diffraction from the grating. To observe near-ultraviolet lines, the glass lens must be replaced, since glass is opaque to ultraviolet light. Use the ultraviolet lens and refocus the mercury lamp on the slit. Find the Hg 546.2 nm line and optimize the lamp position and gain settings. Now scan for a line at 508 nm. Once you find the line, move to the line center using the *manual* dialog and adjust the high-voltage and gain. Note how strong this line is. Does the NIST database list a very strong Hg line at this wavelength? What color is 508 nm light? Now block the slit with the “clear” filter and note the change in the signal. Should 508 nm light be stopped by the filter? What is the actual wavelength of this line? What order are you observing it in at 508 nm? What does the NIST database list at this wavelength? Attempt to detect this line in higher orders (it’s not too hard to find it even in 5th order).

The hydrogen lamp also has some interesting near-ultraviolet features. The lamp emits spectra of water and the OH radical as well as atomic hydrogen and oxygen. The near-ultraviolet spectrum of OH (a very complicated spectrum near 308 nm) can be used to estimate the bond length and therefore the size of an atom. A brief write-up about this topic is available in the lab.

Look at and identify some absorption lines in sunlight. These are called the *Fraunhofer* lines (after the early 19th century German optician Joseph von Fraunhofer, who invented the spectroscope in 1814 and used it to observe several hundred solar absorption lines). Do a broad, continuous scan of the visible spectrum to find the wavelength with maximum intensity. Use this wavelength to estimate the temperature of the sun’s bright surface.

DATA ANALYSIS

What is your best estimate of the uncertainties in your Hg line positions you will use to calibrate the monochromator and how did you arrive at them? Since you have not repeated the scan of each line several times, it is impossible to determine an accurate, independent line position uncertainty for each line. Calibrate the spectral line positions by fitting the actual vacuum Hg line wavelengths versus your observed wavelengths. The slope b and intercept a should provide corrections for the observed line wavelengths.

$$\lambda_{\text{corrected}} = b \lambda_{\text{observed}} + a$$

Perform the fit with no uncertainty values for either the observed or atom wavelengths. In this case *CurveFit* will calculate a *standard deviation* of the points from the fit, and the calculated uncertainties in the fit parameters a and b are determined by assuming that the uncertainties in the data points are given by this standard deviation. Look at the difference plot. What is the maximum error in the linear fit? Is the fractional error (error/wavelength) of the fit small? Should a nonlinear fit be used? Can the slope of the linear calibration be explained by the nonzero index of refraction of the air in the lab, or must there be some other source of error as well? Correct your observed hydrogen line wavelengths using your calibration formula. How will you incorporate the calibration uncertainties for a and b into your final results? Are these uncertainties systematic? What about the *standard deviation* from the calibration fit: could this standard deviation be used to assign uncertainties to your individual Balmer line positions?

Equation (7) can be rewritten as

$$\lambda_{mn} = \lambda_1 \times \left(\frac{1}{n^2} - \frac{1}{m^2} \right)^{-1} = \lambda_1 \times \left(\frac{1}{4} - \frac{1}{m^2} \right)^{-1}; \quad m \in \{3, 4, 5, \dots\}$$

Test the theory by fitting your observed lines to this formula (λ_1 is an unknown constant, and the index term multiplying it is not a measured value, but is a pure number calculated for each observed line). Should you fit your corrected data to a line plus a constant or just a strict proportion? The fit will provide a value for λ_1 which can be compared to the theory's prediction. How do the standard deviation and the fit parameter uncertainties of the calibration affect the uncertainty in your determination of λ_1 ?