

EXPERIMENT #AM-1:

- (A) PRINCIPLES OF GRATING SPECTROMETERS;
SPECTROSCOPY OF ONE AND TWO ELECTRON ATOMS; and
(B) SPECTROSCOPY OF ONE AND TWO VALENCE ELECTRON ATOMS**

OBJECTIVES: *To become familiar with the SPEX spectrometer, photomultiplier sensitivity, photon counting detection, and the PCLabs card. To examine the spectra of simple one and two electron atoms (H, D, and He). To measure and explain the isotope shift in hydrogen. To construct a Grotrian diagram for the He atom.*

EXPERIMENT #AM-1A: PRINCIPLES OF GRATING SPECTROMETERS

INTRODUCTION:

The two commercial spectrometers we use in this course (the Heath and the SPEX – we'll use the Spex for this lab, AM1) both utilize a Czerny-Turner optical design (see Appendix I). The incident and diffracted beams have a fixed angle between them and the grating is rotated to scan a spectrum. (See Appendix I, Fig. A1-1.) In this case, a generalized diffraction equation must be used:

$$m\lambda = d(\sin\alpha + \sin\beta), \text{ where:}$$

α is the incident angle
 β is the diffracted angle
 d is the grating spacing
 m is the diffraction order, and
 λ is the wavelength.

Make sure you can derive this (see lecture notes for assistance). Note the implied sign convention for the diffracted angle β which may be unfamiliar: α is always positive and β is positive if it is on the same side of the normal as is α . In case you've not previously encountered the terminology, "normal" (or "surface normal") refers to the direction perpendicular to the plane defined by a surface.

Take some time to examine the spectrometer and become familiar with the operating characteristics. Pay particular attention to the proper use of high voltages (negative bias) present on the PMT detector (> 1000V), and to taking proper care to avoid exposure of the photocathodes to high light intensities while voltage is applied! Note that both the SPEX and the Heath are set up to utilize photon counting detection -- you will be using both systems so learn the rudiments of each the first time you use them. Instructions are provided on all of these steps in Appendices II-VI.

a. SYSTEM SENSITIVITY CALIBRATION WITH A BLACK BODY SOURCE

1. We will use a small tungsten-halogen bulb for a black body radiator and calibrate the efficiency of the instrument (photons in vs. photon counts or electrons out). Set up the tungsten-halogen lamp with the Variac set at 65V and, TAKING THE USUAL

PRECAUTIONS TO SAFEGUARD THE PHOTOMULTIPLIER TUBE FROM OVEREXPOSURE, set up the system to obtain a reasonable response at 5000 Å. [This means using narrow slits (~10 μm) and probably 1 meter lamp distance from the slit, or a neutral density filter may be used.] Then record a spectrum from 3500 Å to 8000 Å in 10 Å steps. Note that the slit settings may occasionally included an offset. As of spring 2010 with the Spex, the entrance slit appears to be zero-width at 30 μm, and the exit slit appears to be properly zeroed.

ANALYSIS:

- a) Compute a predicted blackbody spectrum in the form of photons incident on the entrance slit vs. wavelength for T~ 6250 K.

Recall the Planck black body spectrum for **energy density** (see Eisberg and Resnick p. 17; or J.T. Verdeyen, Laser Electronics, chap. 7, or Wikipedia - http://en.wikipedia.org/wiki/Planck%27s_law) in terms of wavelength:

$$\rho_T(\lambda)d\lambda = \frac{8\pi c}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

Converting to intensity, we find that the emitted power per unit area of emitting surface, per unit solid angle, and per unit wavelength is given by

$$I_T(\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

Intensity is defined as energy per unit time and per unit area,

$$I = (dN / dt)(hc / \lambda A) \Rightarrow (dN / dt)d\lambda = (I\lambda / hc)d\lambda$$

where dN/dt is the number of photons per unit time, hc/λ is the photon energy, and A is the area. Recall that the spectrometer bandpass is approximately constant in wavelength units dλ. Furthermore, the photon flux from your lamp will be proportional to the filament area and to 1/(lamp distance)². Therefore, we can replace these factors to arrive at the wavelength dependence of the **spectral photon flux** (units of *photons/(time-area-Δλ)*) from a blackbody emitter, given as

$$\frac{dN}{dt} \propto \frac{B}{\lambda^4 (e^{hc/\lambda kT} - 1)}$$

where B is a constant value. For convenience in our case, it is recommended that you use the mixed units *photons/(sec-cm²-nm)*.

- b) Obtain the efficiency of the system by dividing your data (counts/sec) by the incident photon rate (photons/sec) through the entrance slit for the spectral bandpass at the slitwidth used. Because we do not have an absolute calibration for this lamp, for convenience you should normalize your efficiency curve to

unity at the highest computed efficiency.

b. THE HYDROGEN SPECTRUM -- WAVELENGTH CALIBRATION, CORRECTION FOR THE INDEX OF REFRACTION OF AIR, RESOLUTION

1. In order to use any spectrometer for quantitative work it is necessary that the wavelength scale of the instrument be accurately calibrated. You should therefore begin by carrying out such a calibration using the known spectral lines of hydrogen (i.e., using the hydrogen lamp). You should compare your measurements with your calculation of the line positions. See detailed discussion following:

One of the triumphs of the old Bohr Theory and, later, of modern quantum mechanics was the ability to give a quantitative explanation of the observed atomic spectrum of hydrogen.

- a) Recall that the predicted energy of a hydrogen atom with principal quantum number n can be written

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}$$

where μ is the reduced mass of the hydrogen atom, $Z = 1$ for hydrogen, and n is the principal quantum number. Defining the quantity α (the fine structure constant) as

$$\alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \cong \frac{1}{137}$$

one can write the H atom energy levels as

$$E_n = -\frac{\mu\alpha^2 c^2}{2} \frac{1}{n^2}$$

The reduced mass, in this case, is arrived at by using the mass of the electron, m_e , and the mass of the nucleus, M , to compute μ :

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

Use this to compute the expected wavelengths of the first 5 or 6 Balmer transitions (transitions which end on the $n=2$ level, so $n=3$ to $n=2$ for example). In your write-up, compare the calculated values for the H-alpha line as computed using the electron mass (assuming infinite nucleus mass), and with the reduced mass (the more accurate approach). By how many Å do the two values differ, and is the H-alpha line at shorter or longer wavelength for the actual (correct) reduced mass?

The Balmer series of transitions is shown in Table 1. Note that the wavelength precision shown in Table 1 is relatively low – you'll calculate and measure these values to the sub-

Angstrom level in this lab.

Table 1. Balmer series transitions for the hydrogen atom. From http://en.wikipedia.org/wiki/Balmer_series

Transition of n	3→2	4→2	5→2	6→2	7→2	8→2	9→2	∞ →2
Name	H- α	H- β	H- γ	H- δ	H- ϵ	H- ζ	H- η	
Wavelength (nm)	656.3	486.1	434.1	410.2	397.0	388.9	383.5	364.6
Color	Red	Blue-green	Violet	Violet	(Ultraviolet)	(Ultraviolet)	(Ultraviolet)	(Ultraviolet)

b) Now proceed to accurately measure the wavelengths (i.e., peak wavelengths) of the H α , H β , and H γ lines using the Spex. When measuring the H α line, investigate how the spectral resolution, as indicated by the FWHM of the peak, depends on the vertical-limiting shutter setting (for a fixed slit width). The manually-adjustable entrance shutter offers the ability to control the *vertical size* of the slit (if the shutter positioning is finicky, ask the instructor or TA to change the setting). Note the shutter setting readings (“2”, “.1”, “.2”) for three successive spectra acquired at 0.5 Å stepsize or smaller, and include the plots in your write-up. Choose the best shutter setting (it ought to be “.2”) and use this for the remainder of your measurements.

Compare the peak wavelengths for the H α , H β , and H γ lines with your calculations. Assess the uncertainty in your results -- do your experimental values and uncertainties give a result in accord with the accepted values? Include the correction for the index of refraction of air discussed below.

c) It is an indication of the accuracy of atomic spectroscopy that the results are sensitive to the index of refraction of air (normally considered to be unity) and-- in fact-- even to its wavelength dependence. You will need to correct your observed wavelengths measured in air to the vacuum wavelengths by using the formula for the index of refraction of air due to Edlén

$$n = 1 + 6.4328 \times 10^{-5} + 2.94981 \times 10^6 / (1.46 \times 10^{10} - \nu^2) + 2.554 \times 10^4 / (4.1 \times 10^9 - \nu^2)$$

where ν is the “wavenumber” in cm^{-1} ($\nu = 1 / \lambda_{\text{VAC}}$). For additional information on the use of “wavenumbers” as an energy unit, see part **d.** on Helium atom spectroscopy below.

At this point, based on your measured wavelengths of the H α , H β , and H γ lines and how they compare with the calculated values (using the correct reduced mass equation) you should be able to construct a wavelength correction plot for the SPEX spectrometer. This plot should show the offset $\Delta\lambda$ in angstroms vs. wavelength (also in angstroms) from 3500 to 8000 Å. Save this plot for later use. Note: the spectrometer will likely have some systematic offset which must be accounted for in your measurements – that is the point of this wavelength correction plot.

c. DEUTERIUM--ISOTOPE SHIFTS

The expression for the energy levels of hydrogenic-like atoms written in A-1 above shows explicitly the dependence on reduced mass. Thus it is quite easy to calculate the reduced mass contribution to the "isotope shift" of energy levels or spectroscopic lines. In the case of hydrogen and deuterium, of course, the reduced mass contribution is relatively large and accounts essentially for all of the isotope shift. The deuterium atom differs from the standard hydrogen atom only in that the nucleus contains both a proton and neutron (rather than just a proton). So in the equation for the reduced mass, the mass of the nucleus becomes the sum of m_p and m_n .

[An aside: for heavier nuclei (and larger Z) a second contribution becomes more important; this is the nuclear size contribution. Of course, for heavy nuclei the reduced mass effect becomes relatively small because $\Delta m/m$ is small. Meanwhile, because the nuclear radius increases and inner shell electron radii decrease, the extent of electron wavefunction overlap with the nucleus becomes larger. Thus for Hg, for example, the nuclear size effect dominates. This effect must be considered in the high resolution spectra obtained, e.g., during the Zeeman spectroscopy of Hg and in the Doppler-free spectroscopy with the diode laser and is discussed in Appendix XI. However, picking out the isotope shifts in heavy atoms is complicated by the presence of other effects such as hyperfine splitting (see the Doppler-free experiment and Appendix XI) unless an isotopically pure spectral source is available for comparison.]

1. Install the H_2/D_2 lamp in place of the H_2 lamp and record the α , β , and γ lines for the hydrogen-deuterium lamp. Each of the spectra should show a doublet (i.e., two closely-spaced peaks). It is highly desirable to calculate the isotope shift first, before scanning so that you can plan for a good range to scan over and so that you can decide on the resolution necessary to resolve the lines well! Scan both the H and D lines in one continuous scan to minimize backlash and other resetting errors.
2. Determine the intensity ratio of the D_α line to that of the D_β line. You can accomplish this by measuring the two lines (in successive measurements) while carefully controlling any experimental parameters which affect the count rate (e.g., slit widths must not be altered, and the integration time must be held constant). Use the spectral sensitivity correction factor determined above to correct for the system's varying sensitivity. If you use any neutral density filters, you'll have to determine how to correct for those by measuring explicitly the attenuation factor each one introduces.
3. To get a feeling for the resolution obtainable with the Spex monochrometer, return to the D_α - H_α line and make "high resolution" (step size of $\sim 0.1 \text{ \AA}$ or less) studies of the line profile for a variety (three or four) of slit widths between $5 \text{ }\mu\text{m}$ and $100 \text{ }\mu\text{m}$. If necessary, use one or more neutral density filters (which absorb all wavelengths approximately equally) to keep the pulse counting system used with the SPEX from overloading. The point here is to see how the slit width affects the spectral resolution (e.g., the width in \AA) of your measurements.

ANALYSIS:

- i. Use the full width at half maximum (FWHM) to quantify the width of the line. How does the observed linewidth depend upon slit width?

- ii. Compute the reciprocal linear dispersion (see Appendix I); for larger slit widths, how do the observed linewidths compare with what you predict from the instrument geometry and the grating constant?
- iii. For small slit widths, how does the observed slit width compare with the theoretical limit on resolution?

d. HELIUM

Helium, the next simplest atom with just two electrons, introduces a number of complications. In fact, it is in many ways more complicated to discuss than the one-valence-electron alkalis. Before beginning to study it, you may wish to review some terminology of atomic spectroscopy.

A common (but initially strange) “energy” format utilized in spectroscopy is that of the “wavenumber”, most often in units of cm^{-1} or “inverse centimeters” (formally, SI units would be m^{-1}). One can arrive at the wavenumber by multiplying the standard energy result by $1/hc$ where h is of course Planck’s constant and c is the speed of light (see <http://en.wikipedia.org/wiki/Wavenumber>). The wavenumber “energy” is then simply $1/\lambda$.

The level structure of atoms can be conveniently displayed on Grotrian diagrams such as the partial level scheme sketched (not to scale) on page AM1-7. All energies there are given in terms of the wavenumber (in cm^{-1}) and the ground state is arbitrarily assigned the value zero.

Measuring the wavelengths of the emitted radiation is the easy part of constructing such a diagram; identifying the transition which gives rise to a given emitted photon is more difficult. In this task, the spectroscopist may be guided by theoretical calculations, observed and predicted line intensities, previous measurements of corresponding transitions in isoelectronic systems, regularities which are observed along a Rydberg series or as a function of l and intuition. The unequivocal test of line identifications lies in consistency checks when the system is overdetermined and the energy of a given level can be determined in more than one way.

1. Measurements of the quantities needed to locate the three lowest-lying excited singlet levels on this diagram lie outside the range of the Spex. Therefore, values measured elsewhere for the three transitions which determine their energies are shown in the diagram. Use the wavelengths furnished to find the energies of these levels. Remember that all quoted wavelengths below 2000 Å are vacuum values, but those above 2000 Å are air wavelengths and must be corrected for the index of refraction of air.
2. The energies of the next two ^1S levels (shown as dashed lines on the diagram) can then be established by measuring the wavelengths of the 2p-4s and 2p-5s transitions. Scan quickly through the region 5045-5050 Å to locate the approximate position of the 2p-4s line and then accurately measure its wavelength. Similarly, accurately measure the wavelength of the 2p-5s transition which should be found between 4435 and 4440 Å. Obtain the energies of the 4s ^1S and 5s ^1S levels.
3. In a similar fashion the energies of the np $^1\text{P}^0$ levels for $n=3,4$ and 5 can be obtained by

experimentally determining the wavelengths of the 2s-3p, 2s-4p and 2s-5p transitions. If time is short, you may use the accepted wavelengths of these transitions

2s-3p	5015.68 Å
2s-4p	3964.73 Å
2s-5p	3613.64 Å

in place of values measured in the lab. Find energies for 3p ¹P⁰, 4p ¹P⁰ and 5p ¹P⁰ levels.

4. As a check on the values which you obtained, predict the wavelengths of the photons which would be emitted in the transitions 1s-3p, 1s-4p and 1s-5p. Again, these wavelengths lie outside the range of our instruments, but that region has been studied by others. A partial line list from their work follows:

505.5, 505.684, 505.912, 506.2, 507.058, 507.718, 508.643, 509.998, 512.098, 515.616, 522.213, 537.03, 584.334, 591.412 (all in Å).

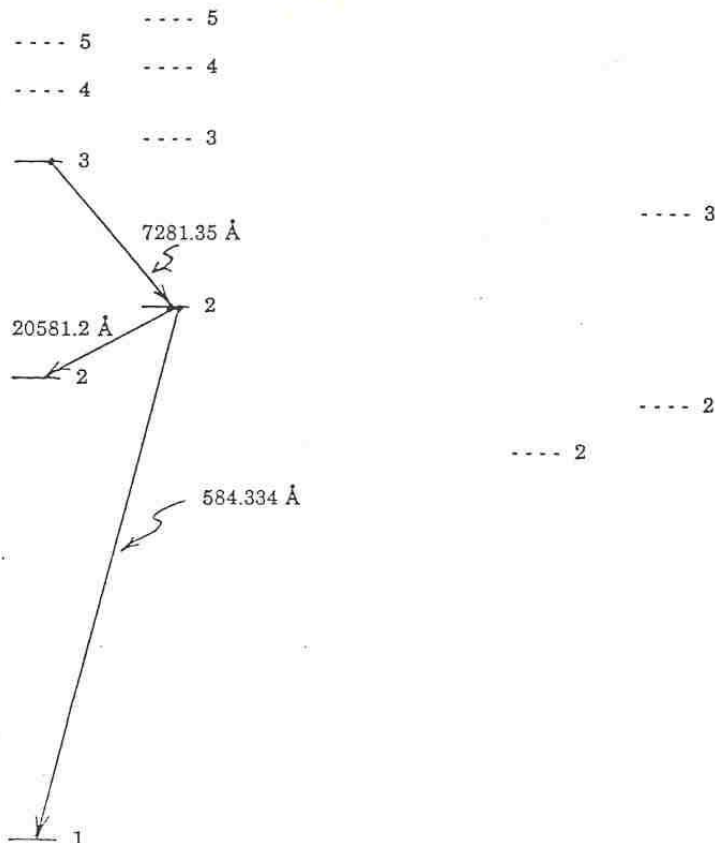
Have the lines predicted by your level scheme been observed? This is the real test of the validity of your Grotrian Diagram.

5. The partial Grotrian Diagram also shows a few triplet levels (why do they tend to lie below the corresponding singlet levels?) In general, so-called "intercombination" lines connecting the two series are weak (they are "forbidden" in LS coupling). However, two such transitions have been observed in the vacuum ultraviolet:

1s ¹S - 2p ³P @ 591.4121 Å, and
~~1s ¹S - 2p ³P @ 591.4121 Å~~

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	ns ¹ S	np ¹ P ^o	nd ¹ D	ns ³ S	np ³ P ^o	

Summariz
clearly in



e energies given

Fig. AM1-1: Partial Grotrian diagram of He I

**EXPERIMENT #AM-1B:
SPECTRA OF ONE AND TWO VALENCE ELECTRON ATOMS**

Objectives: *To study the spectra of the alkali atom, sodium, and two alkaline earth atoms (such as Cd and Hg) and explore various aspects of the Hartree approximation. To measure carefully "term values" for Na and to obtain values for the "effective principal quantum number" and "quantum defects." To observe the effect of residual Coulomb interactions and of spin-orbit coupling on the spectra.*

Note: This section of the AM1 lab guide has **not** been updated and likely contains inconsistencies with part A (Experiment #AM-1A).

Introduction:

Term values are defined as energies measured downward from the ionization limit (IL)

$$T_n = IL - E_n .$$

If there were no corrections for core penetration or polarization, the value of T_n would be hydrogenic

$$T_n = R_{yNa} / n^2, \text{ where } R_{yNa} = [\mu(Na)/m]R_\infty.$$

In a real alkali, T_n can be written as

$$T_n = R_{yNa} / n^{*2}$$

where $n^* = [R_{yNa}/T_n]^{1/2}$ is called the effective quantum number. This is simply a phenomenological way of accounting for the effects of the core seen by the outer electron in the alkali. The deviation from the hydrogenic value,

$$\delta_l = n - n^*$$

is called the quantum defect. It is very nearly constant along a Rydberg series (i.e. for a given value of l), and this can provide a procedure for determining the ionization limit:

- a) guess a value for IL
- b) compute the T_n 's from the energies
- c) then compute n^* and δ_l
- d) finally, vary IL to find quantum defects which vary the least (or in the most linear fashion) as a function of T_n .

Procedure:

e. SODIUM

As indicated earlier, the structure of Na is much simpler than that of He: it closely resembles that of H, with a single electron moving in the field of an effective central potential due to the nucleus and the core of 10 closed-shell electrons.

1. Measure the wavelengths of the doublet near 5890 Å...the famous Sodium D-Lines which give the Na lamp its yellow color. (The name "D-Lines" arises because these lines are among the prominent absorption features -- the "dark lines" -- of the solar spectrum which were first observed by Fraunhofer in 1817; he assigned letters of the alphabet to the most prominent lines, and these were assigned "D"). Your measurement will establish the energy above the $3s^2S$ ground state of the $3p^2P_{1/2}$ and $3p^2P_{3/2}$ levels. (Don't forget the index of refraction of air).
2. Next, accurately measure the wavelengths of the transitions from $3p^2P$ to the $5s^2S$ (~6160 Å) and the $6s^2S$ (~5155 Å) levels to establish the energies of these levels. The energies of $7s^2S$, $8s^2S$ and $9s^2S$ have been determined to be:

7s	38012 cm ⁻¹
8s	38968 cm ⁻¹
9s	39575 cm ⁻¹

3. Apply the procedure described previously to your energies for ns^2S (n=5,6,7,8,9); use IL = 41400, 41410, 41420,.....41500 cm⁻¹. What is the Ionization Limit you determine? How does it compare with the tabulated Ionization Potential of 5.138ev (use the most recent recommended value of hc to make the necessary units conversion)? What is δ_l for l=0 ?

This procedure also can be very helpful in making line identifications. Misidentified members of a Rydberg series generally do not give values of δ_l which agree with those obtained for properly identified lines.

4. The same procedure applied to the nd^2D series gives $\delta_l=0.015$. Explain why this value is so much smaller than the one you obtained for l=0.
5. The validity of LS couplings for Na can be explored by studying intensity relationships within a multiplet as discussed in Appendix VII. Measure the intensities of the transitions listed below in arbitrary -- but consistent -- units. For each multiplet, compare your measurements with the theoretical predictions of LS coupling. (The Ornstein-Burger-Dorgelo sum rule) What do you conclude?

$\lambda(\text{Å})$	Transitions
5688	$3p^2P_{3/2} - 4d^2P_{5/2}$ $^2P_{3/2} - ^2D_{3/2}$ (unresolved)
5683	$^2P_{1/2} - ^2D_{3/2}$
5154	$3p^2P_{3/2} - 6s^2S_{1/2}$
5149	$^2P_{1/2} - ^2S_{1/2}$
4983	$3p^2P_{3/2} - 5d^2D_{5/2}$

4979	${}^2P_{3/2} - {}^2D_{3/2}$ ${}^2P_{1/2} - {}^2D_{3/2}$
4752	$3p^2P_{3/2} - 7s^2S_{1/2}$
4748	${}^2P_{1/2} - {}^2S_{1/2}$
4669	<hr/> $3p^2P_{3/2} - 6d^2D_{5/2}$ ${}^2P_{3/2} - {}^2D_{3/2}$
4665	${}^2P_{1/2} - {}^2D_{3/2}$

f. L • S COUPLING AND TWO-VALENCE-ELECTRON ATOMS (IIB METALS)

We shall now study the fine structure splitting of several terms in the neutral spectra of either Zn, or Cd, or Hg. Except for core penetration and polarization effects, these spectra can be considered as spectra of two-electron systems where one electron always resides in its lowest energy state (4s for Zn, 5s for Cd, and 6s for Hg). One obtains here a singlet and a triplet system exactly as with helium. Through comparison of experimental fine structure splitting with predictions of the Landé interval rule, one can obtain an idea of how well LS Coupling describes these various systems. We shall here study transitions of the type ${}^3P_{0,1,2} - {}^3S$ and ${}^3P_{0,1,2} - {}^3D_{1,2,3}$.

In Cd we can study the multiplets $5p^3P - 5d^3D$ and $5p^3P - 6s^3S$. The wavelengths are given in the table below.

Cd I

$\lambda(\text{\AA})$	<u>Transitions</u>	$\lambda(\text{\AA})$	<u>Transitions</u>
3397	$5p^3P_0 - 5d^3D_1$	4678	$5p^3P_0 - 6s^3S_1$
3466	${}^3P_1 - {}^3D_2$	4800	${}^3P_1 - {}^3S_1$
3468	${}^3P_1 - {}^3D_1$	5086	${}^3P_2 - {}^3S_1$
3611	${}^3P_2 - {}^3D_3$		
3613	${}^3P_2 - {}^3D_2$		
3614	${}^3P_2 - {}^3D_1$		

- Carefully measure the wavelengths of these lines. For unresolved lines, note all contributions in decreasing order of intensity. From your measurements, compute the fine structure splitting in ${}^3P_{0,1,2}$ and ${}^3D_{1,2,3}$ and record the results.

In Hg one can study the $6p^3P-6d^3D$ and $6p^3P-7s^3S$ transitions.

Hg I

$\lambda(\text{\AA})$	Transitions	$\lambda(\text{\AA})$	Transitions
2967	$6p^3P_0 - 6d^3D_1$	4047	$6p^3P_0 - 7s^3S_1$
3126	$^3P_1 - ^3D_2$	4358	$^3P_1 - ^3S_1$
3132	$^3P_1 - ^3D_1$	5461	$^3P_2 - ^3S_1$
3650	$^3P_2 - ^3D_3$		
3655	$^3P_2 - ^3D_2$		
3655	$^3P_2 - ^3D_1$		

1. Compare the measured fine structure splittings for each case with the predictions of the Landé interval rule. What do you conclude about the validity of LS coupling?

In the case of Zn one may study the multiplets $4p^3P - 4s^3D$ and $4p^3P - 5s^3S$. There should be a Zn lamp available if you wish to explore....

ZnI

$\lambda(\text{\AA})$	Transitions	$\lambda(\text{\AA})$	Transitions
3282	$4p^3P_0 - 4d^3D_1$	4680	$4p^3P_0 - 5s^3S_1$
3303	$^3P_1 - ^3D_2$	4722	$^3P_1 - ^3S_1$
3303	$^3P_1 - ^3D_1$	4811	$^3P_2 - ^3S_1$
3345	$^3P_2 - ^3D_3$		
3346	$^3P_2 - ^3D_2$		
3346	$^3P_2 - ^3D_1$		

A third possibility to study the extent of LS coupling is the comparison of intensities for intercombination lines--which are forbidden for pure LS coupling--with intensities of transitions within a system of the same multiplicity. Such intensity comparisons without calibrating the system can be dangerous if pushed beyond a qualitative study. However, the mere detection of an intercombination line is significant. We choose the resonance line in Cd $5s^1S_0 - 5p^3P_1$ at 3261 Å and $5s^1S_0 - 5p^1S_1$ at 2228 Å where the former is an intercombination line and the latter is of course allowed. Measure the relative intensities of these transitions and comment on the results. [Note that glass begins to absorb at wavelengths below about 3300 Å so that optics transmission is an important consideration in this experiment. Also the tungsten lamp used for the efficiency calibration has very little output below 4000 Å so we did not try to calibrate in this region. It would require a special UV-rich standard lamp.]