

## **Introduction**

In this experiment you will obtain an emission spectrum for atomic sodium. The emission is produced in a sodium vapor lamp and then dispersed into "lines" by a monochromator. These spectral lines are detected by a photomultiplier, a device that changes light into an electric current. A computer equipped with a data-acquisition interface will control the monochromator and acquire the spectrum as signal intensity vs. wavelength data. Other software will then be used to analyze the data and to graphically display them. The wavelength range of the spectrum you will probe is 3000 to 6200 Å (1 nm = 10 Å). Using current theories of atomic structure you will interpret the spectrum and calculate from your data the Rydberg constant and the ionization potential of the atom. You will also predict the position of lines beyond the recorded range and construct an energy level diagram for sodium.

## **References**

1. Concise accounts of the Bohr atom and the results of the solution of the Schrödinger equation applied to the hydrogen atom can be found in most good General Chemistry texts.
2. D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld, *Experiments in Physical Chemistry*, third edition, McGraw Hill, 1974, pp. 459-465. Theory of the hydrogen atom spectrum. (On Reserve)
3. G. Herzberg, *Atomic Spectra and Atomic Structure*, Dover, 1944, pp. 1-28, Bohr theory of hydrogen spectrum; pp. 54-59, Alkali spectra. (On Reserve)
4. R. M. Hochstrasser, *Behavior of Electrons in Atoms*, Benjamin, 1964. This is the most comprehensive discussion of the background material for this experiment. (On Reserve)
5. G. R. Harrison, editor, *MIT Wavelength Tables*, Wiley, 1938.
6. A. N. Zaidel, *Tables of Spectrum Lines*, Pergamon, 1961.
7. D. M. McQuarrie, *Quantum Chemistry*, University Science, Sec. 8-11. (On Reserve)

## Theory

Familiar features of the several named series of emission lines in the hydrogen spectrum (i.e., Lyman, Balmer, etc.—see Fig.11.1 on p. 351 of Winn) are observable in spectra of other atoms; in each series the lines decrease in intensity and lie closer together at shorter wavelengths. The interpretation of the spectra of many atoms including sodium is complicated by the overlapping of the series. For all atoms, each series converges to a limit corresponding to an energy above which the electron is removed from bound atomic states (i.e., the atom becomes ionized).

Bohr's original quantum theory successfully explained the spectra of hydrogen and other one-electron systems (e.g.,  $\text{He}^+$ ,  $\text{Li}^{++}$ ). The more detailed and accurate quantum theory of Schrödinger and Heisenberg has provided a quantitative explanation of the spectra of multi-electron systems as well, though the mathematics are complicated and entail approximations. One such useful approximation is contained in the *aufbau* (German for "building-up") principle. From the exact theory there emerges the existence of stationary quantum states of the atom as a whole. It is a good mathematical approximation and immensely useful conceptual approximation to consider each atomic state as composed of an appropriate number of one-electron states (called "orbitals") in which each electron has its own unique set of quantum numbers,  $n$ ,  $l$ ,  $m_l$ , and  $s$ .

The solution of Schrödinger's wave equation for the hydrogen atom leads to an orbital angular momentum with the magnitude:

$$\text{orbital angular momentum} = \hbar\sqrt{l(l+1)}$$

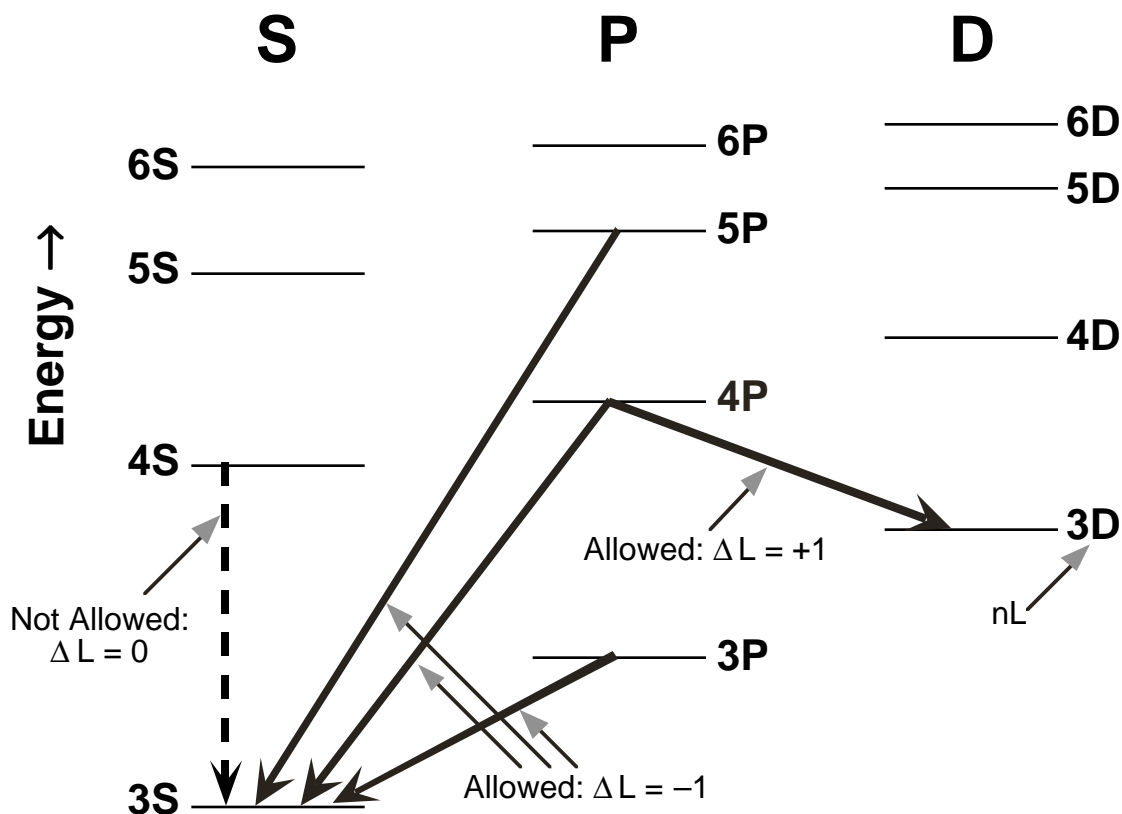
where  $l$  takes positive integral values including zero and  $\hbar = (\text{Planck's constant, } h)/2\pi$ . In a many-electron atom the total orbital angular momentum of the atom is characterized by a **quantum number  $L$**  with allowed values governed by the **individual electron orbital angular momentum quantum numbers,  $l$** .  $L$  may only have integer values **0, 1, 2, 3, ...**, and the letters **S, P, D, F, ...** are used to denote atomic states with the corresponding  $L$  values. For instance, the association of the letter S with an  $L = 0$  state is analogous to the single electron case where values of  $l$  are denoted by the lower case analogs **s, p, d, f, ...**. The composite spin angular momentum quantum number,  $S$ , is also derived from the values of  $s$  for the individual electrons. In atoms having two or more electrons, the spin and orbital angular momenta are coupled, and the resultant total angular momentum is represented by the quantum number  $J$ . The resultant of **contributions from electrons in closed electron shells** to the total value of the orbital angular momentum of an atom is **always zero**; therefore, for alkali atoms the value of  $l$  for the single

valence electron alone determines the allowed  $L$  values of the atom. In other words, **the  $L$  value for an alkali atom is exactly the same as the value of  $l$  for its valence electron.** When there is more than one electron beyond filled shells in an atom, there are rules which you will not need to consider here for combining electronic  $l$  values to obtain the resultant  $L$  for the atom.

The single valence electron in alkali metals is relatively distant from the nucleus and from the inner core of electrons with an inert gas configuration. One would expect, then, that spectra of alkali metals would resemble those of hydrogen and hydrogen-like one electron ions. Differences between alkali metal spectra and truly one-electron spectra arise from the effects of the inner core of electrons in the alkali metals. In one-electron atoms, the energy of each state depends only on the value of the **principal quantum number,  $n$** . That is, although the electron may have various values of orbital angular momentum in excited states, the energy is virtually the same for all values of  $L$ . (There is some observable "fine structure," as it's called, in hydrogen spectra at high resolution due to relativistic effects.) When an inner core of electrons exists in an atom, the energies of the electronic orbitals having the same principal quantum number but different  $l$  values are no longer the same. This is true because the wave functions for the various allowed  $l$  values have different shapes and are therefore shielded to different extents by the inner core of electrons.

The emission lines of hydrogen, you will recall, originate in the transition of the electron from a level with principal quantum number  $n \geq 2$  to a lower level. The original and final  $l$  values of the electron making the transition do not affect the energy of the emitted photon (except for the fine structure mentioned earlier). In the alkali atoms, the energy levels associated with a given quantum number,  $n$ , have different values depending on the value of  $l$  for the valence electron (or  $L$  for the atom). Thus, each energy level is labeled with both an  $n$  and  $L$  value.

The emission spectra of atoms having such a large number of energy levels would be complicated indeed were it not for the existence of "selection rules" which limit the allowed transitions to those between certain energy levels with quantum numbers which satisfy the rules. Other "unallowed" transitions simply do not occur or occur so infrequently that their inherent low intensities make them difficult to observe experimentally. There is no selection rule on  $\Delta n$  so that  $\Delta n$  may equal zero or any other integer. But the selection rule for orbital angular momentum values is  **$\Delta L = \pm 1$** . In other words, in a sodium atom, transitions to an S level ( $L = 0$ ) can originate only from a P level ( $L = 1$ ); transitions to a P level can originate from an S or D level; those to a D level may be from a P or F level, and so on. This is illustrated in Figure 1 which shows the approximate energy levels in atomic Na.



**Figure 1.** Approximate energy level diagram for sodium.

In the region of the spectrum studied in this experiment, emission lines from three series<sup>1</sup> of the sodium spectrum can be observed. One is the so-called principle or P series, and the most intense line of these (and of the entire spectrum) is the 3P to 3S transition<sup>2</sup>, giving rise to the well known intense yellow-orange color of Na lamps. Of the other two series, one originates in transitions from S levels (S series) and one from D levels (D series). One of the goals of this experiment is to assign the observed lines to these three series.

Most of the lines you see are truly due to emissions from one upper level to one lower level, but for a few lines, our instrumental wavelength resolution, while quite high, is not high enough to show that what appears to be a single line is in fact two lines that have nearly the same wavelength. Spectroscopists call the appearance of two (or more) lines from one apparent line as instrumental resolution is

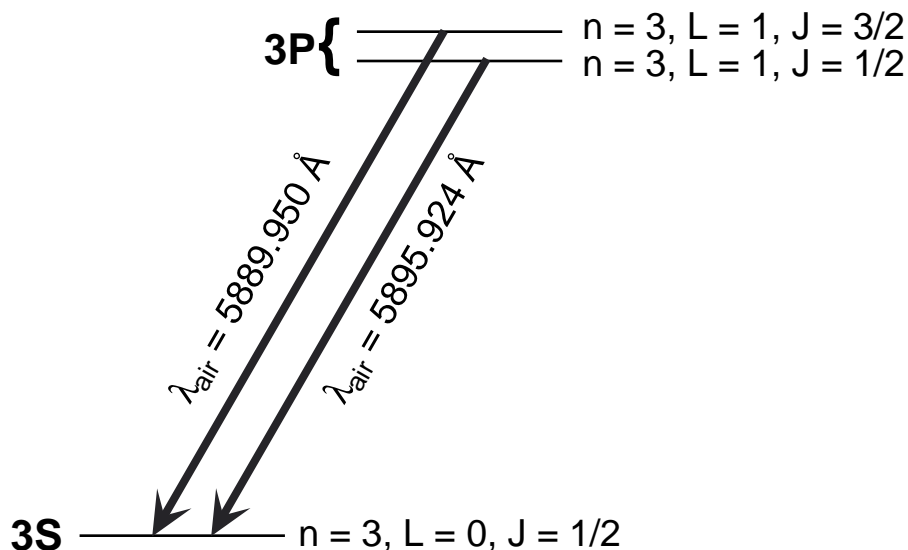
<sup>1</sup> Recall that a "series" is defined as a collection of lines which are assigned to a collection of transitions all of which terminate in a common level, but the series name is based on the transitions' originating levels.

<sup>2</sup> Note how the levels are designated: 3S means  $n = 3$  and  $L = 0$ .

increased line splitting. The splitting here (some which you will observe and some which you will not) originates because in addition to the  $n$  and  $L$  dependence of the various energy levels, there is also a small dependence on the total angular momentum quantum number,  $J$ . As noted earlier, the  $J$  quantum number arises because orbital angular momentum,  $\mathbf{L}$ , and spin angular momentum,  $\mathbf{S}$ , are coupled to produce a resultant total angular momentum,  $\mathbf{J}$ . Since  $\mathbf{L}$  and  $\mathbf{S}$  are vectors and thus have direction, they may be combined in more ways than one. The general theory of angular momentum requires that allowed values of  $J$  (the quantum number that governs the magnitude of the vector  $\mathbf{J}$ ) be positive and differ from one another by integer numbers. The possible values for  $J$  are related to  $L$  and  $S$ :

$$J = (L + S), (L + S - 1), (L + S - 2), \dots, |L - S|.$$

For example, for sodium, the 3P level ( $L = 1$ ,  $S = 1/2$ ) may have  $J$  values of  $(L + S) = 1 + 1/2 = 3/2$  and  $(L + S - 1) = |L - S| = 1 - 1/2 = 1/2$ , whereas the 3S level ( $L = 0$ ,  $S = 1/2$ ) has only one  $J$  value,  $J = S = 1/2$ . The familiar yellow sodium "line" near 589 nm can originate in either of the 3P sublevels and, since these sublevels have slightly different energies, the "line" is actually a pair of lines—a "doublet" in the language of spectroscopy—when observed at sufficiently high resolution<sup>3</sup>. You will easily resolve this splitting in your spectra. The diagram below describes this doublet and gives air wavelengths that will be useful to you as you begin to analyze your spectrum.



According to Bohr's theory, as well as to exact wave mechanical calculations for a single-electron atom of atomic number  $Z$ , the wavenumber  $\tilde{\nu}$  (expressed traditionally in  $\text{cm}^{-1}$  units) of emitted spectral lines (i.e., the emitted photon energy in wavenumber units) can be expressed

$$\tilde{\nu} = \frac{1}{\lambda} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1)$$

where  $\lambda$  is the emitted photon's wavelength,  $R$  = **the Rydberg constant** =  $\mu e^4 / 8\epsilon_0^2 c h^3$ , and  $\mu$  = the reduced mass, defined as  $\mu^{-1} = m_e^{-1} + M^{-1}$  where  $m_e$  is the electron mass and  $M$  is the nuclear mass. Other symbols in the expression for  $R$  refer to well-known physical constants. For an infinitely heavy nuclear mass,  $M = \infty$ , we have  $\mu = m_e$  so that  $R = R_\infty = 109\,737.315\,685\,48\text{ cm}^{-1}$ , one of the most precisely known fundamental constants.

No exact series relationship can be found for the alkali metal spectra because the energy separation between s, p, and d orbitals having the same value of  $n$  varies with  $n$ , decreasing as  $n$  increases. The fact that converging series do exist suggests that the transition wavenumbers (or frequencies, but not wavelengths—do you see why?) may be written as differences between two quantities called **terms**.

One method of writing energies of the alkali atoms can be derived as follows. Expressed in  $\text{cm}^{-1}$ , the energy of the  $n^{\text{th}}$  level of a one-electron atom is

$$W_n = -\frac{RZ^2}{n^2}. \quad (2)$$

In the energy difference expression, Eq. (1),  $W_{n_1}$  has been subtracted from  $W_{n_2}$ . Note that in Eq. (2) the zero of energy is taken to be that for the **completely ionized electron**, i.e., for the state with  $n = \infty$ . For any atom, the energy of a given atomic level can be expressed in terms of an **effective quantum number**,  $n_e$ :

$$W = -\frac{R_{\text{eff}}}{n_e^2}. \quad (3)$$

Here,  $R_{\text{eff}}$  is the **effective** Rydberg constant for the atom of interest. The difference  $n - n_e$  is often called the **quantum defect**,  $\delta_L$ . As the subscript  $L$  indicates,  $\delta_L$  depends on the orbital angular momentum quantum number,  $L$ .

As long as the screened nuclear charge "seen" by the electron in a level of energy  $W$  is fairly near unity, i.e., nearly 100% effective screening by the inner elec-

trons, we may expect that  $n_e$  will not be too different from  $n$ . In the alkali atoms, the magnitude of the quantum defect will measure the extent of penetration (in toward the nucleus) of the orbital occupied by the outer electron, and hence the extent to which the inner core of electrons are ineffective at screening the nucleus.

An empirical equation related to (3) above which often appears in texts is  $W = -RZ_{\text{eff}}^2/n^2$  where  $n$  is the actual integer quantum number and where corrections for imperfect screening are contained in  $Z_{\text{eff}}$ , the effective nuclear charge. Such an equation is just as legitimate as Eq. (3), but it happens not to be as useful in spectroscopic analysis because while  $\delta_L$  is only weakly dependent on principal quantum number,  $Z_{\text{eff}}$  depends more strongly on  $n$ .

If  $n_e$  in the previous equation is expressed as  $n - \delta_L$ , Eq. (3) becomes

$$W_n(\delta_L) = -\frac{R_{\text{eff}}}{(n - \delta_L)^2} \quad (4)$$

where the dependence of  $W$  on  $n$  and  $\delta_L$  has been indicated explicitly. The wavenumber of an emission line from a state with quantum numbers  $n_2L_2$  to a state  $n_1L_1$  can then be written

$$\tilde{\nu}_{21} = W_{n_2}(\delta_{L_2}) - W_{n_1}(\delta_{L_1}) = R_{\text{eff}} \left\{ \frac{1}{(n_1 - \delta_{L_1})^2} - \frac{1}{(n_2 - \delta_{L_2})^2} \right\}. \quad (5)$$

For Na the values of the quantum defects are nearly independent of  $n$ , but vary significantly with  $L$ . The weak dependence of  $\delta_L$  on  $n$  is illustrated for the P terms of Na in Table I.

Table I. Values of Quantum Defects for P Terms ( $L = 1$ ) of Neutral Sodium<sup>4</sup>

$n$	3	4	5	6	7
$\delta_1$	0.883	0.867	0.862	0.859	0.858

You will calculate quantum defects for S and D terms from your experimental measurements.

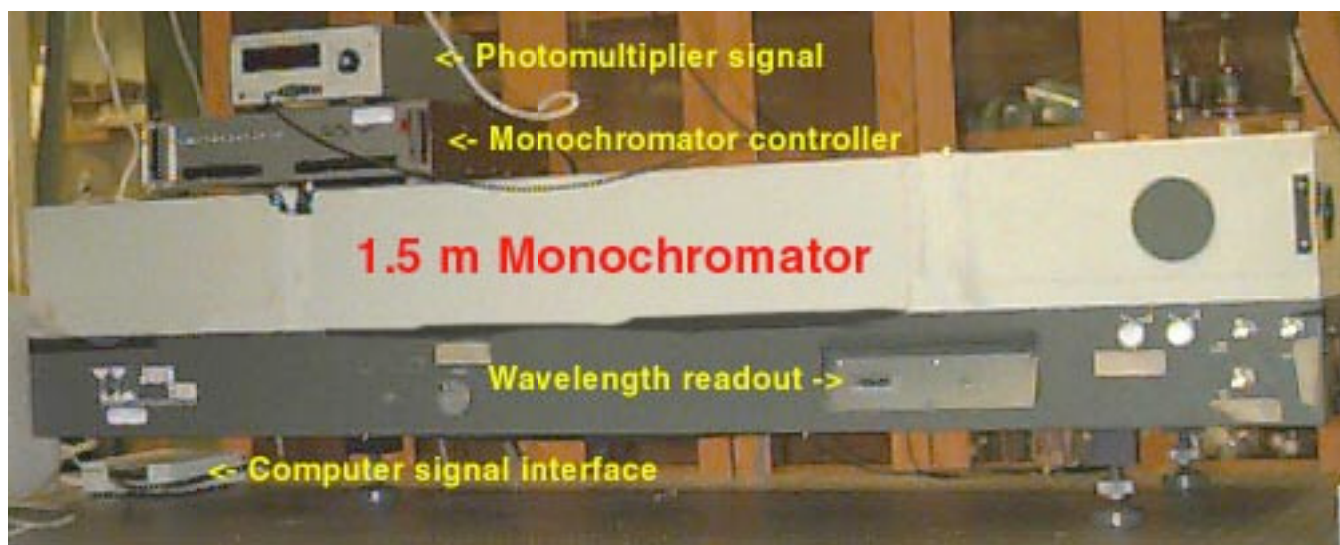
<sup>4</sup> Values of  $\delta_L$  for higher values of  $n$  may be obtained by extrapolation.

## **Experimental**

Using a high resolution research-grade grating monochromator and photodetecting equipment, you will record the emission spectrum from a sodium vapor lamp. A mercury spectrum will also be recorded and used to calibrate the wavelength scale of the monochromator in the spectral range 3000–6200 Å.

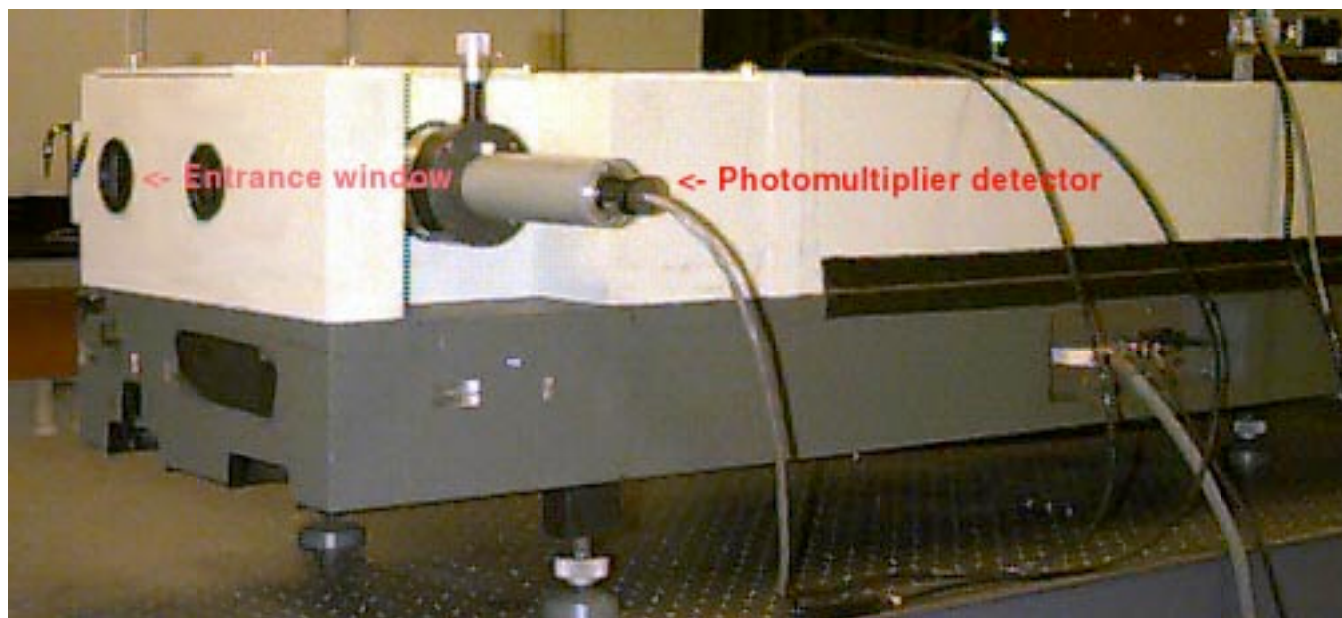
Figures 3a and 3b show two views of the monochromator. (Color versions are on the course web site's page for this lab, or in the pdf version of this handout.) The front view shows the monochromator's wavelength readout, a mechanical dial that changes as the grating is rotated. This readout is not guaranteed to be highly accurate, and thus you will calibrate your Na spectrum's wavelength scale against a Hg atomic spectrum of known wavelengths.

The monochromator is a 1.5 m instrument—the optical path from the grating to the exit slit is 1.5 m long, mostly empty space. Figures 3c and 3d show the internal optical layout of the monochromator, and Fig. 3e shows a schematic top view of the optical system in the monochromator.

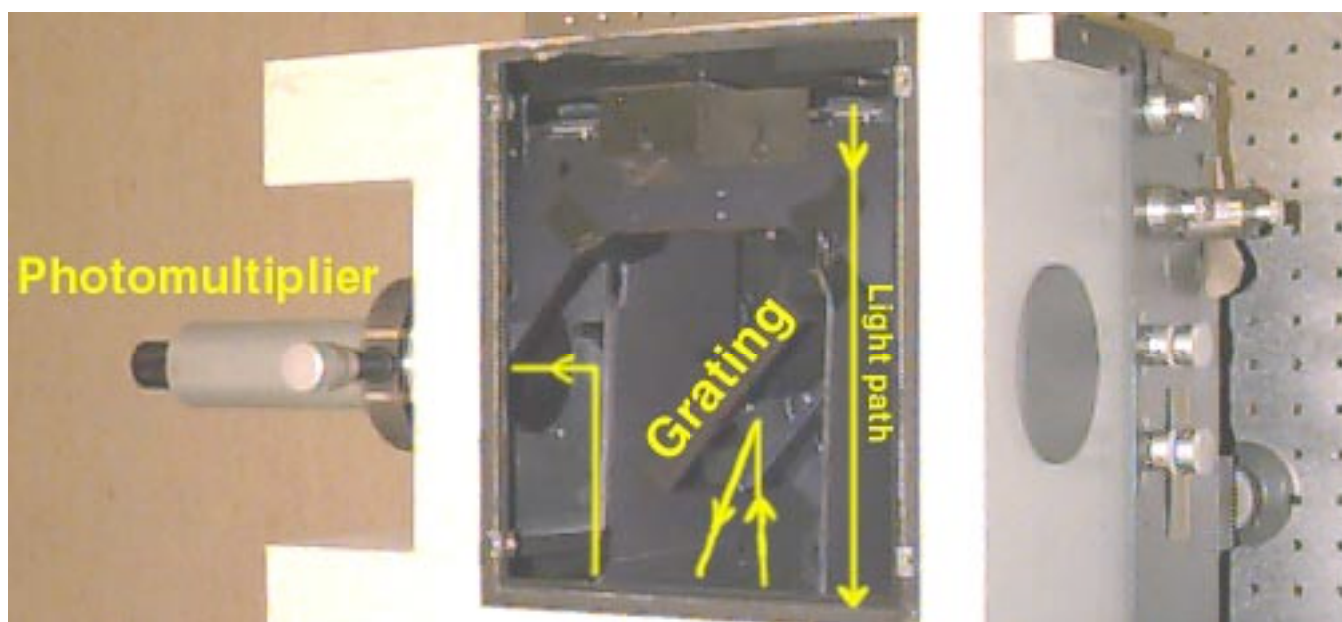


**Figure 3a.** Front view of monochromator.

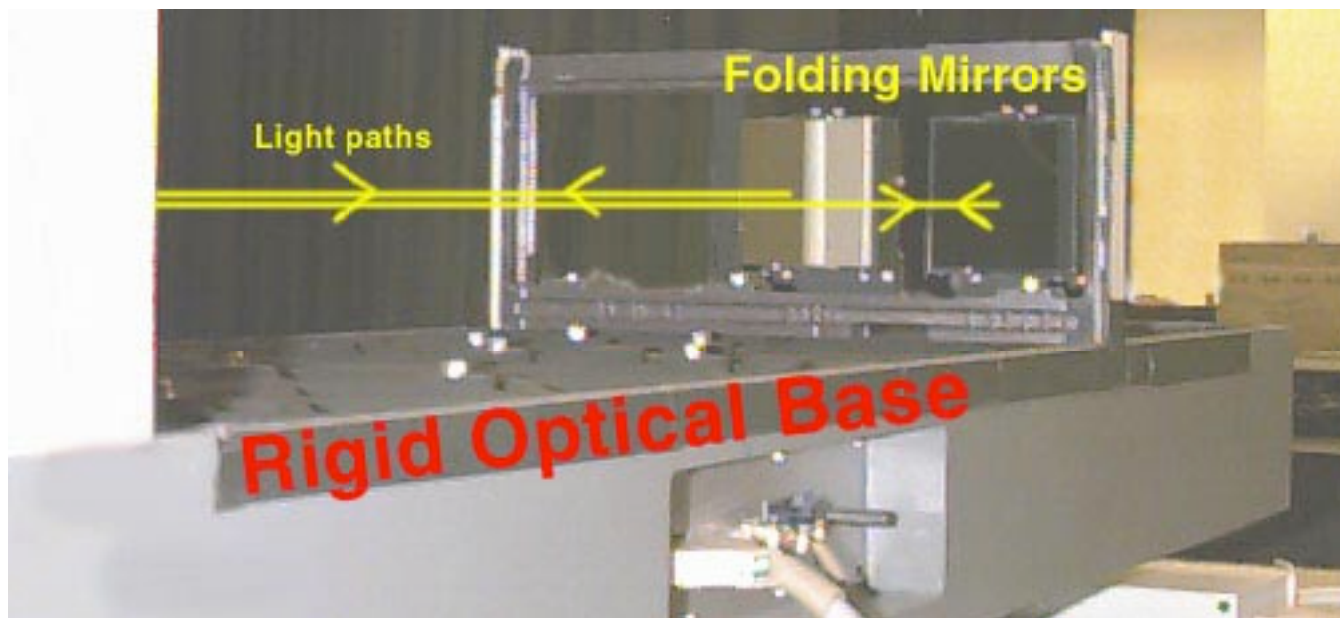




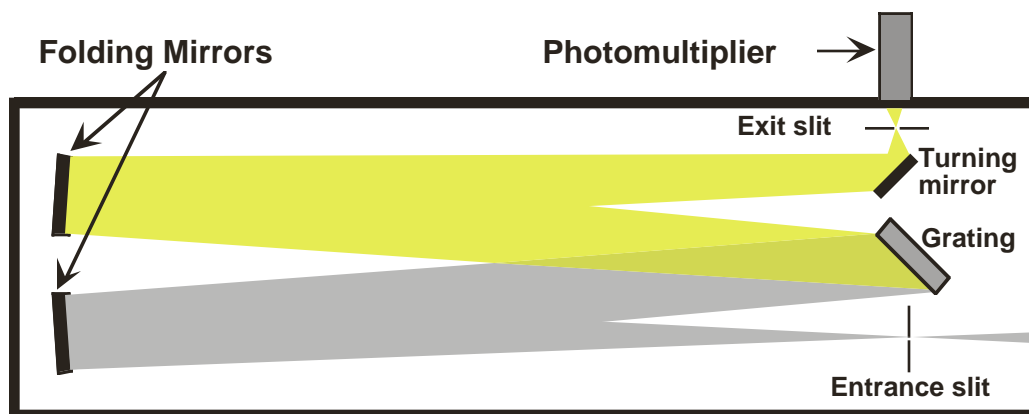
**Figure 3b.** Back view of the monochromator showing the entrance window and the photomultiplier.



**Figure 3c.** Top view of the head end of the monochromator showing the grating and the light path.



**Figure 3d.** View of the tail end of the monochromator with the cover removed. The left folding mirror directs the incoming light back to the grating, and the right mirror directs the dispersed light back to the exit slit and detector.



**Figure 3e.** Schematic top view of the monochromator. The undispersed light is focused on the entrance slit in such a way that it just “fills” the grating after reflection from the lower folding mirror. Light of a particular wavelength then leaves the grating on just the right path so that on reflection from the second folding mirror, it is focused on the exit slit and detected by the photomultiplier.

This optical layout is called a “Czerny-Turner” mounting, a very common monochromator design. The folding mirrors increase the path length between the grating and the exit slit while keeping the whole instrument a reasonable size. Increasing this length increases the resolution, and our instrument has a resolving power  $>10^5$  (i.e., wavelengths differing by one part in  $10^5$  can be resolved).

## Calculations

Your data, as described at the end of the “Running the Sodium Emission Experiment” handout, is a file of raw wavelengths and associated emission intensity. Your first task should be to import the data into Excel and plot intensity versus wavelengths. Tabulate the raw wavelengths of the most intense peaks in your data. (What constitutes “intense” is up to you; some small peaks may really be useful data, but some may be impurities or noise. Noise is usually easy to distinguish. Noise lacks the characteristic peak shape of real data.) You should use the list of impurity peaks in the other handout to eliminate these spurious peaks, and likewise, you should use the list of Hg emission calibration wavelengths to identify the Hg peaks.

At this point, you should have on the order of 20 to 25 features that are likely all due to Na. (Many of these will be closely spaced doublets, as discussed earlier in this handout.) Follow the steps below to (1) correct the raw wavelengths to corrected air wavelengths using the Hg calibration lines, (2) correct air to vacuum wavelengths and thus to vacuum wavenumbers, and (3) assign each Na transition wavenumber to its upper and lower state quantum numbers.

1. Calibrate the wavelength scale of the monochromator from a least-squares fit (you decide if it should be a linear or polynomial fit) of  $\lambda_{\text{true}}(\text{Hg})$  against  $\lambda_{\text{obs}}(\text{Hg})$  (i.e., find the function  $\lambda_{\text{true}} = f(\lambda_{\text{obs}})$  where  $f(\lambda_{\text{obs}})$  is a linear or polynomial function of  $\lambda_{\text{obs}}$ ). Wavelengths  $\lambda_{\text{true}}$  (in air) of the intense mercury lines in your spectral range are given below.

5790.66 Å	5769.60 Å	5460.74 Å	4358.33 Å
4046.56 Å	3650.15 Å	3131.55 Å	3125.67 Å

Given  $\lambda_{\text{obs}}(\text{Na})$ , the least-squares fit function will give you  $\lambda_{\text{true}}(\text{Na})$  for any wavelength in the spectral range. You can use the fitting function's parameters in Excel to calculate corrected wavelengths directly from observed ones.

2. The Na wavelengths as well as the Hg calibration wavelengths were, of course, recorded in air. In order to calculate accurate transition wavenumbers for the Na lines, the Na wavelengths must first be converted to the values that would have been measured with an evacuated monochromator. Light travels more slowly in air than in vacuum, but the frequency of light stays fixed (from energy conservation plus  $E = h\nu$ ). Thus since  $\lambda_{\text{air}}\nu = \text{speed of light propagation in air} = v_{\text{air}}$  and  $v_{\text{air}} < c$ , a wavelength measured in air is smaller than is the corresponding value in vacuum. The ratio  $c/v$  is called the **index of refraction**. As you can easily see, wavelengths measured in air may be corrected to vacuum values by multiplication by the refractive index of air. The refractive index of air is about 1.0003 in the visible and UV spectral ranges, making the correction small (ca. 1 Å). The table below gives correc-

tions to **add** to air wavelengths to convert them to vacuum wavelengths. Use LeastSquares or Excel to fit them to a linear function of  $\lambda$ , and use this function to convert your air wavelengths to vacuum wavelengths. Then compute vacuum wavenumber values ( $\text{cm}^{-1}$ ) for each of your spectral lines, arrange the lines according to decreasing wavenumber, and number each line (i.e., the highest wavenumber line is #1, etc.).

Air wavelength/Å	Correction/Å	Air wavelength/Å	Correction/Å
3000	0.872	5000	1.391
3500	0.998	5500	1.524
4000	1.127	6000	1.658
4500	1.258	6500	1.792

As mentioned above, you will find many closely-spaced doublets because of the spin-orbit interaction that splits the  $nP$  levels into  $J = 3/2$  and  $J = 1/2$  components. For example, the Na D-line is split by about  $17 \text{ cm}^{-1}$ . (See the Sample Calculation below.) To assign your lines to  $n$  and  $L$  values for the upper and lower levels, however, this splitting is not important. Instead, you will find it satisfactory to use a mean wavenumber for these doublets. Theory places the  $J = 3/2$  component of the  $3P$  level at  $+5.7 \text{ cm}^{-1}$  and the  $J = 1/2$  component at  $-11.3 \text{ cm}^{-1}$  with respect to the hypothetical energy of a  $3P$  level that has no spin-orbit interaction. The mean value of the displacement from the unsplit position of  $3P$  is thus  $-2.8 \text{ cm}^{-1}$ . Thus when doublets are observed, you may simply use the mean value of the doublet wavenumbers as the value of the spin-orbit-free energy; rounding mean wavenumbers down rather than up would tend to compensate for the lack of symmetrical displacement of the  $J$ -labeled sublevels.

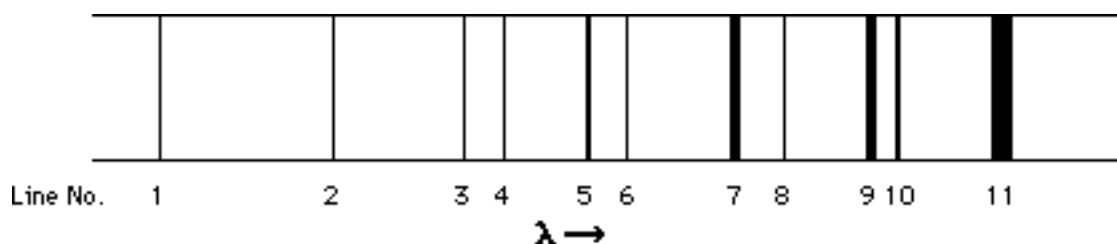
---

### **Sample Calculation:**

We know the air wavelengths of the Na D lines from Figure 2:  $5889.950 \text{ Å}$  and  $5895.924 \text{ Å}$ . From the table above, we can see that the corresponding vacuum wavelengths are  $\sim 1.6 \text{ Å}$  greater. A linear fit shows (and you should verify these numbers from your fit) that the precise additive corrections are  $1.628 \text{ Å}$  and  $1.629 \text{ Å}$ , giving vacuum wavelengths of  $5891.578 \text{ Å}$  and  $5897.553 \text{ Å}$ . (These quantities have more significant figures than your data will warrant. What is the wavelength precision of your data?) Converting these vacuum wavelengths to vacuum wavenumbers gives, respectively,  $16973.38 \text{ cm}^{-1}$  and  $16956.18 \text{ cm}^{-1}$ . We calculate the average vacuum wavenumber for this doublet to be  $(16973.38 \text{ cm}^{-1} + 16956.18 \text{ cm}^{-1})/2 = 16964.78 \text{ cm}^{-1}$ , and we calculate the doublet splitting (the energy difference between the two upper levels in Figure 2) to be  $16973.38 \text{ cm}^{-1} - 16956.18 \text{ cm}^{-1} = 17.20 \text{ cm}^{-1}$ .

---

3. The next problem is to identify the series to which each line belongs. In the jargon of spectroscopy, you must assign the spectral lines. A systematic approach to assignment is outlined in the following. Using your corrected wavelengths, draw a schematic representation of the visible spectrum of sodium with the intensity indicated approximately by the line thickness. For illustrative purposes, we consider the following example (not the Na atom spectrum).



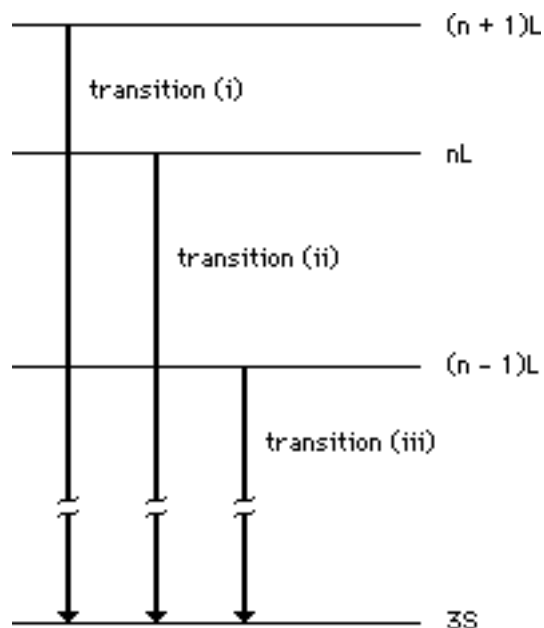
**Figure 4.** Schematic representation of a visible atomic emission spectrum.

Recalling the general observations that the lines in a series decrease in intensity and lie closer together at shorter wavelengths, one might guess that lines 2, 3 or 4, 5 or 6, 7 or 8, 9 or 10 and 11 form a series.

To illustrate how one proceeds further, consider the spectral lines for the  $nP$  to  $3S$  transition series, which are allowed by the  $\Delta L$  selection rule. The wavenumber values are given by the difference in energy (expressed in wavenumber units) between the upper and lower energy expressions of Eq. (4):

$$\tilde{\nu}_{3S,nP} = \frac{1}{\lambda_{3S,nP}} = W_n(\delta_P) - W_3(\delta_S) . \quad (6)$$

Obviously the value of  $\tilde{\nu}_{3S,nP}$  depends on  $n$ ,  $\delta_P$ , and  $\delta_S$ . Thus, to assign the transition, i.e., to specify  $n$ , we need to know  $\delta_P$  and  $\delta_S$ . At this stage, we have too many unknowns ( $n$ ,  $\delta_P$ , and  $\delta_S$ ) for the information available. Since all the members of the  $nP$  to  $3S$  series terminate at the  $3S$  state, as illustrated in Figure 5 below, we can eliminate the dependence on  $\delta_S$  by taking the difference in  $\tilde{\nu}$  values for transitions to  $3S$  from successive levels  $nP$  and  $(n + 1)P$  (transitions (ii) and (i) in the figure below, respectively).



**Figure 5.** Method of combining transition wavenumbers that have a common lower level.

We have

$$\tilde{\nu}_{3S,(n+1)P} - \tilde{\nu}_{3S,nP} = W_{n+1}(\delta_P) - W_n(\delta_P) \equiv R\Delta_{n+1,n}(\delta_P) \quad (7)$$

where we define the quantity  $\Delta_{n+1,n}$  through Eq. (8):

$$\Delta_{n+1,n}(\delta_P) = \left[ \frac{1}{(n - \delta_P)^2} - \frac{1}{(n + 1 - \delta_P)^2} \right] \quad (8)$$

and the weak dependence of  $\delta_L$  on  $n$  has been used to write  $\delta_L(n) \approx \delta_L(n + 1)$ . Note that  $\Delta_{n+1,n}(\delta_L)$  is independent of  $\delta_S$ , the quantum defect for the  $3S$  level. From equation (8) we can calculate an array of  $\Delta$  values for various choices of  $n$  and  $\delta$ . A partial collection of such values is given in Table II.

**Table II** Table of the function  $\Delta_{n+1,n}(\delta) = \left[ \frac{1}{(n - \delta)^2} - \frac{1}{(n + 1 - \delta)^2} \right]$

$\delta$	0.00	0.10	0.20	0.30	0.40
$n = 1$ :	0.7500	0.9576	1.2539	1.6948	2.3872
$n = 2$ :	0.1389	0.1581	0.1811	0.2089	0.2427
$n = 3$ :	0.0486	0.0532	0.5830	0.0641	0.0708
$n = 4$ :	0.0225	0.0241	0.0259	0.0278	0.0299
$n = 5$ :	0.0122	0.0129	0.0137	0.0145	0.0154

Rewriting equation (7) as

$$\frac{\tilde{\nu}_{3S,(n+1)P} - \tilde{\nu}_{3S,nP}}{R} = \Delta_{n+1,n}(\delta_P) \quad (9)$$

shows that for some value of  $\delta_P$ , there should be a correspondence between  $\Delta_{n+1,n}(\delta_P)$  and  $(\tilde{\nu}_{3S,(n+1)P} - \tilde{\nu}_{3S,nP})/R$ ; i.e., the difference in wavenumbers for some pair of lines in the measured spectrum divided by the Rydberg constant should correspond closely to some entry in the  $\Delta_{n+1,n}(\delta)$  array. (Note: you are not likely to get an exact numerical match, but comparisons which differ in the first significant digit should be discarded.) Once such a correspondence is found, this will indicate the values of the upper level quantum numbers  $n$  and  $n + 1$  and the approximate value of the quantum defect  $\delta$  for all the  $nP$  levels. At this stage you will have identified the quantum number for the upper level in transition (i) and the quantum number for the upper level in transition (ii). Note that we have exploited our knowledge of the Na atom ground state (it is  $3S$ , so that we know the lower state  $L$  value), and once we find one pair of excited  $P$  levels that we can analyze and assign this way, *we can work our way up in energy from the uppermost level we first assign, adding only **one** new level at a time*, until we run out of experimental transitions. For the next member (in order of decreasing frequency) of the series, (call it transition (iii)),  $(\tilde{\nu}_{(ii)} - \tilde{\nu}_{(iii)})/R$  should match the  $\Delta_{n,n-1}(\delta)$  entry in the array for the same values of  $n$  and  $\delta$  as those associated with transition (ii).

This procedure is repeated until all the observed lines of a given series have been assigned. For series involving the  $L = 2$  (or  $D$ ) levels, we can use our  $P$  level assignments in a similar way, as we can do for those transitions that start from the  $L = 0$  (or  $S$ ) levels.

Thus, to summarize, the basis of the approach is to:

(1) use the ideas behind Figure 5 to identify possible series of lines and

(2) compare differences between  $\tilde{\nu}/R$  for pairs of spectral lines (in what you believe to be a series) with  $\Delta_{n+1,n}(\delta)$  to assign quantum levels. If you cannot find a close correspondence for any reasonable value of  $\delta_L$ , this indicates that the pair of lines chosen are not members of a series.

Now that we have discussed the general method of analysis, we go over the explicit steps you will take with your data.

(i) Construct a table of  $(\tilde{\nu}_i/R - \tilde{\nu}_j/R)$  for all pairs of Na lines  $i$  and  $j$ . For this purpose, use the theoretical Rydberg constant  $R_{Na}$  for sodium. This may be calculated

from  $R_\infty$  and the appropriate reduced mass ratio. (See Eq. (1); the nuclear mass of  $^{23}\text{Na}$  is 22.989 767 atomic mass units.)

(ii) Construct a table of  $\Delta_{n+1,n}(\delta_L)$  for  $n = 3$  to 12 and  $\delta = 0$  to 1.5 in steps of 0.1. (The easy way to generate both tables (i) and (ii) is with Excel; if you need help, please ask the instructor.)

To illustrate how one uses such tables, consider again the P series. The most intense line in this series is the Na D-line at about 5893 Å, and we have the very great advantage of knowing the  $n$  and  $L$  assignments for both levels involved in this (average wavenumber) transition. If there is more than one member of this series observed in your data (i.e., if the  $4P \rightarrow 3S$  transition is seen), then there should be some  $(\tilde{\nu}_i/R - \tilde{\nu}_j/R)$  value (where  $i$  or  $j$  is the line number of the Na D-line) which corresponds closely with the  $\Delta_{4,3}(0.9)$  entry in your table (ii), which should be 0.1227. The value of  $\delta_L \equiv 0.9$  was known here, since the  $\Delta_{n+1,n}$  values depend on the quantum defect of the upper levels, the P levels in this case. From Table I, we see that such values are approximately 0.9. Once such a match is found, this identifies the next line in the series. This is continued until all the lines in the P series have been assigned. *Be sure to cross off those entries in your table (i) as you make them.* (An easy way to do this is to italicize or display in a different color each assigned entry. You should see a pattern of such assignments emerge quickly as you work your way through your data.)

Following Figure 5, one then attempts to identify another series of lines. Start with  $(\tilde{\nu}/R)$  differences for the low wavenumber members of the series, begin with  $\delta = 0.0$ , and determine if a matching  $\Delta_{n+1,n}(0.0)$  value can be found for some value of  $n$ . If not, repeat the process for the  $\delta = 0.1$  entries, etc. (Remember:  $\delta_L$  stays approximately constant for a series.) In this way you should be able to identify lines from two more series, D and S.

This method, of course, only provides directly the principal quantum numbers of the upper levels. The orbital angular momentum quantum number  $L$  for the upper levels will have a common  $\delta$  value, and it is the magnitude of  $\delta$  that lets you deduce  $L$ . Such a determination is important, since it will allow you to distinguish between the D and the S series of lines.

To complete the assignment of each line, you must specify the values of  $n$  and  $L$  for the level at which the transition terminates. Once  $L$  for the upper levels is known, the  $\Delta L$  selection rule defines possible  $L$  values for the lower level. The values of  $n$  and  $L$  can then be determined by comparing the observed transition wavenumber with  $\tilde{\nu}$  calculated from Eq. (5).



4. Our next step, once the assignment is complete for all Na transitions, is to improve  $\delta$  values, which we do in the following way. Referring to Eq. (5), we see that for any series terminating in a particular level, the value of  $(n_1 - \delta_{L_1})$  is constant. Eq. (5) then has the simpler form

$$\begin{aligned}\tilde{\nu}_{n_2L_2, n_1L_1} &= T - \frac{R}{(n_2 - \delta_{L_2})^2} \\ &= (\text{intercept } T) + (\text{slope of } -R) \times \frac{1}{(n_2 - \delta_{L_2})^2} \\ &= \text{linear function of } \frac{1}{(n_2 - \delta_{L_2})^2}.\end{aligned}\tag{10}$$

To improve our preliminary value for  $\delta_D$ , we make a series of plots of  $\tilde{\nu}$  versus  $1/(n_2 - \delta_D')^2$  for transitions from various excited D levels that all terminate on a common P level. In these plots,  $\delta_D'$  represents a series of approximate value of  $\delta_D$  close to (and including) our preliminary value. We then make least-squares fits to each plot and look at the standard errors of the fitting parameters to decide which value for  $\delta_D$  gives the best fit. Use the parameters of the best plot to determine an experimental value for (1) the Rydberg constant, and (2) the ionization energy from the 3P level. We could repeat this procedure for the P series to improve our value for  $\delta_S$  (recall we know  $\delta_P$  from Table 1), but a linear least-squares fit requires three or more data points. Here's a *big hint*: you will *not* find three or more transitions that terminate on the 3S level!

For the S series, calculate values of  $\delta_S$  for each S series value of  $\tilde{\nu}$  using Eq. (10). (Hint: how does T for the S series compare with T for the D series?) Tabulate the values of  $\delta_S$  and report an average value. Using your experimental values of R, T,  $\delta_S$ , and  $\delta_D$ , predict the energies of the first transitions in the S and D series, both of which are at wavelengths beyond the limits of your spectrum.

5. Once we have best experimental values for R and the quantum defects, we can calculate the ionization potential for the unexcited atom (in units of eV as well as  $\text{cm}^{-1}$ ). Please do so, and include your values in your write-up.

6. Using all the data for sodium that you have recorded and calculated, prepare a detailed energy level diagram, similar to that of Fig. 1, but drawn more accurately to scale. Indicate energies in  $\text{cm}^{-1}$  with the 3S ground level at zero. (Such diagrams are called **Grotrian diagrams** after the spectroscopist who first assembled a large number of them.) Identify the experimentally observed transitions.

7. As mentioned earlier, an alternate approach is to write  $W_n = -RZ_{\text{eff}}^2/n^2$  where  $n$  is the actual integer quantum number and where corrections for imperfect screening are contained in  $Z_{\text{eff}}$ , the effective nuclear charge. For the  $nS$  ( $n = 3$  to  $9$ ) levels of sodium, calculate and tabulate the values of  $Z_{\text{eff}}$  required to reproduce the energies ( $\text{cm}^{-1}$ ) presented in the figure you have just prepared. Compare the dependence of  $Z_{\text{eff}}$  values on principal quantum number  $n$  with the sensitivity of  $\delta_S$  to changes in  $n$ .

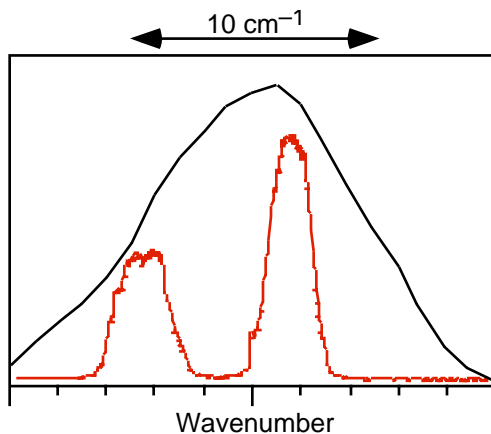
## Discussion

1. Using the value of  $R_\infty$  given earlier and multiplying by the appropriate reduced mass ratio, calculate the theoretical Rydberg constant  $R_H$  for hydrogen. Are your experimental data accurate enough to distinguish among  $R_H$ ,  $R_{Na}$ , and  $R_\infty$ ?

2. Compare your experimental values with the more accurate theoretical value of the Rydberg constant and the literature value of the ionization energy of sodium,  $41449.65 \text{ cm}^{-1} = 5.139 \text{ eV}$ . Are the values consistent within your least squares estimates of uncertainty? Do those least squares error estimates appear to be consistent with the accuracy of your own wavelength data?

3. Compare the values of  $\delta_S$ ,  $\delta_P$ , and  $\delta_D$ . How do these values correspond with what you know about the differences in orbital penetration among the s, p, and d orbitals?

4. The accurate spin-orbit splitting of the 3P level is  $17.196 \text{ cm}^{-1}$ . For the 4P level, it is about  $5.63 \text{ cm}^{-1}$ , but your spectrum won't resolve this due to the compromise made in the slit settings of the monochromator. (Smaller slit widths would allow this doublet to be resolved, but at a significant decrease in signal. The figure below shows this splitting, recorded at a much smaller slit width than you used, compared to the signal you will observe.) For the nD levels, the spin-orbit splitting is around  $0.05 \text{ cm}^{-1}$  or less, which is far below our resolution (but still just within the capabilities of our apparatus). What experimental 3P splitting does your spectrum suggest? Which lines do not give you information on this splitting?



**Figure 6.** The 4P to 3S transition recorded with  $10 \mu\text{m}$  slits (the doublet) compared to the same region recorded with the  $50 \mu\text{m}$  slit width you used (the single broader peak). The entire spectrum spans  $20 \text{ cm}^{-1}$ .

5. What electronic transitions produce the so-called fundamental or F series<sup>5</sup> in sodium? Estimate the value of  $\delta_F$ . Calculate the wavelength of the first member of this series.

---

<sup>5</sup> The letters **s p d f** come from the old spectroscopic nomenclature **s**harp, **p**rincipal, **d**iffuse, and **f**undamental. They are just names that can be viewed as historical accidents nowadays.