

Atomic and Molecular Spectroscopy

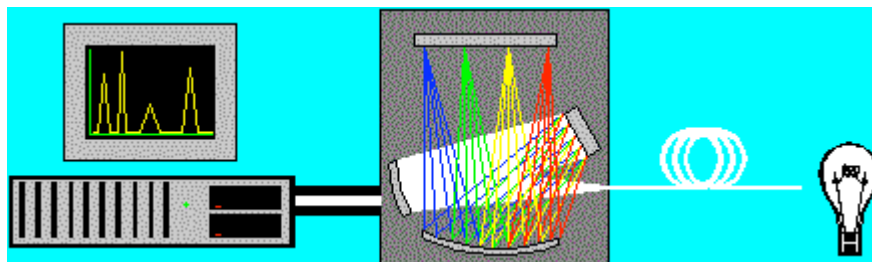


Figure 1: Spectroscopy schematic from Ocean Optics

1. Introduction

Much of our knowledge about atomic structure is derived from the way atoms emit or absorb visible light. When dispersed with a prism or a grating, the light from atomic processes is seen to consist of collections of very narrow, discrete “lines”, at wavelengths characteristic of the atoms involved. The discrete spectrum is a direct manifestation of quantization in atomic systems.

In hydrogen, the regularities in the line spectra can be used to verify the quantized energy levels predicted by the simple Bohr model. More complicated atoms display numerous additional effects, including the screening of the nucleus by inner shell electrons, the interaction of the electron spin with internal atomic magnetism, and the restriction to only those transitions allowed by certain “selection rules”.

When atoms combine into molecules, additional energy terms arise from the vibrational and rotational normal modes of the structures. Transitions between these states lead to a complex “band spectroscopy” which allows study of the inter-atomic potential and the elucidation of the chemical bond.

All of these effects are found to be in complete accord with the Schrödinger theory, and bring us to a deep understanding of atomic structure and molecular structure. Beyond this, modern techniques reveal further small corrections associated with the quantum theory of fields, and some of the most precise measurements in science

In this experiment you will measure the Balmer series, the “spin-orbit” coupling in sodium, and the spectrum of the N_2 molecule. Your instrument is a compact, computerized spectrometer, built for applied and industrial settings, which is easy to use and characterize.

Some brief enlargement on spectroscopic physics and technique is offered below, but this is the barest minimum to get started. Atomic spectroscopy is a famous chapter in the history of physics, and there are numerous excellent treatments. Haken and Wolf and Eisenberg and Resnick are particularly lucid on the physics.

2. The Spectroscopy of Hydrogen: the Bohr Model

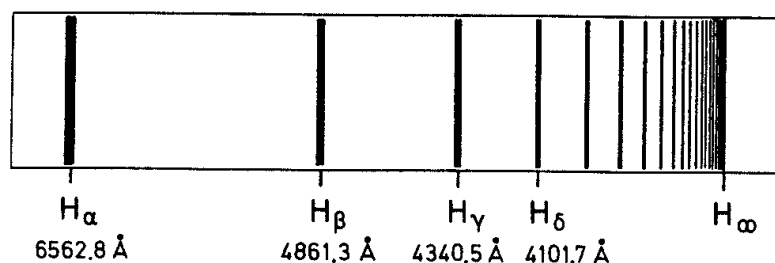


Figure 2 The Balmer series (from Haken and Wolf)

Hydrogen atoms can be excited with an electrical discharge in vessel containing the gas at low pressure. In the visible region, the line spectrum is the famous converging series, as seen in Fig. 2. In 1885 the Swiss schoolteacher Balmer showed that the spectrum was well described by the geometric series

$$\lambda = G \left[\frac{n^2}{n^2 - 4} \right]$$

where G is an empirical constant. In 1889, Rydberg suggested that the Balmer formula was a special case of the expression

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where $n_1 = 2$. The redefined empirical multiplier R_H has come to be known as the Rydberg constant. In 1906 and 1908 Lyman and Paschen confirmed this expression by finding additional series (in the ultraviolet and infra-red) described by the same expression with $n_1 = 1$ or $n_1 = 3$.

In 1913, Bohr invented a simple model of atomic quantization. If the angular momentum of circular orbits was fixed in units of \hbar , the energy of the orbits would also be fixed, and indexed by a quantum number n , according to

$$E_n = - \left(\frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} \right) \frac{1}{n^2}, \text{ with } n = 1, 2, \dots$$

In a transition between states n_1 and n_2 , the energy difference would be balanced by emission or absorption of a photon with wavelength given by the Planck formula

$$\Delta E = h\nu = \frac{hc}{\lambda} = E_2 - E_1 = - \left(\frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} \right) \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

so we have derived “from first principles” the Rydberg equation and the Rydberg constant.

$$R_H = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi\hbar^3 c} = 109737.318 \pm 0.012 \text{ cm}^{-1}$$

The “modern value” of R_H is given in order to convey the kind of precision that is typical of atomic spectroscopy. Note that, following convention since the days of early spectroscopy, the units of “the Rydberg” are in terms of “wave number”, or inverse length.

The value of R_H given above is actually the value that would be appropriate if the nucleus were “fixed” or, equivalently, of infinite mass. In practice, the mass of the electron should be replaced by the “reduced mass”, $m/(m+M_p)$, where M_p is the mass of the nucleus, in this case of the proton. Thus the spectrum has a slight dependence on the mass of the nucleus. It is easy to show that the frequency shift between hydrogen and deuterium is

$$\frac{\Delta\nu}{\nu} = \left(1 - \frac{m}{M_D}\right) - \left(1 - \frac{m}{M_p}\right) \cong \frac{m}{2M_p}$$

where we approximate M_D by $2M_p$. Thus we can measure m/M_p by comparing the spectra of hydrogen and deuterium.

Bohr’s derivation of the Rydberg formula using quantized atomic orbits is one of the landmarks of physical science. Bohr’s is a classic calculation using very simple mathematics. You should follow the treatment in your references and learn to do it yourself. We now know that the more sophisticated Schrödinger treatment, solving for the electron wavefunction in the spherically symmetric Coulomb potential, gets the same energy “eigenvalues”. In retrospect, Bohr’s simple model is not much more than dimensional analysis built around the quantum hypothesis. That fact that it works contains a deep lesson about the fundamental simplicity and solvability of nature.

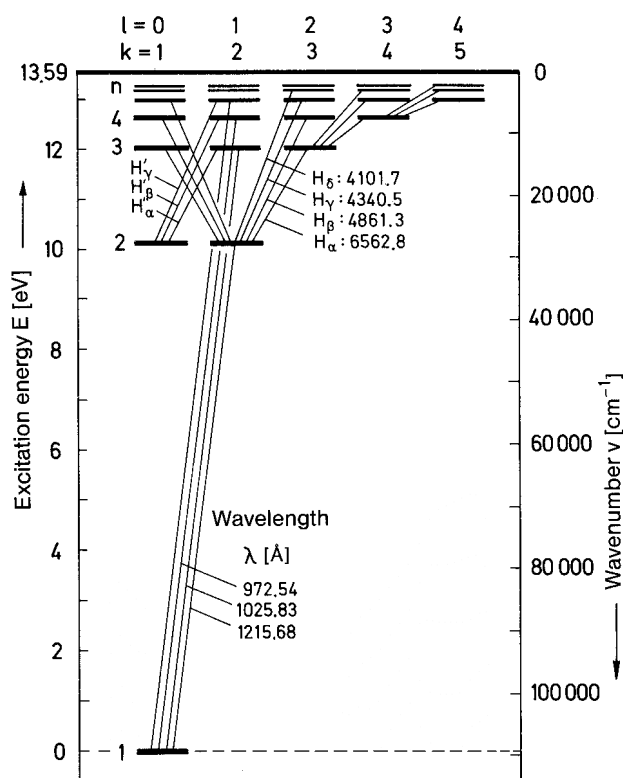


Figure 3 Hydrogen term diagram (Haken and Wolf)

In the Schrödinger solution, we find that each electronic state is specified by three quantum numbers, n , l , and m . The “principle quantum number” n specifies the radial form of the wavefunction and the energy, and is logically similar to index for the quantized “Bohr orbits”. The quantum number l is restricted to the range $l \leq n - 1$, and specifies the angular part of the wavefunction and the total angular

momentum for the state: $|L| = \sqrt{l(l+1)}\hbar$. The magnetic quantum number, m , specifies the projection of the total angular momentum on a given axis:

$$L_z = m\hbar, \text{ with } m = -l, -l+1, \dots, l-1, l$$

In the absence of an external magnetic field, we do not expect the energy of the state to depend on its orientation in space; states with different values of m therefore have the same energy and are said to be “degenerate”. What is perhaps a bit surprising is that the energy is also independent of the angular momentum, l . This is an “accidental” consequence of the spherically symmetric, $1/r$ form of the Coulomb potential. The energy levels of hydrogen depend only on n , and all of the states of different l and m for a given n are degenerate.

This is all summarized nicely in a “term diagram”, as shown in Fig 3. The n values read up along the left, and the l values read across. Note that the energy only depends on the index n . Note also that the transitions as specified always involve a change of one unit of angular momentum l . Because the states are degenerate, this “selection rule” does not show up in the radiation spectrum of hydrogen, but it will be of consequence elsewhere.

In the experiment on Atomic Spectroscopy the Balmer series in hydrogen will be measured with a modern “industrial-grade” spectrometer, utilizing fiber optics, precision gratings, and a CCD based readout is used to measure the Balmer spectrum of hydrogen. The richness of the physics and the history can be followed in greater detail in Haken and Wolf, *Chapter 8*, or Eisberg and Resnick, *Chapter 4*.

3. The Spectroscopy of Sodium: Splitting and Spin

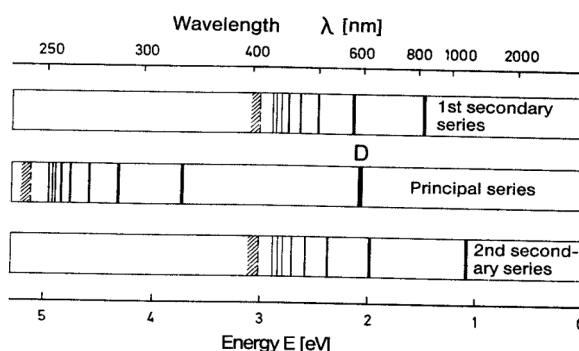


Figure 4 Three series from the sodium spectrum, including the famous Fraunhofer D lines (Haken and Wolf)

a. Nuclear Screening and the Lifting of the Angular Momentum Degeneracy

The distinguishing feature of the alkali atoms is a lone $l=0$ electron outside of all closed shells. Since closed shells are extremely stable, alkali spectroscopy is dominated by the behavior of this outermost “optically active” electron. The electric potential seen by this electron (at its Bohr radius) is the Coulomb field of the nucleus *screened* by the spherically symmetric charge distribution of the inner shells. The net potential is still the Coulomb form, but with the nuclear charge reduced by the amount of the screening charge to give $Z_{\text{effective}} \sim 1$. With one active electron in a Coulomb potential with $Z=1$, we would expect electron wave functions, energies, and spectroscopy similar to that of hydrogen.

The measured energy levels of hydrogen, lithium, and sodium are shown in Fig. 5. The usual spectroscopic notation is employed here, with the angular momentum states specified by the letter s, p, d, f for $l = 0, 1, 2, 3$. The hydrogen like behavior of the alkalis is seen most easily for lithium with large n and l . However, as n decreases, the smaller l states lie below the corresponding hydrogen energy levels. For sodium, the states way out at 6d and 6f are hydrogenic, but the deviations at small n and l are even more pronounced.

The departure from hydrogenic behavior is because only the states with large angular momentum keep the electron out at the large radius of the Bohr orbit, where the simple screening hypothesis obtains. As seen in Fig. 5, for smaller values of l , the electron orbits penetrate within the closed shells, the electron sees more of the nuclear charge, and is more tightly bound, lowering the Coulomb energy. To estimate the magnitude of this effect, one could start with the $Z=1$ hydrogen

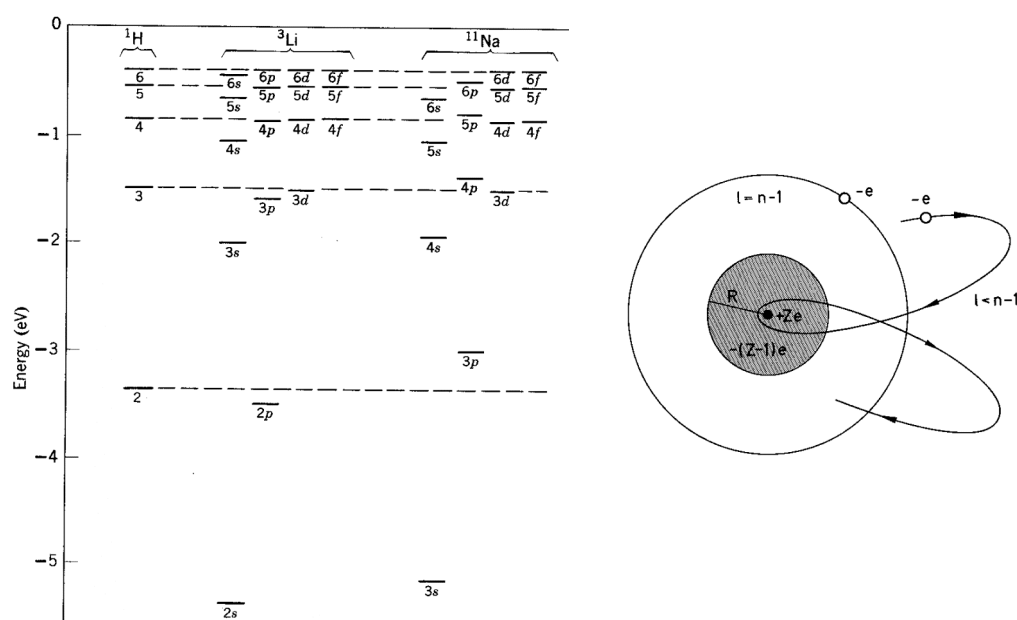


Figure 5 The diagram on the right shows electrons with smaller angular momentum penetrating to smaller radius and seeing more of the nuclear charge (Haken and Wolf). This leads to stronger binding, and lowering of the energy for the low l states, as seen on the left.

wave functions and energies for optical electrons, model the inner shell as a uniform spherical charge of magnitude $-(Z-1)e$, and calculate the energy *perturbation* as the average or *expectation* value of the screening Coulomb interaction:

$$\Delta E_{n,l} = \int \Psi_{n,l}^* \left[\frac{-(Z-1)e^2}{4\pi\epsilon_0 r} \right] \Psi_{n,l} dx^3$$

A more self-consistent technique, due to Hartree, solves for new wave functions and iterates, and converges rapidly to good agreement with the observed energy levels.

b. Spin, Magnetic Moments, and the Spin-Orbit Interaction

When the alkali spectrum is examined with high resolution, many lines are resolved into very closely spaced *doublets*. For instance, the famous sodium “D line” can be resolved into two lines with wavelengths 5896 and 5890 Angstroms. This small 0.1% “splitting” is evidence of the electron spin, and comes about because of the interaction of the spin *magnetic moment* with the internal atomic magnetic field. Since the spin can only point either “up” or “down” with respect to the magnetic field, a state can be “split” into two states of slightly different energy. Transitions from the split state to an un-split state then give two spectral lines in close proximity, a doublet.

The *spin* is a completely non-classical “internal” angular momentum for a particle, as if it were a mass rotating around an internal axis. In the familiar language of angular momentum in quantum mechanics, the spin quantum number, s , specifies the total spin angular momentum and its projection on one axis according to

$$|S| = \sqrt{s(s+1)}\hbar$$

$$S_z = m_s \hbar, \text{ with } m_s = -s, -s+1, \dots, s-1, s$$

For fundamental fermions, like the electron, $s=1/2$, and the projection of the electron spin on any z axis can have precisely two values

$$S_z = \pm \frac{\hbar}{2}$$

Just as if the electron were a classical ball of charge, its internal spin imbues it with a magnetic dipole moment, given by

$$\mu_s = -\frac{g_s \mu_B}{\hbar} S$$

where μ_B , the *Bohr magneton*, is the quantized unit of magnetic moment

$$\mu_B = \frac{e\hbar}{2m} = 0.927 \times 10^{-23} \text{ amp-m}^2$$

The quantity g_s is called the “spin g -factor”, and gives the numerical measure of the magnetic moment in units of Bohr magnetons. For electrons, it is found experimentally that g_s is *very* close to 2. The reason for this is connected with the nature of spin, and predicted by the Dirac theory.

The electron magnetic moment interacts with any local magnetic field. So, what is the local field seen by an electron? In a hydrogenic atom, in the rest frame of the electron, the proton appears to whirling around in a Bohr orbit. This circulating positive current creates a magnetic field at the position of the electron, and then the classic “ $\mu \cdot B$ ” interaction leads to an interaction energy term:

$$\Delta E = -\frac{g_s \mu_B}{2\hbar} S \cdot B$$

The extra factor of $1/2$ is due to the subtleties of a proper relativistic transformation back to the atomic rest frame, and is called the *Thomas precession*. Because the magnetic field is due to the relative rotation of the electron and the atom, its magnitude can be derived in terms of the orbital angular momentum (see references). The expression above term above can then be re-written as a “Spin-Orbit Interaction”:

$$\Delta E = -\frac{g_s \mu_B}{2emc^2 \hbar} \frac{1}{r} \frac{dV(r)}{dr} S \cdot B$$

Evaluation of this expression requires averaging the spatial dependence over the whole atom, weighting by the square of the wavefunction (as at the top of page 6). The size of the splitting is found to depend on the wavefunction as

$$\Delta E \propto \frac{1}{n^3 l(l + \frac{1}{2})(l + 1)}$$

As far as the number of values for ΔE , the projection of the spin along the direction of L or B can have only, and exactly, two values. Reverting to the simple expression in terms of B, the energy of the spin orbit interaction has just two values

$$\begin{aligned}\Delta E &= -\frac{g_s \mu_B m_s}{2} B \\ &= \pm \frac{g_s \mu_B}{4} B\end{aligned}$$

We can think of this as the potential energy of the spin magnetic moment when it is either aligned or anti-aligned with the internal atomic magnetic field. This small energy is then either added or subtracted from the overall energy of the atomic state: for every state with $l > 0$, there become *two states*, with slightly different energies, depending on the relative orientation of the electron spin and the orbital angular momentum.

c. The Addition of Angular Momenta, the Sodium Term Diagram, and Selection Rules

Because it is the total angular momentum that is conserved in the absence of external torques, it is convenient to add the spin and orbital angular momentum into a combined value for a given state. The combined spin $J = L + S$ is specified by the quantum number j , which can have the values $j+s$ or $j-s$, and then, as usual

$$\begin{aligned}|J| &= \sqrt{j(j+1)}\hbar \\ J_z &= m_j \hbar, \text{ with } m_j = -j, -j+1, \dots, j-1, j\end{aligned}$$

In the usual spectroscopic notation, sodium ($Z=11$), has the configuration $1s^2 2s^2 2p^6 3s^1$, and is thus hydrogenic with an optically active electron with ground state $3s$. The $3p$ state has total angular momentum either $j=1/2$ or $j=3/2$; these states are written as $P_{1/2}$ and $P_{3/2}$, and have slightly different energies due to the spin-orbit coupling. The D state has split $j=3/2$ or $j=5/2$, and so on.

The sodium term diagram in Fig. 6 shows all of the effects we have been discussing.

The states of lower l are lower in energy. One might expect the strongest transitions between the ground ($3s$) and first excited states ($3p$), and this is indeed the characteristic yellow light of a sodium lamp, and the famous D lines observed by Fraunhofer in solar absorption spectra. The D lines are one of the most celebrated examples of the fact that states with $l > 0$ are split slightly according to their j values (for clarity this is shown only for the p states). *This is direct evidence of the electron spin.*

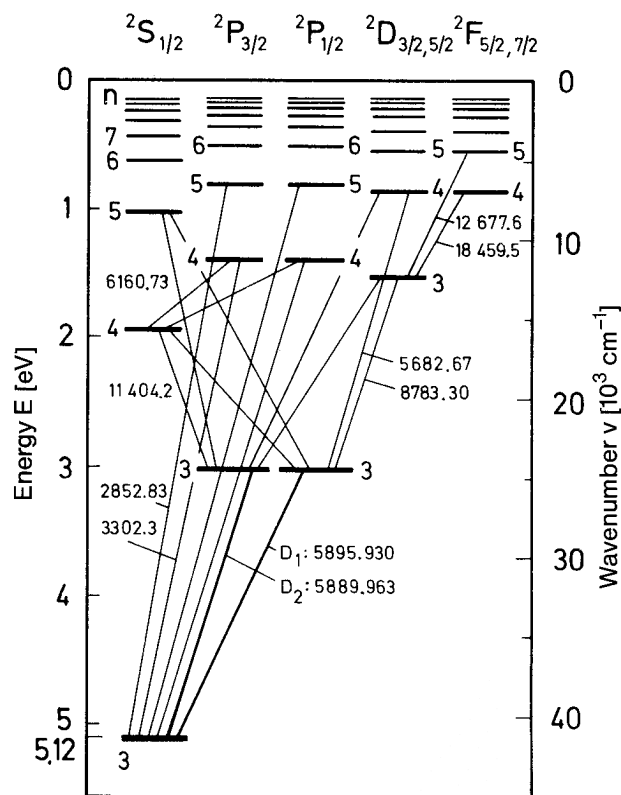


Figure 6 The term diagram of sodium (Haken and Wolf).

A feature seen in this diagram, and not obvious for the case of hydrogen, is that the observed transitions all obey the “selection rule” $\Delta l = \pm 1$. That is, transitions occur between states that differ by one unit of angular momentum. This can be understood very simply in terms of the necessity of conserving angular momentum in the emission of a photon, which has spin = 1!

Alternatively, it can be shown that only states with $\Delta l = \pm 1$ can give rise to the oscillating dipole moment, which must show up at lowest order in the multipole expansion of the radiation field. A *very nice* discussion of this can be found in Eisberg and Resnick Sec 8.7.

4. Molecular Spectroscopy

Thus far we have been mainly concerned with the emission from single atoms, i.e., spectra characterized by sharp lines arising from the emission of photons of particular energies when an electron makes a transition from an excited atomic state to a lower energy state. We will now look at the spectrum of a simple diatomic molecular system: N_2 ,

A cursory inspection of the spectrum of molecular nitrogen (Fig. 7. illustrates what a well-aligned spectrum should look like) reveals not isolated sharp lines but broad ‘bands’ of emission frequencies. This more complicated spectrum is the result of excitation of the additional degrees of freedom that molecules exhibit compared to single, namely the **vibrational** and **rotational** motion of the excited molecule. The emission due to electronic transitions is now convoluted with the spectral features associated with vibration and rotational excitations.

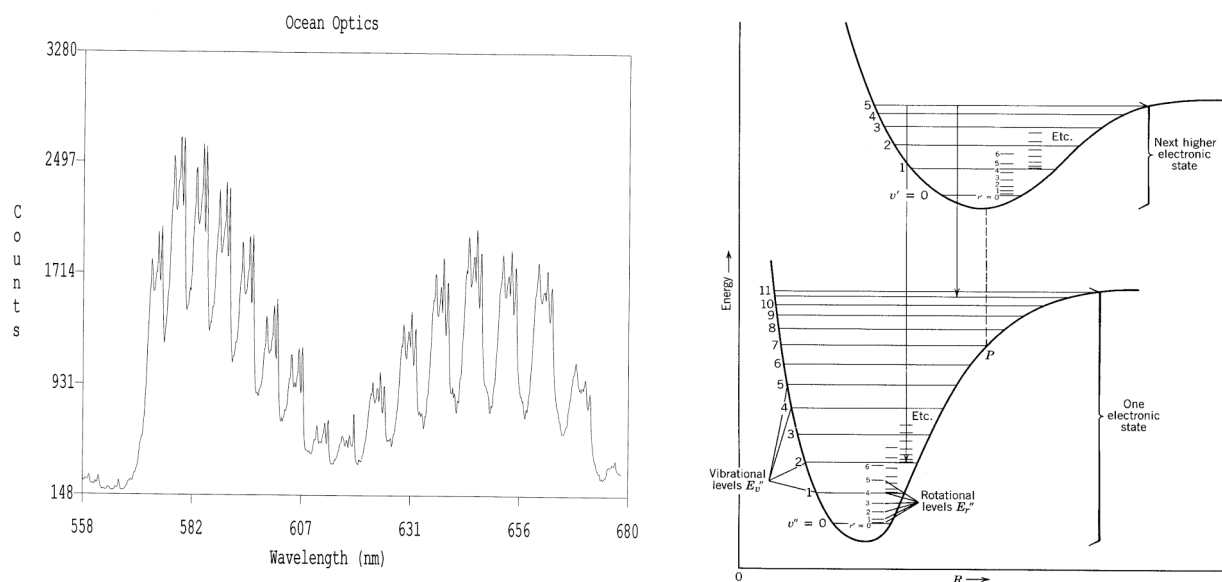


Figure 7 Left: "Band spectrum" of N_2 as recorded with the OO spectrometer. Right: Molecular energy vs. internuclear separation, with the various harmonic oscillator and rigid rotor states superposed (Eisberg & Resnick)

The details of this arrangement are explained in the references, particularly Eisberg and Resnick, Herzberg, and Banwell; however, it is easy to extract some overall features of the spectrum for an intuitive understanding. Because the energies associated with vibrational and rotational degrees of freedom are quite different, we can easily distinguish these two types of excitation from each other in the spectrum. This separation is embodied more formally as the Born-Oppenheimer approximation (briefly, that the vibrational motion is only slightly perturbed by the rotational motion and *vice-versa*). In this case we can treat the vibrational and rotational features of the spectrum as separate contributions superimposed on the overall electronic transition between molecular states:

Let's start with the vibration of the molecule. A useful model for vibrational excitations is the *quantum harmonic oscillator*, which has energy levels given by:

$$E_n = h\omega_0(n + \frac{1}{2})$$

where n is the vibrational quantum number, an integer, and ω_0 corresponds to the fundamental frequency of the simple harmonic oscillator (SHO). Transitions in which $\Delta n = -1$ lead to an emission spectrum of *equally spaced lines*.

Coming now to the rotational excitations, if you zoom in on one of the peaks in the comb of vibrational lines you will see some fine structure. This fine structure is replicated on top of each vibrational line. It arises from optical emission associated with transitions between the quantized energy levels of a rigid rotator:

$$E_{rot} = \frac{h^2 J(J+1)}{8\pi^2 I}$$

where $J = 0, 1, 2, \dots$, h is Planck's constant, and I is the moment of inertia of the N_2 molecule. Note that the energy levels of the rotational states given by this expression are *not* equally spaced.

5. Experimental Atomic Spectroscopy

a. What you will measure

- The Balmer series in Hydrogen
- The Rydberg constant
- The spectrum of deuterium and from it obtain the ratio of the electron to proton masses
- The spectral lines of sodium and evidence for nuclear screening and selection rules
- The fine structure splittings in sodium and evidence of electron spin
- The spectrum of diatomic nitrogen molecules, revealing information on the chemical bond

b. Spectrometry Basics

i) Dispersion via Gratings

Our principle tool for separating light into discernable spectral lines is the diffraction grating.

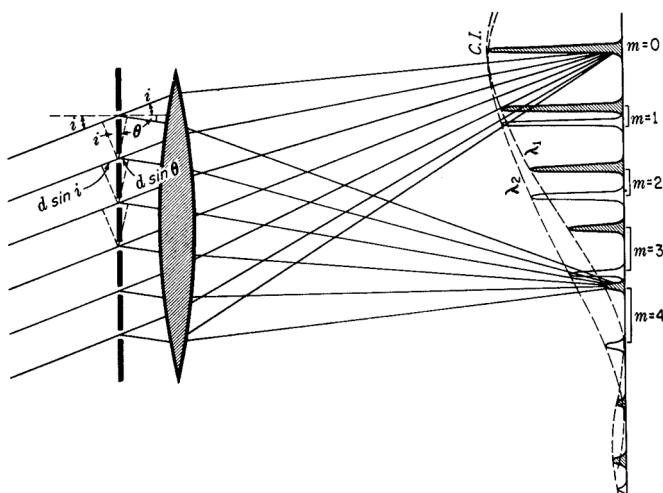


Figure 8 Various orders of diffraction from a simple grating (Jenkins and White)

As seen above, in a figure drawn from the venerable optics book of Jenkins and White, the wavelengths are separated according to the grating equation:

$$m\lambda = d(\sin i + \sin \theta)$$

Notice that as the order number m increases, the separation of nearby lines improves. This feature of the angular dispersion follows from the grating equation, and you will calculate it below. For now, read up on gratings in your favorite optics book. Jenkins and White or Hecht are great. Also study gratings and common spectrometer configurations in Chapter 2 and Section 6.2 in the *Diffraction Grating Handbook 4th Edition*, by the Richardson Grating Laboratory on our web site. Be sure you understand how to calculate dispersion and resolving power.

ii) Photometry via CCDs

In Fig. 8, the dispersed line spectrum is projected onto an “image plane” at the right of the figure. The remaining experimental challenge is to record the intensity here as a function of position. Older systems used film. In a *monochromator*, each line is imaged one-at-a-time by sweeping a single channel of light detection, such as a photodiode or photomultiplier along the line, recording intensity *vs* position. Alternatively, a position sensitive light detector, such as a Charge Coupled Device, or CCD, can be placed in the image plane. A CCD can be thought of as a pixilated photocell. Each pixel, or “bucket”, stores an amount of charge proportional to the integrated light intensity at that location. At the end of the integration period, the charge is shifted out, bucket brigade style, in a raster-like scan over the whole device. A single charge- integrating amplifier on the last bucket records the amount of charge after each shift, and this is easily translated into a map of light intensity vs. pixel. CCD’s are the enabling technology for digital cameras and camcorders, and are revolutionizing spectrometry, astronomy, and all image driven sciences. Read up on CCDs in Chap. 6 and 7 of McLean, and also at the following websites:

<http://www.kodak.com/US/en/digital/ccd/appNotes.shtml>.

<http://www.oceanoptics.com/products/howccd detector works.asp>

c. The Ocean Optics Fiber Spectrometer

The device used in this experiment is an Ocean Optics SD2000 fiber spectrometer. This is a compact, computerized device built for applied and industrial settings. Fiber optics is used to transmit the light from the “specimen” to the instrument, allowing remote measurements of absorption, transmission, and reflectance spectra. The resolution is modest, roughly 0.5 nm at $\lambda = 500$ nm. For comparison, the Fabry-Perot interferometer used in the Zeeman effect experiment in this course can achieve resolutions of fractions of an Angstrom. However, the resolution of the OO-SD2000 is more than adequate for the purposes of this lab, advantageous in its ease of use, and also a thought provoking example of how our laboratory techniques can evolve into applied and entrepreneurial outgrowths. Check out the Ocean Optics website www.oceanoptics.com, especially the topics under

<http://www.oceanoptics.com/technical/systemspecifications.asp>

The SD2000 uses two gratings to cover the complete optical spectrum. One, covering the range 632-880 nm, is directly attached to the DAQ system, and called “Master”. The other, covering the range 371-677 nm, is piggy-backed on the DAQ, and is called “Slave”. These names are just about the DAQ hookup; the two gratings are functionally equivalent over their respective wavelength ranges.

Each grating has 1200 lines/mm, and is mounted in a crossed Czerny-Turner configuration. See Fig.1, the Richardson manual, or your optics book. The first mirror focuses the light on the grating; the second mirror is to focus the slit image on the CCD. The input slit width is fixed at 10 μ m, the effective focal distance from the second mirror to the CCD is 50mm, and the system has an effective magnification of $M \sim 2.0$. Spherical aberrations in the mirrors produce the pronounced shoulder or “coma” on one side of the slit image.

The sensor is a Sony Linear CCD with a single line of 2048 pixels, each 14 μ m wide, for a total sensor length of 2.86cm. For details on the CCD see the discussion and link under “CCD detector response” at

<http://www.oceanoptics.com/technical/systemsensitivity.asp>

d. Understand Your Resolution/ Questions to Answer

Before setting out on a real measurement, a competent experimenter will first think through the experimental realities, and understand the expected level of success for a given idea. No sense wasting time and money if you can prove beforehand that it doesn't work!

In this experiment, the Balmer series and molecular spectra will be easy to measure. (The molecular spectra are NOT easy to interpret, but that's another matter!). The experimental technique is pushed by the need to resolve the spin-orbit splitting in sodium, a 5 parts in 5000 measurement. Can the device do this?

i) Under the link <http://www.oceanoptics.com/technical/opticalresolution.asp> you will find a discussion of the optical resolution expected for the OO devices. For our configuration, with a 10 μ slit, the size of the slit image in the CCD plane is 3.2 pixels.

ii) Using the grating equation, assuming that the angle of incidence equals the angle of reflection, $i = \theta$, calculate θ for the sodium D line. Note that the spectrometer works entirely in the first order regime, $m=1$.

iii) Starting from the grating equation, show that the *angular dispersion* of the grating is

$$\frac{d\lambda}{d\theta} = d \cos \theta_r$$

iv) For a system with focal length f and magnification M , show that an angular dispersion translates into linear dispersion in the sensor plane according to $\Delta x = Mf \Delta \theta$

v) Calculate the separation in pixels at the CCD plane of the sodium D doublet. Compare to the device resolution. Is this going to work?

vi) Calculate the *spectral range* for this system: how large an interval in frequency can be covered by the configuration of optics and grating? Compare to the sensitivity ranges for the master and slave spectrometer.

vii) Explain briefly how a Czerny-Turner spectrometer works. (A diagram would be appropriate.) How is it possible to build one in such a small box?

viii) Explain briefly why it is not possible to use the Ocean Optics instrument to study the hydrogen Lyman series spectrum.



6. Experimental Procedure

a. Using the Lamps and Spectrometer

Figure out how to take the lamps in and out of the spring loaded holder. Put the mercury lamp in the holder. Turn the variac to zero. Turn on the switch on the bud-box and the variac, and turn up the variac until the lamp comes on. Turn the voltage back down until you are just over threshold.

Be careful, the lamps get hot!

The spectrometer is controlled by a program called OOIBASE. The basic procedure is as follows:

- Open OOIBASE by double clicking the shortcut titled “Ocean Optics Spectrometer.”
- SD2000 used in this lab has two input channels: Master and Slave. Each channel has different spectral range: Master from 620 to 880 nm and Slave from 360 to 680 nm. The scope window can be switched between two channels using channel selection button. (See right.) Note: When the active channel is switched, any captured images will not be translated, i.e., an image taken in Master channel will not appear correctly in Slave channel. Therefore, it is important to include the channel mode used with any spectra. (More on this later.) 
- To acquire a spectrum, point the fiber optics cable to the source lamp, avoiding the saturation, and click the image capture button. (See right.) You can vary the intensity by just moving the fiber back. Alternatively, you can experiment with the “Integration Time” using the menu options. Once a satisfactory image is captured, save the image using the procedure below: 
- To save the file for later viewing using OOIBASE, choose “Save Sample Spectrum” under “File.” Save the image using an identifiable name, but no extension is needed. The file will be saved with extension “.ooi” – an OOIBASE readable file.
- To save the file for analysis using IGOR or Excel, choose “Export Spectrum” and “Sample” under “File.” Save the image using an identifiable name, but no extension is needed. The file will be saved with extension “.sco” – an ASCII file readable by both Excel and IGOR. Instructions on doing data acquisition with IGOR are in Appendix 2.
- There are additional parameters associated with the spectrometer that can be used to control the data acquisition process. For more information, refer to OOIBASE online help.

b. Calibrate on Mercury

The ultimate calibration of a grating/CCD system is done using standard reference spectra. The relation between CCD channel number and tabulated wavelength is fit with a calibration function that attempts to give the best interpolation across the whole CCD array. The OO procedure is outlined in Appendix 1. The angular dispersion varies as $\cos(\theta)$, so an obvious calibration function might be quadratic in channel number (why?). OO uses a cubic function to accommodate the tilt of the grating in the optical bench.

Find a spectral reference. The CRC handbook is good, as usual. Or try the NIST website. For mercury, check out the term diagram in Melissinos Fig 2.13, which *is* mercury, not hydrogen as mislisted.

Capture the mercury spectrum and identify lines. If you have started with a good calibration this should be straightforward. Good starting points are the yellow doublet at 576.9 and 578.9, the green line at 546.0 and the purple line at 435.8. Plot wavelength error (residual) vs. wavelength.

How does the accuracy vary over the device? The yellow doublet is very close to the sodium D lines. Is the calibration in this region accurate to get the resolution you will need?

If you want to re-calibrate, use the procedure in Appendix 1, make a new Hg spectrum and compare with the old one, and your reference lines. Try some obvious variations in your procedure as well. Can you get a good calibration over a smaller range by choosing input values just in that range? Or does it help to get three numbers spread as evenly as possible over the spectral range? These comparisons allow you to understand the systematic uncertainty in your calibration, which is probably the largest uncertainty in every measurement here.

c. Measurement of the Balmer series in Hydrogen

- Install a hydrogen tube, and capture the Balmer series. Try to do this soon after your mercury checkout, so that the calibration is preserved.
- Compare the wavelengths of your lines to the accepted values. Identify the transitions they represent.
- Calculate the Rydberg constant from your data. A keen method is to plot

$$\frac{1}{\lambda} \text{ vs. } \left[\frac{1}{4} - \frac{1}{n_2^2} \right]$$

using your “guess” for n_2 . You should get a straight line whose slope is R_H . The straightness of the line tests the Balmer hypothesis. Be sure to estimate the uncertainty on R_H !

- You have measured the quantized energy levels of hydrogen. This is one of the most famous results in modern physics. Autograph your plot and send it to your parents.
- Repeat for deuterium and determine m/M_p .

d. Measurement of Fine Structure in Sodium

- Obtain the sodium spectrum. The sodium lamp requires some time to warm up. Begin acquisition once the sodium lamp is glowing in yellow.
- Measure all of the lines. The D line is whopping, everything else is tiny by comparison. You may have to adjust integration times in order to get good measurements for the other lines. Make sure you can resolve all of the different doublets.
- Identify all of the lines. You may find many lines that don’t seem to belong. Is there something else in the lamp? Check the line listing in the CRC Handbook. Use Fig. 6. Organize them according to final states, and see if you can reproduce Fig. 4. What do the “series” represent? Can you fit a Balmer-like relation using a “quantum defect”? (See Haken and Wolf)
- Measure the splittings of transitions involving the 3P level. In nm and eV! How “fine” is the structure (what % of the total transition energy)? Are they the same across 3P? Can you find split lines corresponding to non-3P transitions? Do the ratios of the splittings scale according to the rule in sec 3b? What is the approximate magnitude of the “internal atomic magnetic field”?

e. Measurement of the Band Spectrum of Diatomic Nitrogen

- Use the N_2 lamp. Carefully measure the positions of the coarser ‘comb’ of lines in the spectrum to check if indeed the vibrational states are uniformly spaced as predicted by harmonic oscillator equation in Section 4. Extract the harmonic oscillator frequency, ω_0 , from your measurements. Pushing this SHO model a little further, we can make an estimate of *the strength of the chemical bond that holds the nitrogen molecule together* from the expression $\omega = \sqrt{(k/m)}$, where m is the reduced mass of the pair of nitrogen atoms coupled to each other by a ‘spring constant’ k , whose stiffness is determined by the strength of the N-N covalent bond. Calculate k in units of newtons per meter.

- Measure the energy levels of the nitrogen quantum rotator from the measured spectrum and compare with the expected energies calculated from the rigid rotor equation in Sec. 4, using a simple classical approximation for the moment of inertia of the N_2 rotator. You can treat the molecule as two point masses connected by a rigid rod, rotating end-over-end. What is the moment of inertia of N_2 ? What is the distance between atoms in the molecule?
- Compare the vibrational and rotational frequencies for Nitrogen.
- Hydrogen and deuterium are both diatomic molecules (H_2 and D_2), so how come we don't see all this interesting molecular structure in these cases?
- If you observed that the vibrational emission lines were not exactly equally spaced, how big is the deviation, in percentage terms, and what do you think causes this deviation from the ideal SHO spectrum?
- There is an extremely useful kitchen appliance that works on the principle of rotational excitations of molecules. Can you explain the operation of a microwave oven in these terms?
- Compare your results with expectations for hydrogen, sodium, nitrogen, ...
- Does your measurement of m/M_p agree with the expected value? Discuss.

(Be sure to answer all questions in the earlier parts of the writeup.)

References

Banwell, C.N., Fundamentals of Molecular Spectroscopy, McGraw Hill, London, 1966, is a readable account of the basics.

Bemath, P.F., Spectra of Atoms and Molecules, Oxford University Press, 1995.

CRC Handbook of Chemistry and Physics, CRC Press: Boca Raton, FL , 2001.

R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, is an excellent source book for modern physics, at a level somewhat above the standard “Modern Physics” texts

H. Haken and H. Wolf, The Physics of Atoms and Quanta, is another excellent source book, not as comprehensive as Eisberg and Resnick, but with deeper discussions of awesome clarity on many of the topics of atomic physics. For instance, here you can find the best discussion of the “quantum defect” as well as the dependence of the spin-orbit splitting on l and n .

Herzberg, G. Molecular Spectra and Molecular Structure: 1. Diatomic Molecules. This is the classic reference, very approachable, in spite of its density.

I. S. McLean, Electronic Imaging in Astronomy: Detectors and Instrumentation, has a very complete discussion of CCD’s from the point of view of their utility in experimental physics.

A. R. Melissinos, Experiments in Modern Physics, has discussions of the physics, and very complete discussions of procedure, data, and analysis for many of the standard experiments in a course of this kind. The book is old, so there are some quaint circuit diagrams with tubes, etc., on the other hand, the principles of grating spectrometers have not changed all that much!

C. Palmer, Diffraction Grating Handbook, 5th Edition, is a comprehensive guide to the business, published by Richardson Grating Laboratory, Rochester, NY. See our web site for a copy.

Appendix 1: SD2000 Calibration

a. Both Master and Slave channel require separate calibration processes. To calibrate the spectrometer, an element with at least 3 peaks of known wavelength within the range of each channel is needed. Check CRC Handbook of Chemistry and Physics under section E. Krypton and Mercury satisfy the above requirement for Master and Slave channels, respectively.

b. Begin calibration by resetting coefficients to the original factory-supplied values:

| Coefficients | Master Channel | Slave Channel |
|--------------------|----------------|---------------|
| First Coefficient | 0.147333 | 0.176653 |
| Second Coefficient | -1.081E-5 | -1.171E-5 |
| Intercept | 627.921 | 365.655 |

c. For each channel, capture the spectrum of calibration element, being careful not to saturate the peak. Make sure that there are more than 3 visible peaks and their rough wavelength to match the theoretical values found in CRC. (Spectrometer can be assumed to be reasonably calibrated at the onset.)


d. Using the cursor mode button (see right), identify the *pixel number* of each peak at the *highest intensity*. The pixel number and the intensity can be read from the data bar at the bottom of the screen. (Note: It is useful to zoom into each peak by dragging the cursor to enlarge the region of interest. To go back to the full spectrum view, use the zoom out button.) (See right.)



e. Tabulate the calibration data on an Excel worksheet as follows:

| True Wavelength (nm) | Pixel Number | (Pixel Number) ² |
|----------------------|--------------|-----------------------------|
| 404.66 | 226 | 51076 |
| 435.83 | 409 | 167281 |

f. OOIBASE relates the pixel number to the wavelength by using a second-order polynomial: $\lambda_p = I + C_1p + C_2p^2$. The goal of the calibration is to determine the values of I – the intercept, C_1 – the first coefficient and C_2 – the second coefficient. These values can be obtained by performing a linear regression analysis on Excel:

- Under “Tools,” choose “Data Analysis.” In the menu, choose “Regression.”
- Use true wavelength column for “Input Y Range,” and *both* pixel number and pixel number squared as “Input X Range.” (Data range can easily be chosen by pressing the button  within the input field. See right.)
- The regression analysis result will be output into another worksheet. Under “Coefficients:” “Intercept” is the value of I
 “X Variable 1” is the value of C_1
 “X Variable 2” is the value of C_2
- In addition, the value of “R squared” should be very close to 1. (Why?)

g. In OOIBASE, under “Setup,” choose “Configure Spectrometer.” Under “Spectrometer Channel,” select “Master” and enter appropriate values of three coefficients, then switch to “Slave” and repeat the procedure. Close the window by clicking “OK.”

h. Restart OOIBASE for new calibrated coefficients to take effect.

Appendix 2: Exporting OO Files and Analysis with IGOR

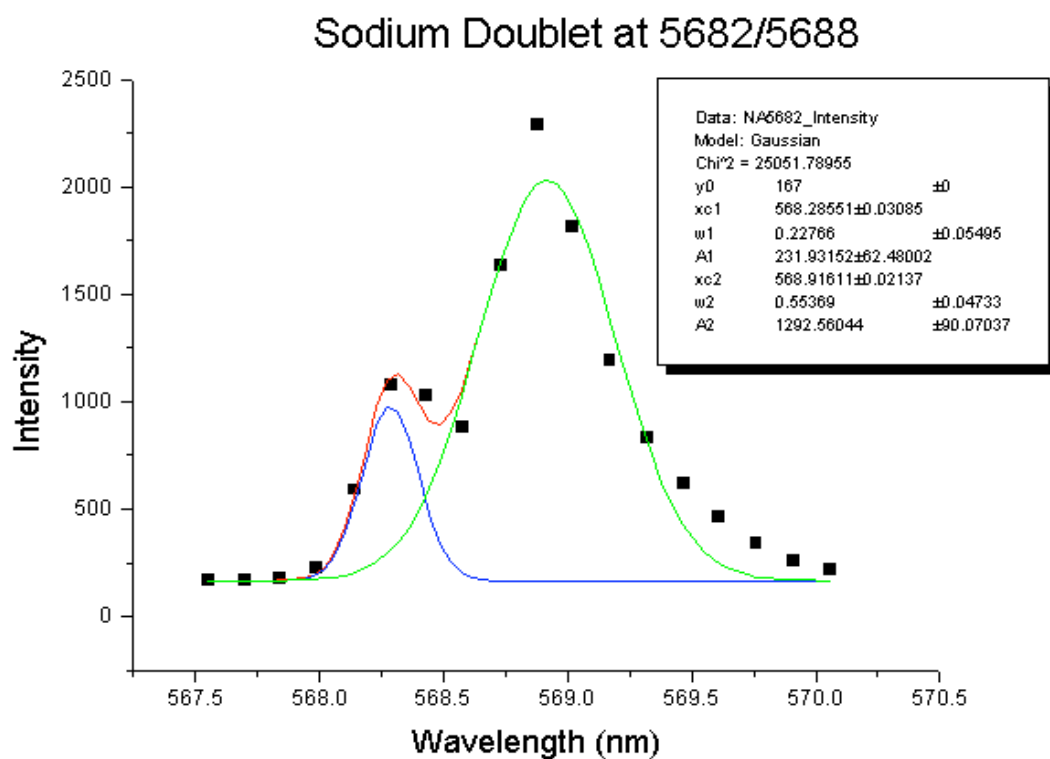
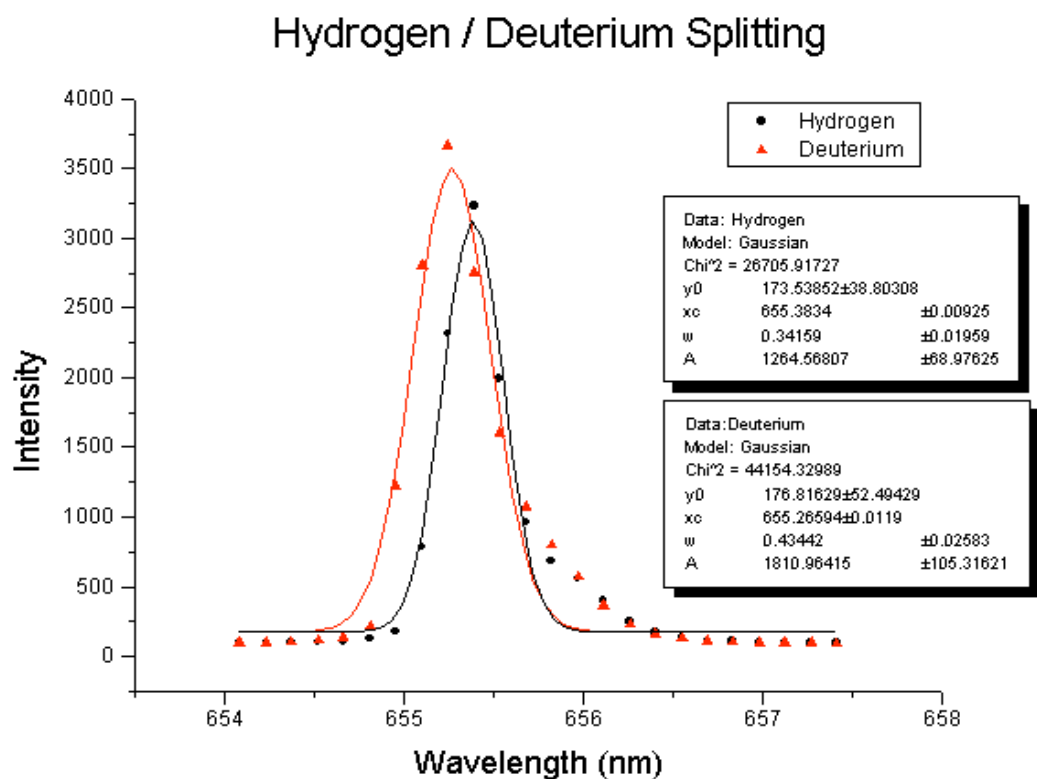
1. Any OOIBASE spectrum saved as the scope output (with .sco extension) can be imported directly into Origin worksheet. [Origin is no longer available in the labs, but use of IGOR is similar.
 - a) Start Origin. There should be three windows present: Data1 sheet, Toolbox and the Script Window.
 - b) Making sure Data 1 window is highlighted, under “File,” choose “Import,” then “ASCII.”
 - c) To display “.sco” files, “Files of Type” needs to be changed to display all file types, *i.e.*, by selecting “*.*”. Locate the target file and open.
 - d) To enter both hydrogen and deuterium spectrum under one worksheet, import two sets of data into two different worksheets. Add a new column to the hydrogen data worksheet (“Add New Column” under “Column”), cut the deuterium intensity data from the other worksheet and paste into the new column.
2. To plot the entire data sheet, simply choose “Scatter” under “Plot” while Data worksheet window is highlighted.
3. To plot each peak
 - a) First, identify the peak by zooming into the plot using “zoom” function from Toolbox (Magnifying lens icon). Click and drag the rectangle around the peak. Once the peak is sufficiently magnified, identify the starting and ending wavelength.
 - b) From Data window, highlight the data range as identified in step 3. Easiest way to do this is to highlight the row of the beginning wavelength, then scroll and highlight the ending wavelength while depressing the “shift” key. This procedure will automatically highlight all rows in between the beginning and the ending wavelength.
 - c) Once the desired data region is highlighted, plot the peak by choosing “Scatter” under “Plot.” Choose “Wavelength” as “X column” and “Intensity” as “Y column.”
4. To fit the lineshape: it turns out that, except for the **coma** on one side, the lineshape is Gaussian. This has nothing to do with normal statistics, but instead with the way the slit image is made from light propagating down the fiber. To do the fit, simply choose “Fit Gaussian” under “Analysis.” A textbox with relevant information will show up. Origin defines a Gaussian function as:

$$y = y_0 + \frac{A}{w \cdot \sqrt{\frac{\pi}{2}}} e^{-\frac{2(x-x_0)^2}{w^2}},$$

where y_0 is the baseline offset, A is the total area under the Gaussian from the baseline, x_0 is the center of the peak and w is 2σ , approximately 0.849 of FWHM. Be

5. To fit multiple Gaussians on one set of data points (*i.e.*, sodium), choose “Fit Multi-peaks” then “Gaussian” under “Analysis.” Enter the number of peaks and the initial half width. (The estimate given by Origin works fine.) Select the rough location of each peak by double clicking the mouse on the plot. A textbox with complete specifications of each Gaussian will appear. The one additional line is the sum of all Gaussians. It is useful to color code each fit. Simply double click each fit line to specify its color. (See sample 2 at the end of this write up.)

Sample 1: Origin resolution graph of hydrogen-deuterium doublet



Sample 2: Origin analysis graph of sodium doublet

