

Spectroscopy

Reading Your text books. Look under spectra, spectrometer, diffraction.

Consult Sargent Welch Spectrum Charts on wall of lab. Note that only the most prominent wavelengths are displayed on these charts. Wavelengths obtained from these charts are accurate enough for comparison with your data.

Equipment DataStudio, optical bench with scale facing students, one pair bases and rods to raise optical bench 4 cm off lab bench, PASCO spectrophotometer with collimating lens at left end of optical bench, PASCO CI-6604 high sensitivity light sensor, discharge power supply with cardboard shield, hydrogen and helium discharge tubes, sodium discharge unit removed from supply and raised by rod and clamp, 6 inch ruler, red bulb bench light

Room Lights The room lights should be off for this experiment as they will give a signal in the light sensor. Use the red bulb light source to illuminate the computer keyboard.

Light From Monitor Light from the computer monitor can give a signal in the light sensor. Turn the monitor away from the light sensor, and if necessary, shield the monitor.

PRECAUTIONS

1. Be sure the high voltage for the gaseous discharge is OFF and the installed discharge tube is COOL before changing discharge tubes.
2. The sodium light source gets hot. Do not touch it when it is on or has recently been on.
3. Please keep fingers off the diffraction grating and lenses. Handle these items by their edges or holders to avoid contaminating them with finger oil.

1 Purpose

To use a grating spectrometer to observe and measure the line spectra of various atoms in a discharge. A recording spectrometer which is capable of giving relative intensities is often referred to as a spectrophotometer.

2 Background

Early in the 20th century there were a number of phenomena that could not be explained by classical theories. These phenomena included the photoelectric effect and the electromagnetic spectra emitted by black bodies, atoms, and molecules. Quantum mechanics explains these phenomena to a very high degree of precision. (For the highest precision, quantum electrodynamics or Q.E.D. is necessary.)

Incandescent liquids or solids emit electromagnetic radiation that have continuous spectra. Gases that are not too dense or too large in spatial extant and have been excited by some means such as an electrical discharge emit light at discreet frequencies or wavelengths. In a

spectrometer, a device which measures these wavelengths, a particular wavelength or color usually shows up as a thin line of color which is separated from lines of different wavelength or color. Lines arise because the input light to the spectrometer is from a thin slit. The emitted spectra are often referred to as line spectra or “lines.” The wavelengths emitted are uniquely characteristic of the kinds of atoms and molecules that make up the gas or discharge, and measuring the spectrum of a discharge is a standard way of determining the composition of a substance.

An atom or molecule has an infinite number of energy levels, including the lowest or ground state. If the atom or molecule is in an excited state and makes a transition to a lower energy state, where the energy difference between the states is E , it will usually emit a photon with frequency ν whose value is given by the Einstein formula

$$E = h\nu, \quad (1)$$

where h is Planck’s constant whose value is $h = 6.6 \times 10^{34}$ joule-seconds. (The atom or molecule can also give this energy to another particle.) In a discharge some of the transitions or lines are stronger than others and are easier to observe.

3 The Diffraction Grating

Due to their superior resolving power, diffraction gratings have replaced glass prisms in spectrometers. Refer to Fig. 1. A plane monochromatic wave with wavelength λ is incident normally on a thin plane which has a large number of identical parallel slits each separated by the distance d from its two neighbors. This arrangement of slits is called a diffraction grating. The long dimension of each slit is perpendicular to the page, and the slits are narrow enough so that the single slit diffraction pattern of each slit is very broad. Assume that the transmitted light is observed on a screen that is far enough away so that the light rays arriving at a given point on the screen from all parts of the grating are essentially parallel. The resulting diffraction is called Fraunhofer diffraction. On the screen will appear a series of narrow lines at angles θ given by

$$d \sin \theta = m\lambda \quad (m = 0, \pm 1, \pm 2, \dots). \quad (2)$$

(Questions: What are appropriate units for d and λ ? For θ ?) All wavelengths will have a line in the forward direction where $\theta = m = 0$. This is called the “zero” order line. For other values of m there are two lines symmetrically placed about the zero order line. The positions of these lines are wavelength dependent. The lines at $m = \pm 1$ are termed first order lines, the lines at $m = \pm 2$ are termed second order lines, etc. When the conditions of this formula are met the light from each slit will be in phase with the light from any other slit, and there will be complete constructive interference. As the angle of observation θ is slowly changed from the conditions of this equation, some destructive interference occurs. This happens faster, as a function of angle, as the number of slits used increases. The observed lines get narrower as the number of slits increases.

In actuality a diffraction grating rarely consists of parallel slits. Diffraction gratings are usually made by scratching many parallel grooves or “lines” on a glass blank which may have been coated with aluminum. The grating in the spectrometer you are using is a replica grating made from using an original grating as a mold. It is a “blazed” grating which means

that the grooves or lines are not symmetrical. This makes the intensity of a given order not the same on either side of the central maximum. Do not confuse the lines (grooves) of a grating with the spectral lines observed with the spectrometer. A grating is blazed to throw more light into desired orders.

If two wavelengths are incident simultaneously on the grating the lines on the screen will be at different locations (except for the zero order line). If the lines are separated enough the two wavelengths can be distinguished. The ability of the grating to distinguish between two closely spaced wavelengths is called the grating's resolving power. As the width of a line on the screen decreases as the number of slits used increases, the resolving power of the grating depends on N , the number of slits used. (Unfortunately, the grating slits are often called grating lines, so "line" can be used in several ways.) If the wavelength difference that can just be resolved by the grating is $\Delta\lambda$ the resolving power of the grating is defined as $R = \lambda/\Delta\lambda$. A reasonable and often used definition of $\Delta\lambda$ is that the maximum of one of the two wavelengths is at an adjacent minimum of the other. It is not too difficult to show that

$$R = \frac{\lambda}{\Delta\lambda} = mN. \quad (3)$$

N is the number of lines of the grating actually used, not the number of lines the grating has. Only part of the grating may be illuminated. The grating just described is a "transmission" type grating. A grating which has thin mirror-like lines is termed a "reflection" grating.

4 The Grating Spectrometer

Refer to Fig. 2, which has all the essential elements of a grating spectrometer. As usual, the long dimension of the slit is perpendicular to the page. A light source, which in this experiment is an electrical discharge, illuminates a collimating slit. The collimating slit is placed at the focal point of the collimating lens, and a ribbon of light whose rays are parallel falls on the diffraction grating. The rays of light are perpendicular to the plane of the grating. Note that the ribbon of light does not have to be unduly thin, but it does have to have a fair amount of coherence. The original light from the discharge is incoherent, which is to say that there is no fixed phase relationship between light emitted from different parts of the discharge lamp. The slit-collimating lens arrangement produces light that is coherent enough for the experiment. The light emerging from the diffraction grating at a given angle θ is focused by a lens onto the detector slit, behind which is a light detector or sensor. The focusing lens, detector slit, and light sensor rotate as a unit so that the angle θ can be scanned. The grating does not rotate. The focusing lens enables the Fraunhofer condition to be satisfied with a shorter grating-detector distance. The focusing lens also increasing the peak intensity of a line. Without it, the spectral line would be unduly spread out and the light intensity at the center of the line low.

The resolving power R of the grating is not necessarily indicative of the spectral line widths observed using the spectrometer. All spectral lines have some width in frequency and wavelength which will appear in the observed line. The width of an emitted line depends on the lifetime of the emitting energy state, the Doppler effect resulting from atom motion, and collisions between atoms. In addition the spectrometer itself may have other imperfections other than the grating, such as imperfect lenses and mechanical motions.

5 The PASCO Grating Spectrophotometer

See Fig. 3 which is a top view of the spectrophotometer. Fig. 4 is an exploded view of the grating, light sensor, and associated components. All components except for the light source are mounted on an optical bench or on the (spectrophotometer) base which is attached to the optical bench. The optical bench has been raised 4 cm above the lab bench to bring it in line with the gaseous discharge source. The optical bench has a scale to help with the proper positioning of components. Taking the perspective of Fig. 3, at the left end of the optical bench are 5 collimating slits of various widths. These slits are in a single plate. The plate is held by a thumbscrew which, when loosened, enables the plate to be slid horizontally and allows the different slits to be brought onto the optic axis of the spectrometer. The collimating slits are attached to one side of a holder that when squeezed near the bottom enables the holder to be slid along the optical bench. A convenient position for this holder is at the 2 cm mark on the optical bench. There is a mark on the holder to facilitate positioning.

The collimating lens and its holder are to the right of the collimating slit. This lens has a nominal focal length of 10 cm, so that taking into account the thickness of the holders (about 2.5 cm), the collimating lens holder should be placed at about 13.3 cm on the optical bench scale

The final component that is directly attached to the optical bench is the (spectrophotometer) base. See Fig. 5. All the components shown in Fig. 4 are mounted on this base. The degree plate (see Fig. 3) mounts on top of the base and rotates about a vertical axis. The degree plate has degree marks on it and its angular position can be determined by the pointer attached to the base. Attached to the degree plate and rotating with it is the (light sensor) arm (see Fig. 3). Attached to the arm and also rotating with the degree plate are the focusing lens, screen, aperture disk, and light sensor. A rod fixed to the underside of the arm and beneath the light sensor is a convenient handle for rotating the degree plate.

Referring to Fig. 5 it is seen that the rotary motion sensor, stripped of its pulleys, is attached to a hinge on the base. The hinge has a spring which pushes the smallest cylinder or pinion¹ of the rotary motion sensor onto the edge of the degree plate. The rotary motion of the pinion is used to measure the angular rotation of the degree plate. For this measurement to be accurate it is important to rotate the degree plate and arm slowly enough so that the pinion does not slip on the degree plate.

In the middle of the degree plate is a holder for the grating. The holder and grating *do not rotate* with the degree plate. The grating holder is held by friction and its rotational position adjusted so that the light beam is normal to the grating. The grating is held magnetically to the holder and should be on the light source side of the holder. The glass blank holding the grating is positioned so that the grating side faces the light sensor.

The screen, aperture disk, and light sensor are mounted on the end of the arm. The screen allows you to look directly at the spectral lines that have been focused by the lens. The aperture disk has 6 slits of various widths plus some other openings that are not of interest in this experiment. The various slits can be brought into operation by grasping the aperture disk at its horizontal extremes and rotating it. The choice of slit width is a trade-off between intensity and angular resolution.

Behind the aperture disk is the photodiode light sensor. A switch on the top of the light

¹A pinion is the smallest gear in a gear train. PASCO uses it to define the smallest of the cylinders on the axle of the rotary motion sensor.

sensor increases or decreases the signal from the light sensor. Gains of 1, 10, or 100 can be chosen. In addition the signal to the display can be changed in the drop-down menu for the light sensor in the experimental set-up window. Sensitivities of low(1x), med(10x), and high(100x) are available. We use the term gain for the switch on the light sensor, and sensitivity for the light sensor menu. PASCO suggests the following. Start with the gain at 1 and the sensitivity at 1x. As necessary, increase the gain to 10 or 100. If still more signal is needed, then increase the sensitivity from 1x to 10x or 100x. PASCO's recommendations are probably based on maximizing the signal to noise ratio.

6 Measuring the Rotation of the Degree Plate

The angular rotation of the degree plate is measured by the angular rotation of the rotary motion sensor. Nominally, the sensor axle rotates 60 times for each rotation of the degree plate. Obtain the actual rotation ratio experimentally. For the best accuracy, set the rotary motion sensor for 1440 divisions/rotation. You can change the divisions of rotation by clicking on the rotatory motion sensor tab and changing the resolution to high. Use the digits display with 3 decimal points. Set the degree plate at $-60\ deg$, click Start and slowly rotate the degree plate to $+60\ deg$. (Which side of the degree plate you call plus or minus is arbitrary.) Record the angle through which the rotary motion sensor has turned and calculate the rotation ratio. Note that you are measuring the pinion rotation in radians and the degree plate rotation in degrees. Repeat this procedure a few times to determine the accuracy of your measurement. With what accuracy can you measure the rotation angle of the degree plate? Try rotating the degree plate at different speeds to see if this has an effect on your accuracy. When measuring the angular position between spectral lines, divide the angular rotation of the rotary motion sensor by the rotation ratio to obtain the rotation angle of the degree plate.

7 The Sodium Spectrum and Calibration

The grating provided with the PASCO spectrophotometer has approximately 600 lines per mm. The well known Sodium D lines will be used in the spectrometer to measure this grating parameter to greater accuracy. The sodium D lines are a doublet with wavelengths of 589.0 nm and 589.6 nm. This doublet is not resolved by the PASCO spectrometer. Use the average value of 589.3 nm in determining the lines per mm of the grating. Proceed as follows.

1. The sodium light source should be separated from its power supply and mounted on its own stand. Turn the source on to allow the source to warm up while adjusting the spectrometer.
2. Center the #3 collimating slit in the rectangular opening of its holder and rotate the aperture disk so that detector slit #3 is in front of the light sensor. These slits choice are suggestions, and you are free to try different slit combinations.
3. Turn the degree plate to zero and keep it there for the following adjustments.

4. Place the 6 inch ruler against the grating holder, and using the marks on the degree plate verify that the plane of the grating is perpendicular to the optical bench. If it is not, rotate the grating holder so that it is perpendicular to the optical bench.
5. Position the end of the tube projecting from the sodium light source near the collimating slit. The tube from the light source should be at the same height as the collimating slit and parallel to the axis of the optical bench. A band of sodium light which is the zero order line should appear in the vicinity of the detector slit. On the screen you should also see the two first order lines on either side of the zero order line.
6. Alternately move the collimating lens and the focusing lens so as to make the zero order line as sharp as possible. The zero order line may not be centered on the detector slit but should not be too far from it. Note that the two first order lines are fuzzy unless you rotate the arm so that the detector slit is near these lines.
7. When the degree plate is set at zero degrees, the two second order sodium lines lie outside of the screen. Move the screen to either side so that you can see these lines.
8. Set up the graph display, with the light sensor intensity on the vertical axis. In the light sensor set-up window set the sensitivity at 1x and set the light sensor gain at 1. Set up the horizontal x-axis of the graph display from time rotation count of the rotary motion sensor, which should be adjusted for 1440 divisions/rotation.
9. Click Start. Move the detector slit back and forth across the zero order line and observe the change in signal strength as the line is “scanned.” Increase the gain of the light sensor until a satisfactory zero order line is obtained. Scan the two first order lines. Increase the light sensor gain if necessary. Now scan the two second order lines and adjust the gain if necessary. If a light sensor gain of 1000 is not enough, increase the sensitivity in the light sensor set-up window. When you have satisfactory signals for the first and second order lines, you may “saturate” the zero order line. This means the amplifiers and/or recorders do not have sufficient range to handle the signal. The signal will have a flat top when the line is scanned.
10. When you have satisfactory signals for the second order lines, move the detector slit a little bit “outside” one of the second order lines and click Start. Slowly scan the detector slit to the outside of the other second order line. Note that zero on the graph display is where you start taking data and does not correspond to zero on the degree plate. Click STOP. If you have scanned slowly and carefully, between the second order and first order sodium lines, you will see lines on your graph that you did not see on the screen with your eyes. We will call these lines “X.” Print out your graph. For each of the lines on the graph, use the graph cross hairs and an expanded horizontal axis to determine the two angles at which the peaks are located. Write these angles in on your graph. Calculate the difference in angle between the two first order peaks and the two second order peaks for the sodium lines. Half of these two angles divided by the rotation ratio should be used in Eq.(2) to determine two values of d , the grating spacing. Use an average of these two values of d in determining wavelengths of other spectra.
11. Calculate the wavelengths of lines X. Speculate what gives rise to these lines. Why do you not see them on the screen?

8 Hydrogen and Helium Spectra

Using the procedures employed for sodium, investigate the spectra of hydrogen and helium using the discharge source. Use the grating spacing you obtained by observing the Na D lines. Review the precautions at the beginning of this write-up. Compare your results with the wall chart.

9 Finishing Up

Please leave the bench as you found it. Thank you.

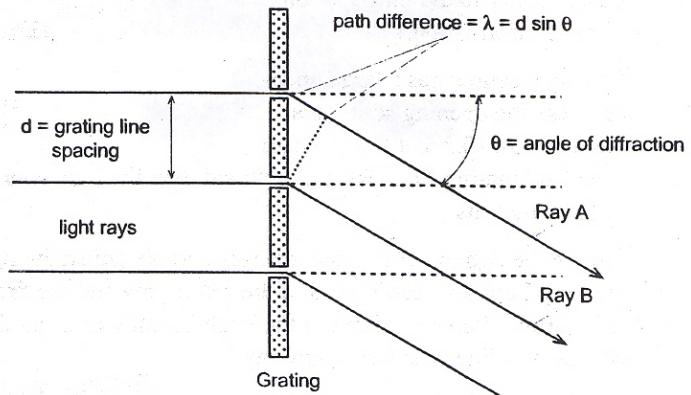


Fig 1 Ray diagram for first order diffraction pattern

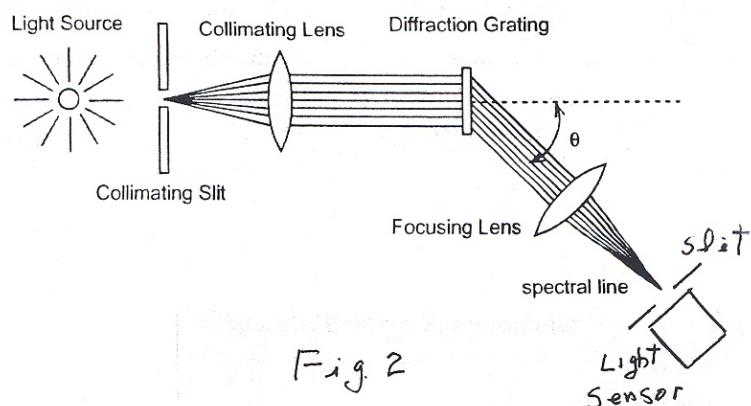


Fig. 2

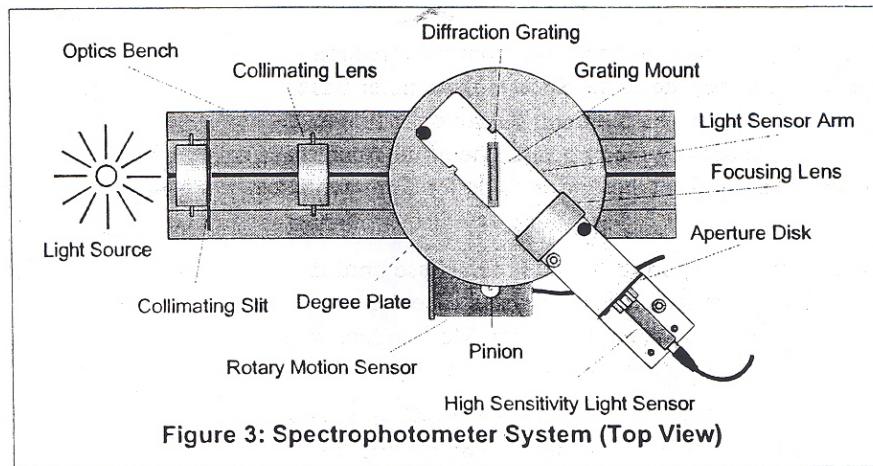


Figure 3: Spectrophotometer System (Top View)

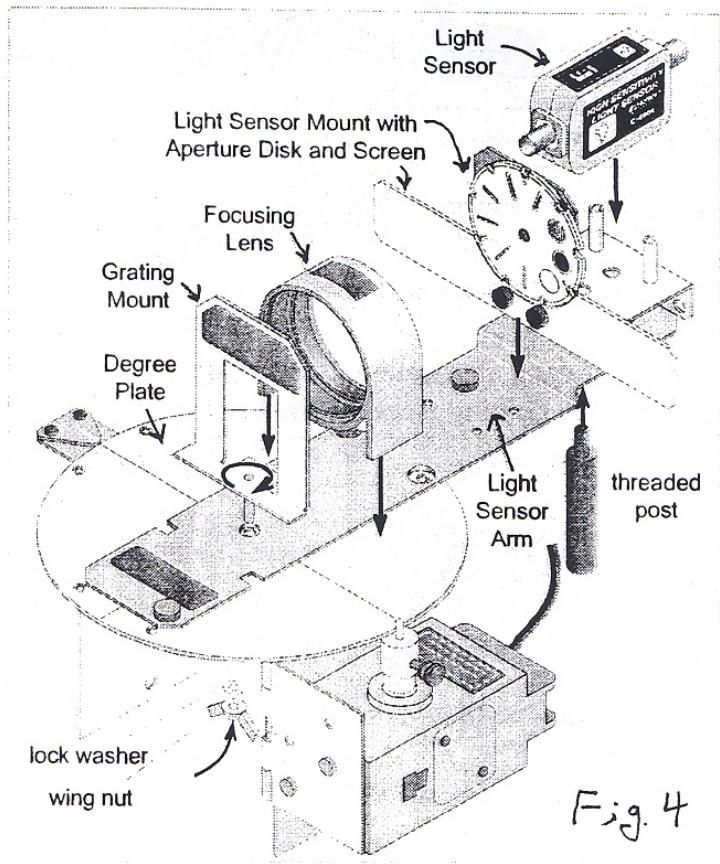


Fig. 4

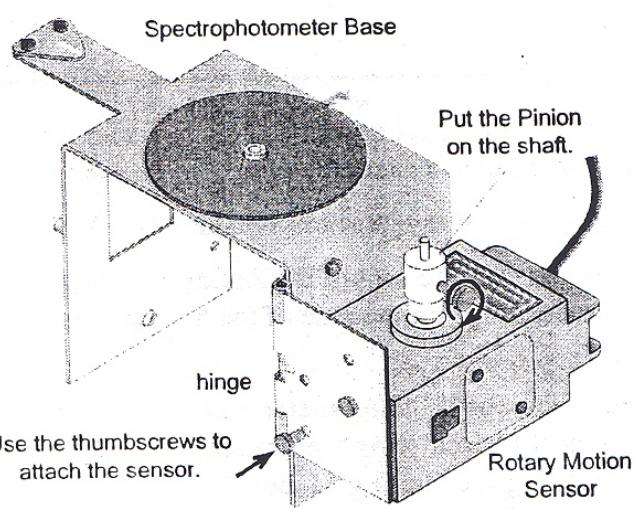


Fig. 5