

Experiment D-7

SPECTROSCOPY USING A DIFFRACTION GRATING MONOCHROMATOR

1. References:

1. J. Loader, *Basic Raman Spectroscopy*, Heyden Press, London (1970).
2. A. Yariv, *Quantum Electronics*, Ch. 23, John Wiley, New York (1967).
3. G. Herzberg, *Molecular Spectra and Molecular Structure*, D. Van Norstrand, New York (1954).
4. F. A. Jenkins, H. E. White, *Fundamentals of Optics*, 4th ed., Chapter 22-11, McGraw-Hill, New York (1976).
5. E. Hect, *Optics*, 3rd ed., Ch. 13.1.4, Addison-Wesley, Reading, Massachusetts (1987).
6. Instruction Manuals for diode laser, monochromator and photomultiplier (on file in lab & on website).
7. Various websites such as https://en.wikipedia.org/wiki/Raman_scattering
8. NIST website: <http://webbook.nist.gov/chemistry/>

2. Precautions:

- a) If you have not worked through the laser safety tutorial on the UI Division of Research Safety webpage, you may start from it now from the homepage: <http://www.drs.illinois.edu/> . Select the tab “Training” and choose *Laser Safety >> General laser Safety*. The training is about 20-30 minutes and worthwhile to learn as part of this lab as well as for any lab that you need to use lasers in the lab.
- b) **NEVER** look directly into the laser beam (even while wearing safety goggles). The diode laser is powerful (55 mW at 450 nm) and can damage your eyes. Use the safety goggles provided to protect yourself from stray reflections!
- c) Do **not** exceed 1000 V on the photomultiplier (PMT). This is its nominal operating voltage. Never expose the PMT to room light or to the direct laser beam when the PMT high voltage is on. It will be *destroyed!!!* When the laser is on, the monochromator can be set at 4500 Å only if:
 - (1) the laser light seen by the monochromator is scattered - not direct, and;
 - (2) the monochromator entrance slit is 20 µm wide or smaller. Do not exceed 1 mA anode current on PMT.
- d) If you open the monochromator top, do **not** touch any of the mirrors or grating optical surfaces. Remember the PMT voltage must also be *off* ! Very low level light

measurements like ours would also require to cover the PMT entrance area cover with black cloth to reduce the background noise when the monochromator box is open. .

3. Introduction

The equipment used in this lab – a computer-controlled diffraction grating monochromator and PMT used in single-photon counting mode enables one to carry out spectroscopic studies on essentially an arbitrary (emission) source of light, such as:

1. Emission lines from Sodium and Mercury discharge lamps.
2. Raman Scattering/Raman Spectroscopy.
3. Fluorescence Studies.
4. Absorption Studies.

4. Equipment:

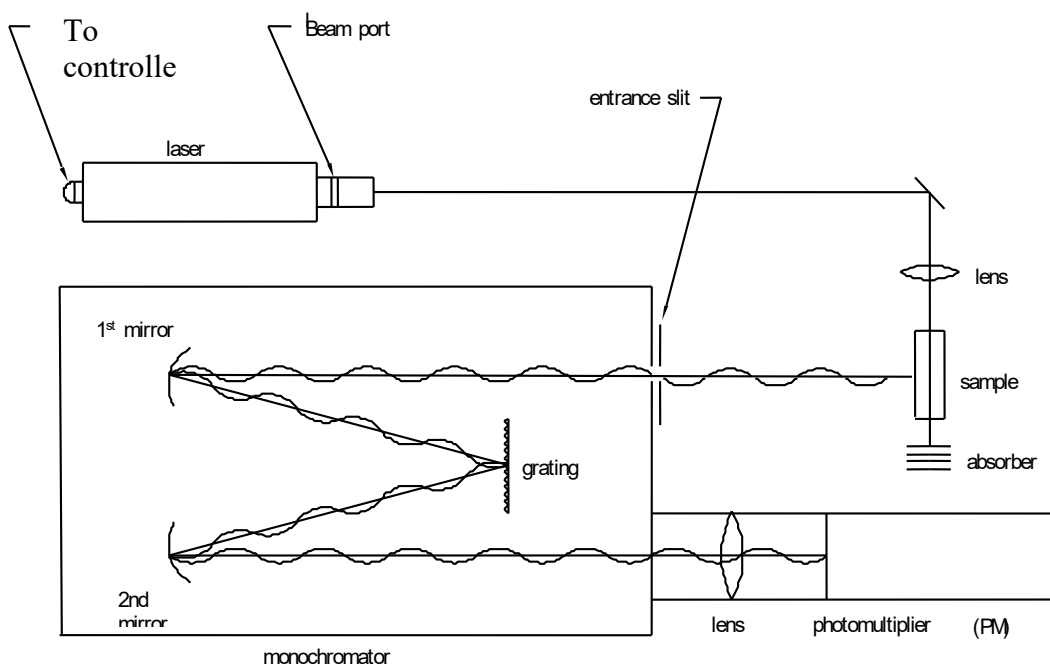


Figure 1. Optical Schematic Diagram. Monochromator dimensions: length of the slit = 2.5 cm; entrance slit to 1st mirror = 43.6 cm, 1st mirror to the grating = 32.3 cm, grating to the 2nd mirror = 32.3 cm, 2nd mirror to the PMT entrance slit = 43.6 cm.

See Figures 1 and 2. Also look up files on Pacific Photometric Instruments' Photomultiplier, Monochromator and Diode Laser. The photomultiplier is Centronic type 24249BA (SN: 7642-129). The PMT high voltage power supply is Pacific Photometric Instruments model 204 (SN: 350). The monochromator is McKee-Pedersen Instruments model # MP-1018B. The diode laser is Power Technology type IQ2C55 (450-80), model LDCU8/A652 (SN: 312088). Its output is rated as 55 mW at a wavelength of 450 nm. The counting electronics is home-made 32-bit scaler interfaced with a Windows PC using

National Instruments LabWindows/CVI software. The program can be accessed from the desktop icon *DGMC2.exe*.

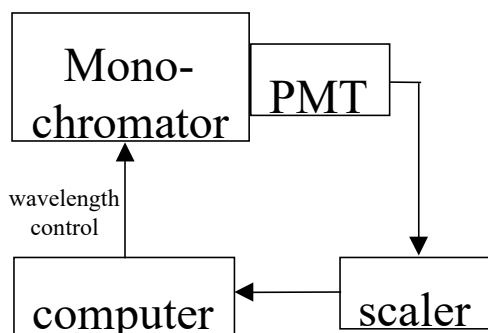


Figure 2. Basic Electrical Circuit

The operating mechanism of this experiment is simple. The monochromatic light ($\lambda = 4563\text{\AA}$) produced by the diode laser is scattered by the sample. Part of the scattered light from the sample enters the entrance slit of the monochromator through a lens which focuses the light. After passing through two mirrors via the grating, light energy pass through the photomultiplier (PMT) which produces a pulse for every $1/\eta$ photons that strike it. (η is the efficiency of the PMT, which depends on wavelength - see PMT manufacturer's specifications listed in the course folder).

The output of PMT is processed through a pulse shaping circuit after which one can view its negative going pulses on an oscilloscope. This signal is fed into a 32-bit 100MHz scaler. The scaler consists of a discriminator which rejects small pulses due to the noise. Then the scaler counts the number of pulses produced by photons received in a given period of time. The counting time is adjustable. The digital output of the scaler, which is the number of pulses counted, is sent to the computer and the program displays it as either counts or counts/sec (Hz).

5. Principles of The Raman Scattering Experiment:

The principle of Raman scattering is illustrated in Figure 3. When a photon interacts with an atom or a molecule in a solid, a liquid, or a gas, it may be scattered in two ways. If it is scattered elastically – also known as *Rayleigh scattering* - the scattered light has the same wavelength as the exciting photon. If it is scattered inelastically - *Raman scattering* - the scattered light has a different frequency ν_s than the incoming light. From Fig. 3,

$$h \nu_s = h \nu \pm h \nu_v$$

where h is Planck's constant and ν_v is the vibrational frequency of the scattering entity. The minus sign applies when the photon excites a vibration in the scattering medium giving rise to what is called the Stokes shift frequency. The plus sign comes about when the energy of a vibration in the medium is transferred to the scattered photon – anti-

Stokes shift. The origin of the Raman scattering is due to the induced dipole moment which is proportional to the strength of electric field. Refer to the references and formulate the Stokes and anti-Stokes frequencies by classical approach in your report. It should be emphasized that Raman scattering is a very weak process. It is about nine order of magnitude smaller than Rayleigh scattering.

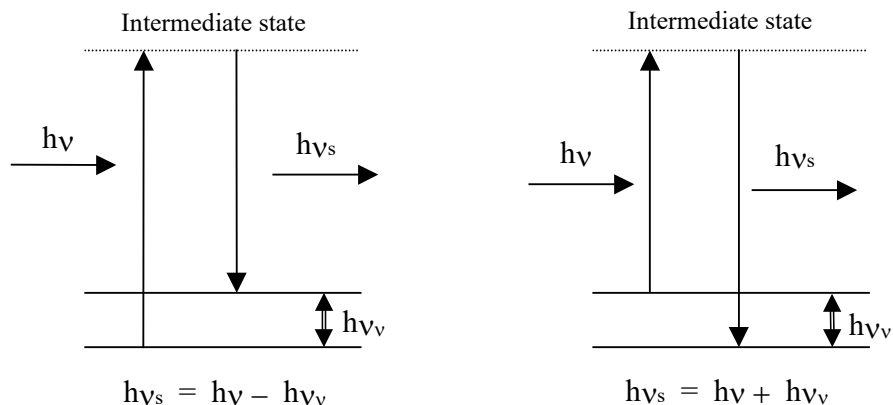


Figure 3. Schematic of Raman Scattering: Stoke (left) & anti-Stoke (right).

It should be noted that the population of the excited state would differ from the ground or lower state by $e^{\frac{-h\nu_v}{kT}}$. Here h = Planck constant = 6.626×10^{-34} joule-second, ν_v = frequency in Hz, k = Boltzman constant = 1.3806×10^{-23} J/K, T = Temperature in K. Note that $h\nu_v = \Delta E$ is the energy difference between the energy levels of the corresponding states.

6. The Raman Scattering Experiment:

- 1) Make sure the slit is open about 20 μm or less. Turn on the laser. It takes about 5 seconds to start. Note that the laser power supply unit is temperature-controlled to keep the wavelength and power from drifting. Make sure the laser or its power supply should not be covered by black cloth or have enough air-cooling when operating. The electronic control unit is on the relay rack. The top unit consists of 32-bit 100-MHz scaler counting electronics. Note that its power switch is located at the rear of the unit. The middle unit consists of stepper motor controller and computer data acquisition electronics (DAQ). Turn on the power of DAQ and then the counting electronics. The bottom unit of the relay rack is the photomultiplier (PMT) power supply. Turn on its power to "Standby" mode (or "0" Volt) without applying any voltage to the PMT tube yet. Remember, when operating the PMT, never exceed PMT supply voltage over $|-1000|$ Volt and PMT current must be always less than 1 mA.
- 2) The laser is aligned to produce vertical polarization (vertical to the optical table). To verify this, first measure the laser power and note it down. Now place the polarizer between the laser and the mirror and set it to 90° . Make sure it is the maximum power. Note this power. Next, turn the polarizer to 0° . This will be horizontal polarization, parallel to the optical table but perpendicular to the beam direction. Power should be minimum at this point. Record that power in your notebook. In case the polarizer readings

are not 0° or 90° for minimum/maximum power meter readings, the laser should be rotated to produce the respective power.

3) Alignment of the laser with the sample cell:

- a) See Fig. 1 for the basic optical path.
- b) The laser should pass through the sample cell at the height of the monochromator entrance slits.
- c) The distance between the sample cell and slit should be set such that the collecting lens will focus the light scattered in the sample onto the entrance slit. Since Raman scattering is very faint, we will use an acrylic rod to simulate the scattering process to show a visible band of scattered light. Place the amber acrylic rod at the sample holder. Cover it with the black sample cover so that the scattered light will fall on the graph paper of the alignment tool. This cover will act as a beam stop for the laser. A beam stop reduces dangerous scattering of the laser beam and helps reduce scattered light being admitted to the monochromator. You would see a straight line on the graph paper of the alignment tool. Focus the light on the graph paper by moving the lens holder back and forth on the rail. Note that the actual focal point should be located at the slit area. We use the amber acrylic for quick alignment but always with the alignment tool covered over the monochromator entrance port. Never allow the strong intensity from its reflections pass into the monochromator to prevent damage to the PMT.
- d) The walls of the sample cell will produce reflections back along the original laser path. For safety, the laser beam area is cordoned off by black card-boards. This will mask stray room light and reduce the scattered laser light. Keep the card-board on the top since room light can pass through the black cloth alone.
- e) If you are not sure about reflections from laser beam, please ask your TA! You may also find information on hazardous reflections from laser beam when you take the online laser safety tutorial. Remember, reflections are dangerous to everyone else in the lab as well.
- f) Turn on the oscilloscope. Its initial settings should be 100 mV/div (X), 10 ns/Div (Y), Normal (Trigger).
- g) Set the slitwidth to 20 μm if you have not done so.
- h) You may start the program, DGMIC. The program initializes when you click at the "INIT DAQ" button. You will be prompted to input the low limit, high limit and current value of wavelength. Since the exact laser wavelength is very close to 4563 Å, you may select LO = 4550 Å and HI = 4575 Å. The computer will offset the recorded value 11.7 Å from the dial reading to calibrate the known offset of the monochromator. This initialization needs to be done only once before you run your experiment. The program is self explanatory and a few sample runs will be required to familiarize for efficient operation. Note down the current wavelength reading at the monochromator. Basic settings for the program are the followings. The boundary settings for the upper and lower wavelengths to scan (Change Monochromator Lo/Hi W-limit), stepper motor speed (Change W/SM Step size), stepper motor pulse width (Change SM Pulse Width), optical signal collection time (Change PMT Gate Time). Use "START W-SCAN" to start the data collection. At this time we do not use the "START T-SCAN" which is reserved for time scanning in future experiments. You may need to save your data after a scan so that you may use other programs such as *Origin* to analyze the data.

- i) Fill the *quartz* sample cell with Benzene (do not include bubbles). Whenever handling any chemical material, always consult the MSDS (Material Safety Data Sheet) to understand the hazards and what to do if things go wrong. Ask your TA for the *proper* quartz sample cell (we have a limited number of quartz cuvettes and they are very expensive). Most other samples can be used in the plastic sample cells located at the sink area.
 - j) Have a flash light handy so you will not bump in the dark. Now turn off the room light or carefully cover the setup area with black cloth.
 - k) Turn on the PMT power to -1000 Volt. Remove the alignment tool from the slit aperture.
 - l) We would like to calibrate the laser wavelength and verify that the laser beam provides adequate scattering light for our spectrum. Take a short scan between the range selected (4550\AA to 4580\AA) with $\frac{1}{4}\text{\AA}/\text{step}$. Use default settings for other parameters. During the scan, observe the oscilloscope signals. The strongest signal should be related to negative going pulses of about 800 mV and 20 ns FWHM (full width half maximum). If you see oscillatory sine waves or count rates in millions, they are probably caused by external interference rf signals, eg. TV tower. You may need to retry or reset the amplifier in that case. Ask your TA for help if the problem persists. Usually disconnecting the BNC connector at the scope eliminates the interference problem, but then you may not observe the signal on the scope. The scope signal can be viewed on the browser using the IP address and save for your report.
 - m) Determine the laser peak wavelength from this scan. At the peak wavelength, you should read maximum photon counts or count rate in Hz. If the peak count rate is in several hundreds Hz or more while the background is about 10 or less, signal to noise ratio would be close to 40 dB. This will assure us that it is aligned. Otherwise you may need to align the collecting lens. As described earlier, the beam is along the z-direction into the monochromator's slit; laser beam strikes the sample in x-direction (parallel to the optical table) from the diode and mirror system; and then the y-direction would be perpendicular to the optical table. To align, set the monochromator position to that wavelength using the button "Go to W = W-User". Manually move the lens along the beam in z-direction keeping it also perpendicular to the beam. You may want to watch the scope or take a single manual scan by clicking at PMT SCAN button to verify your proximity to optimum alignment. For across the beam (i.e. x-direction), move the micrometer (located at the base of the lens on the rail), typically 0.005" at a time, when closer to the peak.
 - n) After the best aligned position is obtained, cover the monochromator aperture with the alignment tool. Now move the monochromator starting wavelength to 4650\AA to proceed with the experiment.
- 3) Some of the important benzene peaks in cm^{-1} (relative intensity in bracket) are (see Ref #1): 406 (7), 606 (38), 781 (2), 825 (4), 850 (5), **992 (100)**, 1180 (31), 1584 (17), 1605 (17), 2618 (2), 2949 (5), 3047 (12), 3063 (29). Note that 992 cm^{-1} corresponds to 4782\AA .
- 4) Open the slit width to $200\text{-}300\mu$ and record it in your notebook. Remove the alignment tool from the monochromator aperture.

- 5) Scan the spectrum at 2\AA per step from 4650\AA to 5350\AA . After the scan finishes, observe the recorded spectrum and note the peaks. Always save your data with 'txt' extension after every scan.
- 6) Install the polarizer (marked H-polarization) between the sample and the monochromator entrance. Set the polarizer to $P=90^\circ$. Re-scan from 4650\AA to 5350\AA with the polarizer (vertical polarization). Note that the polarization state of the laser beam is vertical or in the y- direction. This will allow to pass any scattered light that is vertically polarized. Next, rescan with polarizer set to $P = 0^\circ$. Note that some of the peaks may be suppressed due to the polarization state of the scattered photons.
- 7) Cover the entrance slit of the monochromator with the alignment tool and move the wavelength to 3400\AA . Remove the alignment tool and scan the spectrum to 4425\AA and thus record the anti-Stokes lines for horizontal polarization. Next, change the polarizer to 90° and rescan for Stokes lines.
- 8) Remove the polarizer and scan the spectrum from 3400\AA to 4425\AA . This will be the scan without polarizer.
- 9) Cover the monochromator entrance with the alignment tool. Move the monochromator to 4700\AA . Remove the alignment tool. Adjust the slit width, scan step and counting time to resolve the two peaks of the spectrum at 4908\AA and 4921\AA . What effect does the slit width have on the spectral resolution? How does the counting time affect your signal to noise?

Analysis of Results and Questions:

- 1) Calculate the Stokes and Anti-Stokes shifts you observed (give results on units of cm^{-1}) and the intensity of the lines relative to the highest peak which will be 100. Compare your results to published data and comment.
- 2) Calculate the depolarization factor from your data for the various lines, compare and comment. Note the depolarization factor, ρ , is the ratio of counting rates of a peak at horizontal polarization (I_\perp) to vertical polarization (I_\parallel) i.e. $\rho = \frac{\rho_\perp}{\rho_\parallel}$.
- 3) Note the difference in the spectra obtained with the exciting light polarized vertically and horizontally. Comment on the possible reasons for these differences.
- 4) (a) At what wavelength would the most intense line in the spectrum have appeared if the exciting laser had been red He-Ne ($\lambda = 6328\text{\AA}$)?
 (b) If the two lasers were of the same intensity, what would have been the relative intensity of the most intense line observed with the He-Ne as compared to this line observed with (1) the diode laser and (2) He-Cd laser ($\lambda = 4416\text{\AA}$)?

- 5) Were the Stokes or Anti-Stokes lines stronger? Why?
- 6) Calculate the spectral width in Å and in cm^{-1} that the monochromator allows to pass when the slit opening is 200-300 μm .
- 7) One of the vibrational modes of the Benzene molecule is a breathing mode where the C-C bonds all stretch and contract simultaneously. Another mode is one which the C-H bonds stretch and contract. Which mode would you expect to have the largest Stokes shift. Why?
- 8) CCl_4 and SiCl_4 are molecules of similar geometry (identical symmetry). One would therefore expect that their modes of vibration are similar. What similarities and differences would you expect to find in the Raman spectra of these molecules?

7. Further options to explore for extra credit (may need extra time):

1) Other liquids:

- a) Repeat the procedure for other liquids in the lab such as ethanol (or other alcohol). Mix the liquids in known proportions and observe the spectra. Are the peak intensities proportional to concentration? What are the detection limits of one liquid in the others?
- b) Silicon nanoparticles in isopropyl or tetrahydrofuran may be used to explore the nature of the scattering.

2) Raman spectra of a solid

Ask your instructor for ideas on solids and procedures to use, such as KDP, graphite, graphene, silicon, copper, stainless steel etc.

3) Fluorescence Spectroscopy

You can measure the fluorescence spectrum of whatever fluorescent material (such as the wavelength shift fiber). You may put the material on the sample holder, also use the diode laser to illuminate it, and scan the spectrum of the fluorescence. Since usually the fluorescence is much stronger than Raman scattered light, you should reduce the slit width to much smaller value (such as 40 μ) .

4) Emission Spectroscopy

You can also measure the emission spectroscopy of a Sodium or Mercury lamp. Just put the light source in front of the monochromator and scan. Don't exceed 40 μ on the slit width. To see the more detailed shape of sharp lines, you may use smaller scan step. (The smallest step is 0.25 Å).