D7 - Spectroscopy Using a Diffraction Grating Monochromator

Andrew Kim[1*†] and Kendall Graff[1†]

[1]Department of Physics, University of Illinois Urbana Champaign, Champaign, USA
[*]Writing Student. NetID: andrewk3
[†]These students contributed equally to this lab.

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Abstract

The purpose of this experiment was to observe Raman spectroscopy through the use of a diffraction grating monochromator. We were to observe the emission lines of Stokes and Anti-Stokes shift at vertical, horizontal, and no polarization. We observed that our Stokes shifts were rather accurate to published literature, but our Anti-Stokes shifts were erratic and not highly accurate.

1 Instruments and Apparatus

This experiment had a single set up with two portions: a physical system and a digital system. The physical system began with a diode laser emitting its beam into a lens that directed the beam into a sample, which scattered light into a diffraction grating monochromator. The monochromator selected for specific wavelengths before directing the selected light into a photomultiplier (PMT). The layout of the physical system is shown below in Figure 1:

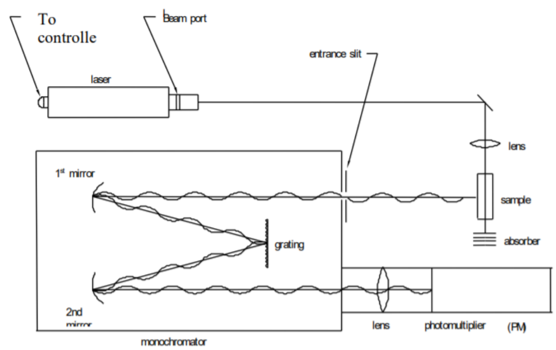


Figure 1: Diagram of the physical system. Monochromator dimensions: length of the slit=2.5 cm; entrance slit to 1st mirror=43.6 cm, 1st mirror to the grating=32.3 cm, grating to the 2nd mirror=32.3 cm; 2nd mirror to the PMT entrance slit=43.6 cm. Note that the lens was after the sample in the set-up used. Figure taken from the lab document.

The monochromator works by directing the incident light into a diffraction grating, which selects for specific wavelengths of light through diffraction. The monochromator can select for a range of wavelengths over several steps between a minimum and maximum wavelength. The monochromator does this by rotating the grating, changing the angle of incidence and therefore the diffracted wavelength that comes out of the monochromator. The function of a monochromator can be seen in Figure 2:

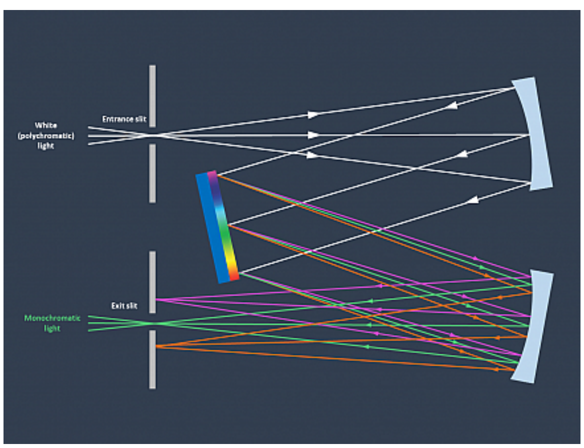


Figure 2: Diagram of a monochromator. The blue panel is the diffraction grating that rotates to select a specific wavelength. Photo taken from Berthold Technologies webpage.

The digital system mainly processed and presented the data the PMT collected. It consisted of a department-made 32-bit scaler interfaced with a Windows computer using the National Instruments Lab Windows/CVI software. The program was accessed as DGMC2.exe. Figure 3 is a diagram of the digital system.

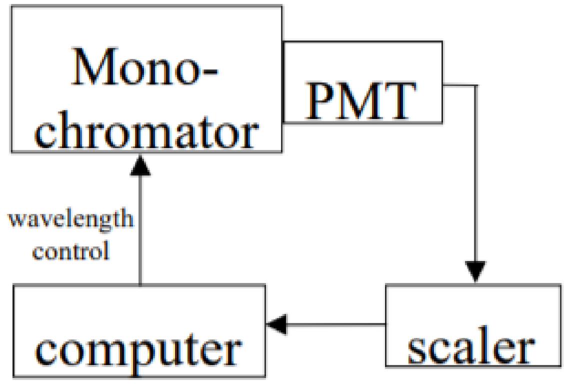


Figure 3: Diagram of the digital system. This shows the connections between the different collection devices. The computer can control what wavelengths the monochromator selects. Figure taken from the lab document

2 Procedure

The initial section of this lab was set-up. After turning everything on, we measured the laser's power at no polarization, vertical polarization, and horizontal polarization to make sure that the laser was vertically polarized. We then used an amber acrylic rod as a sample to set the lens and align the scattered light with the opening of the monochromator.

Now we actually start working with data collecting and the monochromator. We start by initializing the monochromator by having it do a test run from 4550 Åto 4575 Åwith a slit width of 24 μ m. This calibrates the monochromator to the laser's wavelength of around 4563 Å. We then fill a sample with Benzene and do another test run to check if we are providing adequate enough scattering. After determining a peak wavelength for the scatter at 4564.4 Å, we are ready to begin taking our data.

The data collection can be split up into two sections: the Stokes scans and the Anti-Stokes scans. The Stokes scans collect the emissions from the Stokes shifts around the wavelengths 4650 Åand 5350 Åwith a step of 2 Åand a slit width of 400 μ m. The Anti-Stokes scans collect the emissions from the Anti-Stokes shifts around the wavelengths 3400 Åand 4425 Åwith the same step and slit width as the Stokes scans. Both of these collections consist of 3 separate scans at different polarizations of the exciting light: one unpolarized, one at a polarization angle of $\theta = 90^o$ (vertical polarization), and one at a polarization angle of $\theta = 0^o$ (horizontal polarization).[1]

Relevant Equations

There are two directly relevant equations: the calculations of the Stokes and Anti-Stokes shifts and the calculation of the depolarization factor. The Stoke shift comes from the equation for Raman

[1] I have outlined steps 1-8 from the lab document here. We did not have enough time in the lab to complete step 9 and so therefore it has not been included in this report.

scattering:

$$h\nu_s = h\nu \pm h\nu_v \tag{1}$$

Where ν is the frequency of the laser, ν_s is the frequency of scattered light, also called the Stoke/Anti-Stoke shift frequency, and ν_v is the vibrational frequency of the scattering entity. The Stoke shift happens in the negative case and the Anti-Stoke shift happens in the positive case, as shown in Figure 4:

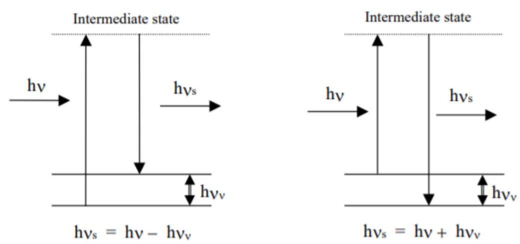


Figure 4: Schematic of Raman Scattering: Stoke (left) and Anti-Stoke (right). Taken from the lab document.

The equation for the depolarization factor is rather simple:

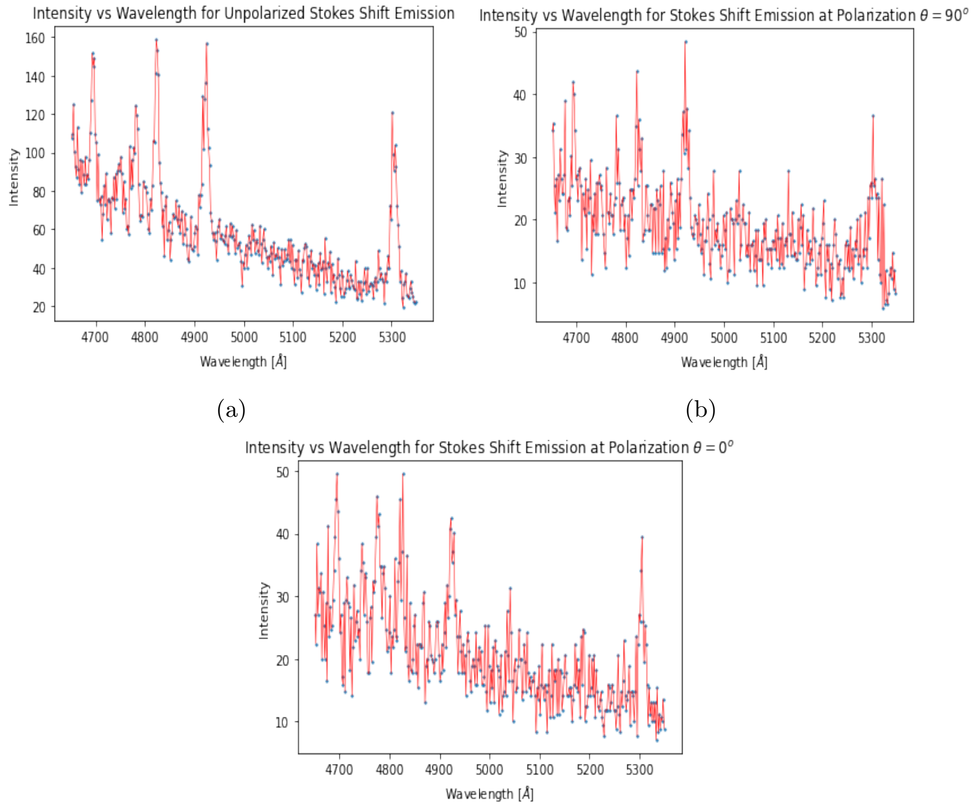
$$\rho = \frac{\rho_\perp}{\rho_\parallel} \tag{2}$$

Where $\rho_\perp$ is the counting rates of a peak at horizontal polarization and $\rho_\parallel$ is the counting rates of a peak at vertical polarization.

3 Results and Discussion

Stokes Shift

The spectrum scan for the Stokes shifts produced the following graphs:



(a) (b) (c)

Figure 5: The graphs generated by the data for the Stokes Shift Emission scans. a is the unpolarized emission, b is the vertically polarized emission, and c is the horizontally polarized emission.

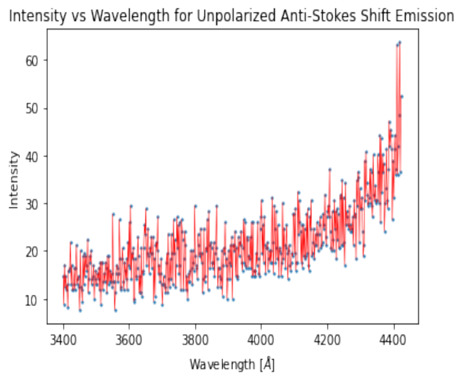
Calculating the Stokes shift is simple, it uses the negative version of the Raman Scattering equation solved for $\nu_v = \nu - \nu_s$. Using the peak of the graph at 4823.10 Å, the Stokes shift for the unpolarized emission is 1181.85 cm^{-1}. For the vertical and horizontal emissions, who's peaks are at 4921.15 Åand 4695.15 Å, respectively, Their Stokes shift is 1594.95 cm^{-1} for the vertical and 616.83 cm^{-1} for the horizontal. These are about 10 cm^{-1} off the values obtained in other literature.

The relative intensity of the three highest emission lines for the unpolarized emission at wavelengths 4693.15 Å, 4823.10 Å(the peak), and 4925.10 Åare: 95.5, 100, and 98.9. For the vertically polarized emission lines at wavelengths 4693.15 Å, 4823.10 Å, and 4921.15 Åthe relative intesities are: 86.6, 90.2, and 100. For the horizontally polarized emission lines at wavelengths 4695.15 Å, 4775.15 Å, and 4821.15 Åthe relative intesities are: 100, 92.9, and 91.7.

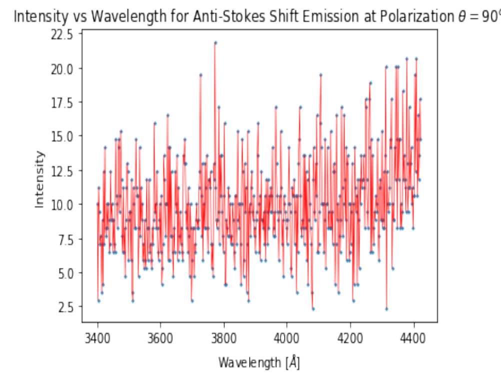
We calculated the average depolarization factor by calculating the depolarization factor for every wavelength and then taking the average. The average depolarization for the Stokes Shift Emission was $\rho = 1.140899$. Taking specific depolarization factors at the wavelengths 4695.15 Å, 4823.10 Å, 4921.15 Å, 5303.15 Å, and 5305.15 Ågave depolarization factors of $\rho = 1.2353$, 0.67567, 0.84146, 0.93548, and 1.5581 for the respective wavelengths. The general trend among both these factors and the average is that they are above 0.75. This means that the emission was depolarized and that the source vibration was anti-symmetric.

Anti-Stokes Shift

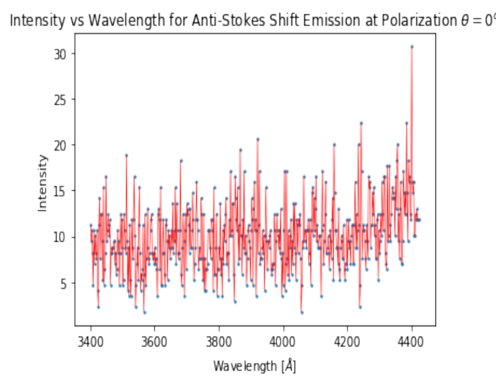
The spectrum scan for the Anti-Stokes shifts produced the following graphs:



(a)



(b)



(c)

Figure 6: The graphs generated by the data for the Anti-Stokes Shift Emission scans. a is the unpolarized emission, b is the vertically polarized emission, and c is the horizontally polarized emission.

The Anti-Stokes shift uses the positive version of the Raman Scattering equation solved for $\nu_v = \nu_s - \nu$. The unpolarized peak is at 4419.15 Å, so its Anti-Stokes shift is 713.38 cm^{-1}. For the vertical and horizontal emissions, who's peaks are at 3773.20 Åand 4401.20 Å, respectively, Their Anti-Stokes shift is 4587.30 cm^{-1} for the vertical and 805.67 cm^{-1} for the horizontal. The horizontally polarized frequency is close to a frequency in the literature, but both the unpolarized and vertically polarized frequencies aren't really found in the literature.

The relative intensity of the three highest emission lines for the unpolarized emission at wavelengths 4411.2 Å, 4419.15 Å(the peak), and 4423.15 Åare: 99.1, 100, and 82.4. For the vertically polarized emission lines at wavelengths 3773.20 Å(the peak), 4379.20 Å, and 4409.15 Åthe relative intesities are: 100, 94.6, and 94.6. For the horizontally polarized emission lines at wavelengths

4243.15 Å, 4387.20 Å, and 4401.20 Å(the peak) the relative intesities are: 73.1, 73.1, and 100. A lot of these ended up giving the same intensities, which is odd to say the least.

It's hard to directly grab peaks, so the specific depolarization factors will come from using each of the polarizations' peaks (3773.20 Å, 4401.20 Å, 4419.15 Å), 4379.20 Åline, and the 4423.15 Åline. The values came out to (in ascending order of wavelength) $\rho = 0.405405$, 0.6, 2.88889, 0.869565, and 0.8. The average came out to $\rho_{average} = 1.14612$. This would indicate the same thing as the Stokes emission: the emission was depolarized and the source vibration was anti-symmetric.

General Observations and Conclusion

The vertically polarized emission spectra for the Stokes shift emission seems to be less noisy than that of the horizontally polarized emission spectra. This could be due to the laser's original vertical polarization carrying through to the emission lines, or it just be that a lot of the noise is horizontally polarized. However, for the Anti-Stokes shift, the vertically polarized emission spectra is much more noisy than the horizontal. There could be a theoretical answer to this conundrum, but I believe it is experimental error. The vertical Anti-Stokes shift scan was done while the system wasn't fully shielded from outside light, so it could be that some outside light interfered with the collection.

The Stokes lines were generally stronger than the Anti-Stokes lines. This is because the Stokes shift starts at the ground state while the Anti-Stokes shift starts at an excited state. Because particles at rest are more likely to be in their ground state than any excited state, it makes sense that emission from that ground state would be more common than emission from an excited state.

Outside of the aforementioned lack of shielding during the vertically polarized Anti-Stokes shift scan, This student does not think that there were many errors during the experiment. However, there is always a possibility of outside light entering the system or rf signal interference. It is also possible that the monochromator was not calibrated properly, which could be a possible explanation for the error by 10 in the calculation of the Stokes shifts.