Raman Spectroscopy

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Abstract

In this report, I examine the Raman spectrum by investigating the shift in the wavenumber for the Silicon and Toluene. The resultant spectrum produced is verified by the available articles published on the Raman spectrum of Silicon and Toluene. This spectrum is the fingerprint of the material itself.

Contents

1 INTRODUCTION

Raman Spectroscopy is a very unique method typically used to determine vibrational modes of molecules, although rotational and other low frequency modes of systems may also be observed. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. It was discovered by Sir Chandrashekhara Venkata Raman in 1928, it was a very famous paper he published in the "Indian Journal of Physics" titled,*"A New Radiation"* [7]. This research got him the Nobel Prize in Physics in 1930, just within two years of his publication. The hidden story also revolves as Sir C.V. Raman didn't have money to buy a spectrograph, thus he sought funding request from Mr. G.D. Birla (Indian businessman) and he said to him that if he gives him funding to buy spectrograph then he will bring the Nobel Prize in India within a year. Hence, Mr. Birla gave him the money, but now Raman was nervous and hence, he wanted to make sure that he is the first one to report these findings. Thus, he sent his first draft to Nature via the expensive mode of postal service known as Telegram. He then also wrote several letters to many notable Nobel laureates, such as Rutherford, Bohr and others stating that,

> *"I believe this is a Nobel Prize winning discovery, you must nominate me for the Nobel Prize"*
>
> — *Sir C.V. Raman* [4]

He also called upon a press conference on February 28, 1928, to report his discovery, which was published in newspapers on next day with articles written in the form that, Raman has discovered an important phenomenon and this might lead him to win a Nobel Prize. Thus, today in India February 28 is celebrated as National Science Day. [4]

In this whole process, Arnold Sommerfeld was a key person to play a role in getting Raman the Nobel Prize. He himself came to Calcutta, India (currently known as Kolkata) to verify if the discovery was indeed true and recognisable enough to be given Nobel Prize. Once, he was convinced, he along with several other Russian scientists recommended Raman's name for the Nobel Prize in Physics. After which, Raman received the Nobel prize winning telegram on November 15, 1930. During a speech at the Royal Society, Lord Rutherford said,

> *"The Raman Effect must be ranked among the best three or four discoveries in exeprimental physics".*
>
> — *Lord Ernest Rutherford* [4]

1.1 Raman Spectroscopy

When light is incident on molecules, the light is scattered by molecules. Most of scattered light has the same frequency with incident light but some fraction of light have different frequency

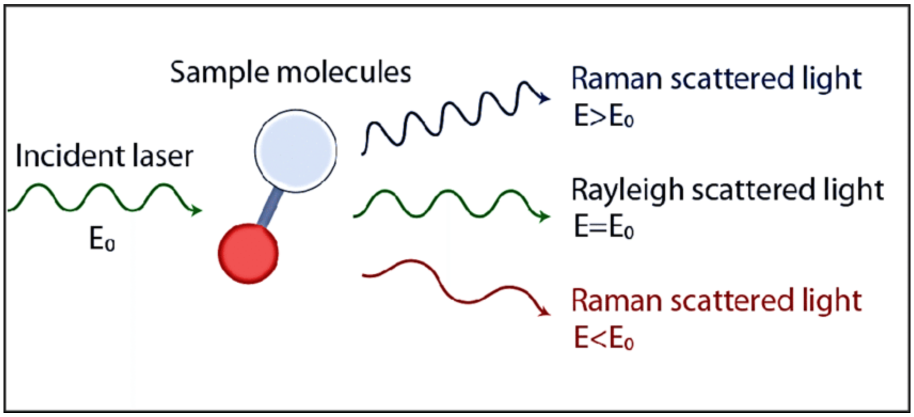


Figure 1: Scattering of light due to a molecule. [1]

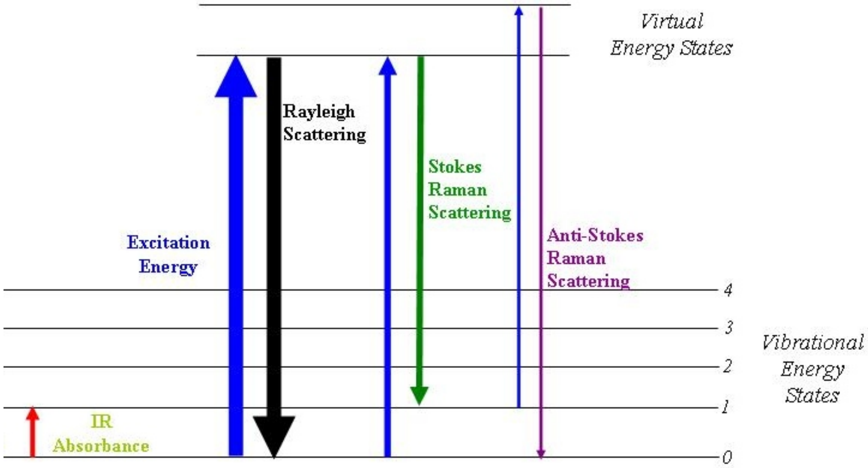


Figure 2: Energy-level diagram showing the states involved in Raman spectra. [2]

due to interaction between oscillation of light and molecular vibration. The phenomenon that the light is scattered with frequency change is called Raman scattering. Because this frequency modulation is specific to molecular vibration and phonon in crystal, it is possible to analyse the composition of material or crystal lattice information by analysing the spectrum of Raman scattered light. This analysis method is Raman spectroscopy. [6]

The Raman shift in the sample can be calculated by an equation,

$$\Delta\nu = \left(\frac{1}{\lambda} - \frac{1}{\lambda_i}\right) \tag{1}$$

where, $\lambda = 632.8$nm, i.e., the incident monochromatic light's wavelength and λ_i are all wavelengths we calculated through the conversions of pixels using the calibration Equation 2.

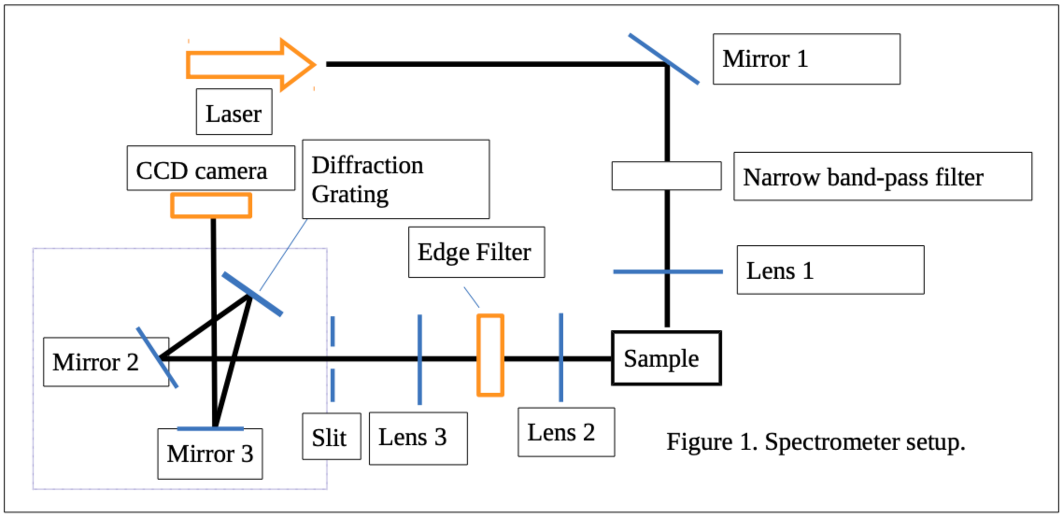


Figure 3: Set up for the experiment

1.2 Application of Raman Spectroscopy

Raman spectroscopy is used in chemistry to identify molecules and study chemical bonding and intramolecular bonds. Because vibrational frequencies are specific to a molecule's chemical bonds and symmetry (the fingerprint region of organic molecules is in the wavenumber range 500-1500 cm^{-1}), Raman provides a fingerprint to identify molecules. For instance, Raman and IR spectra were used to determine the vibrational frequencies of SiO, Si_2O_2, and Si_3O_3 based on normal coordinate analyses. Raman is also used to study the addition of a substrate to an enzyme [2].

2 EXPERIMENTAL PROCEDURE

1. A typical sequence of initial setup steps is:
    (a) Turn ON the main power switch; the laser should turn on after a few seconds. The shutter on the front of the laser can be used to temporarily block the beam while making adjustments. Whenever the laser is on, wear laser safety goggles.
    (b) Turn ON the CCD power. Start the Kestrel software and make sure is starts normally; any startup errors would indicate a problem with computer-to-camera communications. Set Spectroscope wavelength to 654 nm.
    (c) Adjust and align Mirror 1 and Lens 1 to bring the light from the laser to the sample chamber. Lenses 1 and 2 are embedded in the walls of the sample chamber and will

not require any adjustments.

(d) Place a bright scattering sample (a small piece of laboratory tissue works well) onto the sample holder and move it into the laser beam, at grazing incidence. Slide the edge filter aside. Using the scattered light, adjust Lens 3 until the laser light is focused and centered on the slit. This is probably best done in darkness.

The next few steps perform the spectroscope calibration. As you replace the bright white sample with metallic or silicon samples, the amount of scattered light is greatly diminished, and the optical adjustment must be performed in complete darkness after your eyes had a chance to adjust. Small final adjustments of focus (Lens 3) and sample position and orientation will need to be performed slowly and will be difficult to see.

(a) Slide aside the narrow band-pass filter.
(b) Hang a small mirror attached to a wire from the sample holder, at grazing incidence, so that it reflects an extremely small amount of scattered light into the slit. Make final focusing and positioning adjustments to make sure the bright spot is tightly focused and is directly on the slit.
(c) Set exposure time to 10s. Turn off the computer monitor as you click the mouse to run the program so that the only source of light in the room is from the laser.
(d) When you hear the shutter closing on the Spectroscope, or when you have waited an appropriate amount of time, turn the monitor back on to view the results. There should be several significant peaks due to helium discharge in the laser.
(e) Now place a blocker directly in front of the slit and run again using the same exposure time. This will be the background spectrum and must be subtracted from the spectrum found in the previous step. You may need to turn the lights back on, or to use a flashlight, to position the blocker correctly. Refer to the Appendix for information on how to subtract spectra.
(f) Repeat the previous steps until helium discharge peaks are clearly visible. Your spectrum should look similar to the one shown below.
(g) Calibrate Kestrel software by matching the peaks to corresponding wavelength values in Table 1. Refer to the Appendix for information on how to calibrate Kestrel software.

2. Toluene

   (a) Inside the fume hood, fill a small glass vial with toluene and place it inside the vial holder. Position the vile holder on the sample holder so that the laser beam enters the bulk of toluene, and the scattered light hits Lens 2.

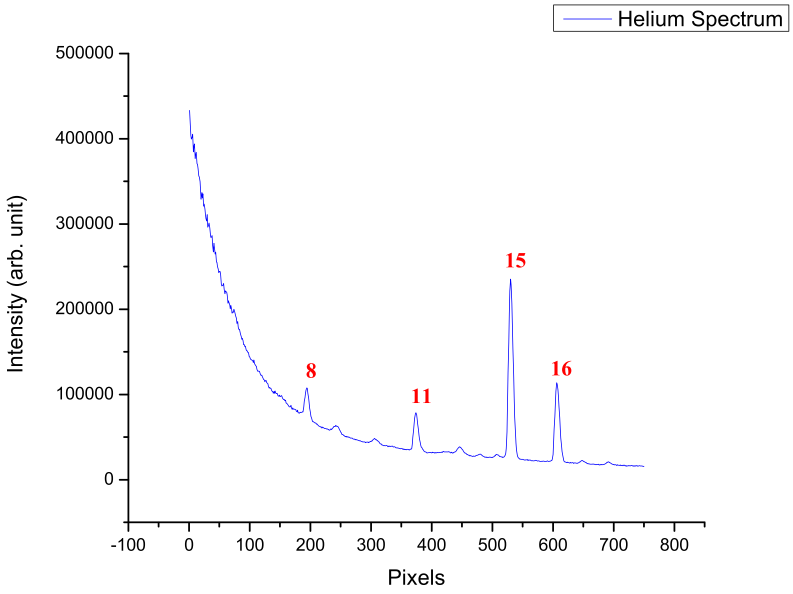


Figure 4: Incident laser light (Helium -He) Spectrum

(b) Select an appropriate exposure time which and turn off all the lights (including the computer monitor) and acquire a spectrum. Repeat, adjusting the exposure time as necessary, until a satisfactory, clearly visible peak is obtained.

(c) Save this spectrum (use a memory stick to transfer the files to your account on the regular workstation).

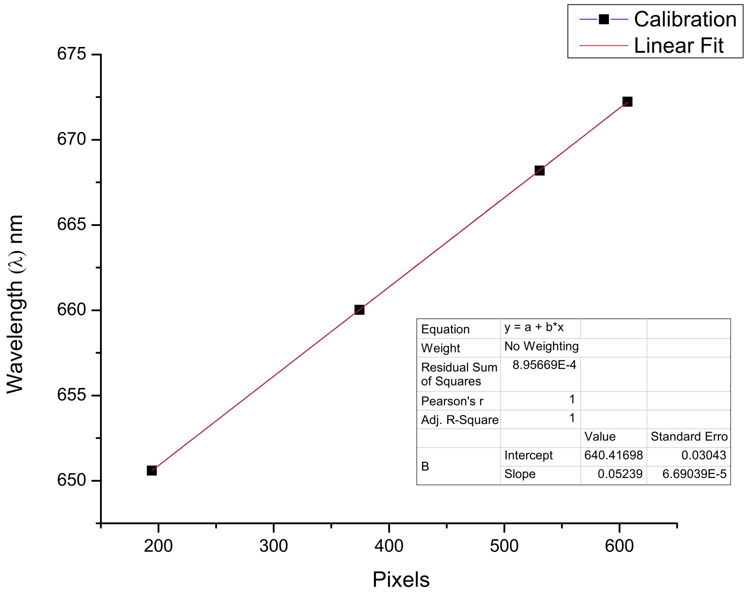
3. Silicon

   (a) Using a small amount of vacuum grease press a sample of silicon to the sample holder. Adjust the sample for grazing incident of the laser beam.

   (b) Select an appropriate exposure time (which should be significantly longer than for toluene), turn off all the lights (including the computer monitor), and acquire a spectrum.

3 DATA ANALYSIS

The Helium (He) spectrum i.e., the spectrum generated by the incident wave of monochromatic light of wavelength $\lambda = 632.8$nm. Using the peaks generated in the He spectra, refer to the Figure 5. We plot the calibration curve and generate the calibration equation through the linear fit. The equation generated through linear fit correspondingly produces, slope and an intercept



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	8.95669E-4		
Pearson's r	1		
Adj. R-Square	1		
		Value	Standard Erro
B	Intercept	640.41698	0.03043
	Slope	0.05239	6.69039E-5

Figure 5: Calibration curve

on y-axis, thus the produced equation is,

$$\lambda = SLOPE(Pixels) + INTERCEPTONY - AXIS \tag{2}$$

Now, keeping the calibration equation 2 in mind we can now manipuate the data obtained from the Silicon and Toluene.

Later we find the wavenumber of the incident light's wavelength and subtract it from the every wavenumber to get the shift at every point. Thus, using the 1 mentioned in the section 1.1. Then when we plot a graph of ν vs Intensity, we can directly analyse the Raman shift corresponding to respective molecular vibration. For example, in case of Silicon the Raman shift can be plotted as,

4 DISCUSSION AND CONCLUSION

In conclusion I would like to make a note saying that, Raman spectroscopy is indeed a very unique detection method which can be used to identify the molecular vibrational modes, resulting in fingerprinting them. This can be used in various other regimes as qualitative analysis of unidentified materials.

Also, the appearance of the unusual spikes in the spectra of silicon and toluene is due to the

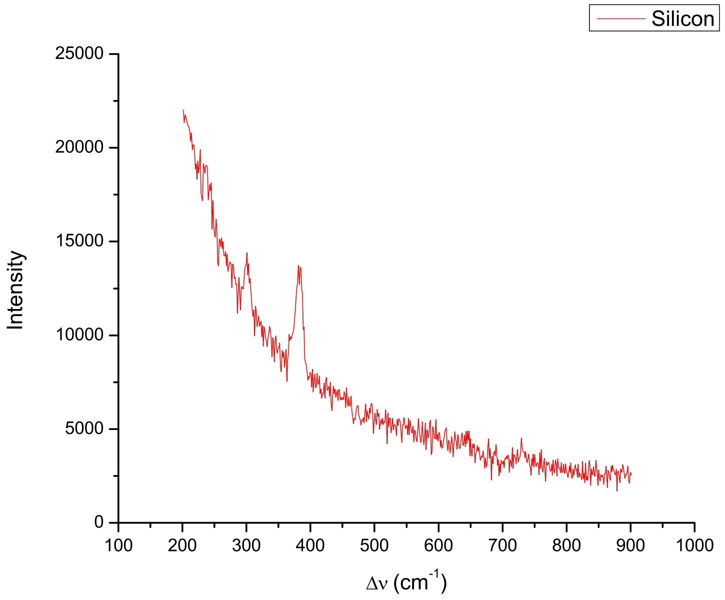


Figure 6: Silicon Raman spectra

cosmic ray events, which discharges and charges the unit cells. These unit cells already have a certain voltage which was a result of the data accumulation, but due to the interference of the cosmic rays, they tend to mend the voltage in the unit cell in an unusual way. Thus, resulting in the appearance of the sudden spike in the data [3]. Thus, to reduce this I deployed the algorithm (refer Appendix A), which in turn manipulates the spikes and replaces it with the anticipated data [5].

A APPENDIX

A.1 Algorithm

The following algorithm was implemented to eliminate the random spikes in the Silicon and the Toluene spectra. The code is written in python.

- For Silicon Spectrum

```
import matplotlib.pyplot as plt
import pandas as pd
data = pd.read_csv('Si_ramanspec.csv')
intensity_val=data["intensity"]
for i in range(len(intensity_val)): #start the for loop for the
execution
if i==0:
data=data.drop([i]) # to eliminate the first value of the data
elif i+1==len(intensity_val): #to consider the last value of the data
continue
elif i<=150 and not((intensity_val[i]) <=
(intensity_val[i-1])*1.15 and
(intensity_val[i]) >= (intensity_val[i-1])*0.85):
data=data.drop([i])
# to remove several continous peaks due to cosmic ray event
elif i>150:
mean = (abs(intensity_val[i-1]) + abs(intensity_val[i+1]))/2
if(abs(intensity_val[i])<mean or
abs(intensity_val[i])<(mean+mean*0.01) or
abs(intensity_val[i])<(mean-mean*0.01)):
# to keep the data without the cosmic event peaks
continue
else:
data=data.drop([i]) #eliminate the cosmic event peaks

plt.rcParams['figure.figsize']=(40,20) #to manipulate the graph size
plt.plot(data["delta v"], data["intensity"]) #to plot graph
plt.xlabel('delta v')
```

```
plt.ylabel('Intensity (a.u)')
plt.savefig('Silicon_graph.eps', format='eps', dpi=1600)
```

- The following code is for Toluene:

```
\footnotesize

import matplotlib.pyplot as plt
import pandas as pd

data = pd.read_csv('Toluene_math_600s.csv')
plt.plot(data["delta v"])
intensity_val=data["intensity"]
for i in range(len(intensity_val)):
#start the for loop for the execution
if i==0:
data=data.drop([i]) # to eliminate the first value of the data
elif i+1==len(intensity_val): #to consider the last value of the data
continue
# elif i<=150 and not((intensity_val[i]) <= (intensity_val[i-1])*1.15
and (intensity_val[i]) >= (intensity_val[i-1])*0.85):
#data=data.drop([i]) # to remove several continuous peaks due to
cosmic ray event
elif i>0:
mean = (abs(intensity_val[i-1]) + abs(intensity_val[i+1]))/2
if(abs(intensity_val[i])<mean or abs(intensity_val[i])
<(mean+mean*0.005) or abs(intensity_val[i])<(mean-mean*0.005)):
# to keep the data without the cosmic event peaks
continue
else:
data=data.drop([i]) #eliminate the cosmic event peaks

plt.rcParams['figure.figsize']=(40,20) #to manipulate the graph size
plt.plot(data["delta v"], data["intensity"]) #to plot graph
plt.xlabel('delta v')
```

```
    plt.ylabel('Intensity (a.u)')
    plt.savefig('Toluene_graph.eps', format='eps', dpi=1600)
```

The other algorithm was also produced similar results which took another approach but sightly different.

```
import matplotlib.pyplot as plt
import pandas as pd
import numpy as np

plt.rcParams['figure.figsize'] = [18, 12]

data = pd.read_csv('buffer1_600s.dat',header=0,sep='\s+')
c=data["#1D"]
light=data["mx+b"]
data = pd.read_csv('buffer2_600s.dat',header=0,sep='\s+')
dark=data["mx+b"]
y=light-dark

#calibration over 4 identified peals
ch=[194.203,374.294,530.651,606.818]
wl=[650.60,660.02,668.20,672.23]
coeffs=np.polyfit(ch,wl,1)

# convert x-axis to Raman shift
rs=1e7*(1/632.8-1/np.polyval(coeffs,c))

N=len(y)
z=np.copy(y)
cutoff=1500
for i in np.arange(2,N-3):
y1=(y[i-1]+y[i+1])/2
y2=(y[i-2]+y[i+2])/2
if abs(y2-y[i]) > 2*cutoff and abs(y1-y2) < cutoff:
z[i]=y2
```

```
#plt.plot(rs[150:],y[150:],'g-',rs[150:],z[150:],'r-')
plt.plot(rs[150:], z[150:], 'r-')
plt.xlabel('Raman shift, cm$^{-1}$')
plt.ylabel('Intensity, arb.units')
    plt.show()
```

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