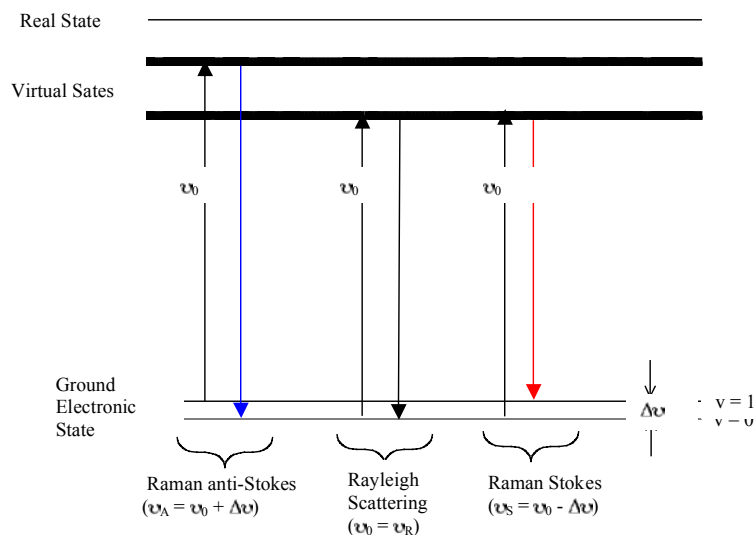


Theory:

Raman spectroscopy, unlike other forms of spectroscopy, focuses on the scattering of light. There are two categories of light scattering: elastic scattering where the scattered radiation is at the same frequency as the incident radiation, and inelastic scattering where the scattered radiation is at a different frequency. Elastic scattering off molecules is called Rayleigh scattering. In Rayleigh scattering, the photon energy and molecular energy are both separately conserved. Rayleigh scattering has the highest probability of occurring and is the scattering that gives rise to the blue color of the sky. Raman scattering is inelastic: the total photon plus molecular energy is conserved but the vibrational energy changes and frequency shifts occur in the scattered radiation.

There are two types of Raman scattering phenomena which are distinguished by whether the frequency of incident light is shifted up or down. When the incident radiation is shifted to a lower frequency (lower energy), the scattered light is called Stokes scattering. Similarly, when the incident radiation is shifted to a higher frequency (higher energy), the scattered light is called anti-Stokes scattering. Figure 1 below shows the energy levels and transitions that are responsible for Rayleigh, Stokes, and anti-Stokes scattering. At room temperature most of the molecules are in the ground vibrational state ($v = 0$) with a much lower population in the first vibrationally excited state ($v = 1$). Since there is a much higher probability the molecule is in the ground vibrational state, the Stokes lines in the spectrum are much more intense than the anti-Stokes lines. When light with frequency, ν_0 , is scattered, a molecule passes through an intermediate level called a “virtual state” which does not correspond to a real energy level of the molecule. The closer in energy the virtual state is to a real excited state, the higher the scattering probability. In essence, virtual states exist because the uncertainty principle says it takes time for the molecule to determine that a photon does not have enough energy to excite the molecule. As a temporary change in bonding, this “virtual” excitation of the electrons may set vibrations into motion. If the incident radiation frequency can excite a real energy level of the molecule, the radiation from of the upper excited state last longer ($\sim 10^{-8}$ seconds) and is radiation from fluorescence or phosphorescence. The fluorescence and phosphorescence

Figure 1- Energy-level diagram illustrating Raman Scattering



spectra is usually independent of the excitation wavelength. In contrast, the Raman shifts are independent of the wavelength of the incident photon. So one will get the same Raman shifts if a HeNe laser is used with photons of 632 nm or if a Ar-ion laser at 514 nm. The spectrum of the Raman scattered light will change with excitation wavelength.

In order to understand the origins of a Raman spectrum, one needs to discuss how a molecule interacts with the incident radiation. In order for a molecule to have a Raman spectrum it must be polarizable in much the same way that a molecule needs to have a change in its dipole moment in order to have an infrared spectrum. Polarizability is defined as a measure of how efficiently a given incident frequency of light induces a dipole in the molecule. A molecule's polarizability will vary with internuclear separation of the atoms in a molecule relative to the equilibrium value, so certain molecular vibrations will cause a change in polarizability. When the polarizability of the molecule changes, the corresponding scattered radiation intensity will change as well. Therefore vibrations in a molecule that will cause a change in polarizability in a molecule are said to be Raman-active modes of vibration. When the incident light frequency is far below the absorption frequency of the molecule, Raman transitions that occur must obey the selection rule $\Delta v = \pm 1$ as seen in infrared vibrational spectroscopy. A detailed derivation of the interactions between the incident light field and the molecule that leads to Raman scattering is given as a supplemental document.

Another type of analysis that can be used to probe the type of vibrations in a molecule that give rise to a Raman signal is the Raman depolarization ratio. When the sample solution is excited by linearly polarized radiation (the light field is all in one direction), scattered radiation is found to be polarized to various degrees that depend on the nature of the active vibration. Knowledge of the depolarization ratio can give structural information concerning the molecule under study. For example, if the molecule being studied is approximately spherical and the vibration is totally symmetric, the scattered incident radiation should be polarized in the same direction as the incident radiation. If the vibration was asymmetric, then the polarization would be changed and the depolarization ratio would be significant (greater than zero). Mathematically the depolarization ratio is shown in Equation 1.

$$\rho = \frac{\Phi_{\text{perpendicular}}}{\Phi_{\text{parallel}}} \quad \text{Equation 1}$$

In Equation 1, $\Phi_{\text{perpendicular}}$ is the power of the Raman scattered light polarized perpendicular to the polarization of the original beam and Φ_{parallel} is that polarized parallel to the original beam. For our measurements, use the intensity of each of the peaks you can distinguish in the spectrum for $\Phi_{\text{perpendicular}}$ and Φ_{parallel} . Using scattering theory, it is predicted that for asymmetric vibrations $\rho = 0.75$, where for symmetric vibrations $\rho < 0.75$. An example of using the depolarization ratio is CCl_4 which has a Raman line at 459 cm^{-1} . This line has a $\rho = 0.005$ which corresponds to the totally symmetric breathing vibration of CCl_4 .

Experimental:

Turning on the laser:

The provided diagram illustrates the basic setup of the laser table and includes all the optics that will be used in the experiment. The HeNe laser used produces approximately 50 mW of power and generates light of 633 nm. The steps for turning on the laser are as follows and need to be done in the given order;

1. Make certain the power switch on the power supply is in the “0” (off) position
2. Check the voltage setting on the voltage selector switch (back of power supply) and make sure it is set to 115
3. Insert the line cord into the receptacle on the back of the power supply and then plug the other end into the laser (if necessary)
4. Plug the male high voltage connector from the laser head into the high voltage receptacle on the back of the power supply – this connection has to be a TIGHT FIT or else the laser will not work properly
 - a. Tighten the high voltage connector retaining screw (under high voltage receptacle) to prevent the possibility of electric shock
5. Turn the power supply on by switching the power switch to “1” (on).
 - a. DO NOT turn on the power supply WITHOUT THE LASER CONNECTED. If you do, turn off the power supply and wait at least FIVE MINUTES before connecting the laser.
6. The indicator light will turn on immediately when power supply is switched on; the laser will take 3 to 7 seconds to begin lasing
7. make sure the safety shutter is in the closed position (slider moved all the way to the right when facing the laser) when turning on the laser

The laser is powerful enough to cause permanent damage if it is directed into a student's eye so never put your eye on the same level as the laser (i.e. don't sit down) and watch for any stray reflections from the optics on the laser table.

Setting up the laser table:

Looking at Figure 3, there are several mirrors, filters, and lenses used to manipulate the laser beam before it reaches the sample and then several more optics before the beam reaches the spectrometer. The first two mirrors are used to redirect the laser beam down the table and towards the sample cell. These mirrors will already be set in place but you must make sure they are aligned by using the irises along the beam line. To do this you want to close down Iris 1 so that the opening is as small as possible, then adjust mirror 1 (M1) so that the beam goes through the pinhole opening in Iris 1. The blackhole beam dump should be positioned behind Iris 2 to “catch” the laser light and prevent any stray reflections. After the laser is aligned through Iris 1, open Iris 1 as much as possible and adjust mirror 2 (M2) so the beam goes through Iris 2. Once the beam is aligned through Iris 2, close Iris 1 down again and make sure it still travels through the pinhole.

If it doesn't, adjust M1 so it does as done previously. This process of aligning the laser beam through the irises is repeated until the beam only goes through the pinhole of each Iris which ensures the laser beam is level. Once the beam is aligned, the other optics can be placed on the table keeping in mind that if the mirrors are adjusted (or bumped) at anytime later, this process of aligning will have to be redone.

The first optic you want to put down is the 633 MaxLine filter which only lets 633 nm light through to ensure no other wavelength are incident upon our sample. The positioning of this filter along the beam path is not too important as long as it is in front of the first focusing lens (L1). L1 is a Plano convex lens with a focal length of 100mm (~4 inches). That means that the laser light will focus to its smallest aperture 100mm after passing through the lens. Make sure the lens is mounted with the adjustment knobs pointing towards Iris 2. Also, when mounting any of the optics to the laser table, make sure to place a washer in-between the screw and the clamping fork as to prevent creating any indentations in the clamping fork.

Once L1 is in place, the sample cell needs to be mounted so that the front of the cuvette (the face of the cuvette where the Raman scattering is leaving as indicated in Figure 3) is placed in tightest focusing section of the laser beam. We do this because we want the largest intensity of light to be the closest to the exit face of the cuvette towards where the light will be collected. The scattered light will be collect perpendicular to the direction of the laser beam so that the laser intensity won't saturate the spectrometer and mask the Raman signal. Before the sample cell is mounted, use a card to find the tightest focus of the laser beam after L1 and try and mount the cell as close to this region as possible.

The last two optics to go on the table, L2 and the F2 unit, are the trickiest to place since their exact position determine the intensity of signal collected. Since the scattering signal is very weak, a Plano convex lens (L2) is used to collimate the light into the collection fiber mounted to F2. First place L2 about 1 to 1.5 inches straight back from the sample cell and see where it focuses using a card. Then adjust L2's position until an optimal position is found where the scattered light is imaged the clearest with the tightest focus. Use a clamping fork to mount L2 into position. The scattered light is collected using a high precision translation lens mount with a notch filter and fiber optic cable attached. The notch filter blocks out all light below 633 nm since we want to see Stokes lines which occur at wavelengths above 633 nm. The translation lens mount is use to adjust the fiber optic cable's position with respect to the focused scattered light. Place F2 in the region where the tightest focus was found (this can be difficult to find) and mount with a clamping fork. At this point, all the optics are roughly where they will be for the rest of the experiment and only fine adjustments will be made from here on out.

Calculating Raman Shifts:

Once a Raman Spectrum is obtained, the Raman shifts can be calculated and compared to the vibrational frequencies of the molecule. From the Raman spectrum, create a table that labels each peak in the spectrum with the wavelength that it occurs. Convert these wavelengths into frequencies (cm^{-1}). As mentioned previously, Raman shifts are

independent of the incident radiation wavelength, but we need to subtract the frequency of each Raman peak in the spectrum from the frequency of the laser light to obtain the Raman shifts. Therefore, convert the HeNe laser wavelength (632 nm) to a frequency (cm^{-1}) and determine the observed Raman shifts for each peak in the spectrum.

We can then compare these observed shifts with those predicted from the known molecular vibrations for benzene. The literature values for the Raman active modes of vibration for benzene are provided below where n is a number for the vibration being described (not all 30 vibrational modes are Raman active). The Raman modes that this lab will be probing are Stokes lines, therefore the scattered light will have a lower frequency than the incident light. To calculate the predicted Raman shift of each vibrationally active mode in the spectrum, the frequency of the vibration must be subtracted from the incident frequency of the laser light. Since the Raman signal is very weak and hard to find, it is very important to know where to expect peaks in the spectrum before starting the experiment. Using Table 1, calculate all the possible Raman peaks for Benzene in units of nanometers. What are possible reasons for differences between observed and predicted Raman shifts for benzene?

Table 1- Literature Values for Fundamental Vibrations in Benzene¹

n	Symmetry	Activity	Frequency (cm^{-1})
1	A_{1g}	Raman	3073.94(5)
2	A_{1g}	Raman	993.063(15)
11	E_{1g}	Raman	847.1
15	E_{2g}	Raman	3056.7(1)
16	E_{2g}	Raman	1600.9764(8)
17	E_{2g}	Raman	1177.776(10)
18	E_{2g}	Raman	608.13(1)

Measuring the Depolarization Ratio:

Once a Raman signal has been obtained, the depolarization ratio can be found by inserting a simple Polaroid film (a polarizer) in the path of the scattering radiation between the L2 and the fiber optic collector. First place the polarizer perpendicular to the incident laser beam and record the spectrum. Then place the polarizer parallel to the laser beam and record another spectrum. Measure the intensities of the Raman peaks visible in both spectrums and calculate the depolarization ratio using the ratio of the two measurements given by Equation 1. From the values of ρ for each peak in the spectrum, determine if the mode of vibration is a symmetric or asymmetric vibrational Raman mode.

The Spectrometer:

One of the most important aspects of any spectroscopy experiment is understanding how your signal is analyzed so that one can understand what the raw data means and where it comes from. The following is a brief description of the Ocean Optics USB2000 spectrometer.

Any scattering that is captured from the sample is focused through L2 and captured in the fiber optic cable attached to the high precision translation lens mount. The fiber optic cables used in this lab have different sizes that can be used (50, 200, 400 micrometer diameters) which controls the amount of light that gets collected. Now referring to Figure 2, the fiber optic cable attaches to connection point at 1 and the light passes through a narrow slit at 2. The size of the slit is preset and controls the resolution in the spectrum. There is a filter at 3 that restricts the optical radiation to a pre-determined wavelength range which has been tailored for this Raman experiment. Once the light has passed through the filter, it traverses across the spectrometer to the collimating mirror at 4 which focuses the light towards the working part of the spectrometer. At 5 is the grating which spatially separates the light by diffracting each wavelength through a different angle in a similar way as a prism refracts different wavelengths through different angles. The refracted light then travels to 6 where a focusing mirror focuses the light onto the Charge Couple Device (CCD) detector at 7. The CCD is an array of 2048 pixels. For each incident photon, the CCD ideally generates one electron, and the total number of electrons each on each pixel is converted to a digital signal. The spectrometer then transmits the digital signal to the Ocean Optics 001Base32 application software through the USB connection.

Figure 2- The Ocean Optics Spectrometer

