

Raman Spectroscopy

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Raman spectroscopy uses the inelastic scattering of monochromatic light to probe molecular structure. In Raman scattering, the frequency of the scattered light is shifted from the frequency of the incident beam. The rotational and vibrational energy levels of the molecule in the sample determine the magnitude of the frequency shifts. In this experiment, you will use a high powered laser scattered off of a gaseous sample to find the rotational constants of the molecules.

I. BACKGROUND

II. THEORY

II.1. Molecular rotational energy levels

The theory chapter of reference [1] gives a thorough and clear explanation of the physics of Raman scattering. Section 1.4, "Origin of Raman Spectra", is particularly relevant.

Molecules have quantized rotational and vibrational energy levels. Raman scattering occurs when light excites a molecule to a virtual energy state and it returns to an energy state different from its initial state. The scattered light is shifted in frequency by the vibrational frequency of the molecule. The intensity of the Raman line is determined by the population of molecules at a given energy level.

Under normal conditions, more molecules are in the ground state than in excited states, so the final energy state of the molecule is more likely to be higher than the initial state. Therefore, Stokes lines (lower wavenumber than incident beam) are typically stronger than anti-Stokes lines. Energy level degeneracy in homonuclear diatomic molecules. The theoretical background of energy level degeneracy and its impact on Raman spectra is explained in Professor Greytak's 8.044 lecture notes [2]. Section 3.2 of reference [3] also discusses features of the Raman spectra of diatomic molecules.

III. LASER SAFETY

The laser used for this experiment is a wavelength of 532 nm, with an adjustable output power of 10mW-2.5W. When taking data, you will use a power of 2W. This is a high power class 4 laser which poses serious safety hazards to anything in its path. One benefit of this laser is that the beam is visible, making it easy to avoid.

Always wear the appropriate safety goggles when the laser is on. Do alignments at low power. Don't obstruct the beam path. Two pre-lab questions on laser safety

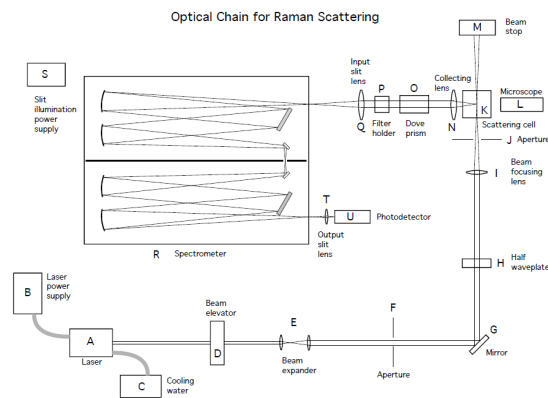


FIG. 1. Schematic of the optical chain.

IV. APPARATUS

IV.1. Optical Chain

Figure 1 is a schematic drawing of the beam path from the 2W laser.

IV.2. Electronics Chain

Figure 2 is the set up of the electronics used in this experiment.

V. RUNNING THE EXPERIMENT

V.1. Initial Steps

- Turn on the laser warning sign
- Check to see that the aperture on the front of the laser is closed. It is closed when the lever on the aperture mount is pushed fully clockwise when facing the laser.
- Turn on the cooling water with the rocker switch on the side of the unit.
- Warm up the laser power supply by turning on the rocker switch on the back of the unit.

Electronic Chain for Raman Scattering

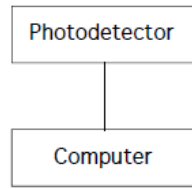


FIG. 2. Schematic of the electronic chain.

V.2. Filling the Cell

Remove the blank-off disk from the cell port on the vacuum panel.

Attach the cell to the vacuum panel.

Hold the cell by the body, not the valve stock.
Support the cell on the adjustable post.
Tighten the vacuum line clamp.

Increase the height of the post to snug it up to the bottom of the cell.

Attach the vacuum pump line to the panel. Open the vacuum valve and the gauge valve on the panel. Start the vacuum pump.

Open the valve on the top of the cell. The inside of the cell is reached through a 1/16 inch diameter tube. Pump on the cell for several minutes to be sure it is emptied of all the previous gas.

Open the panel valve to the desired gas to purge the connecting rubber tubing back to the valves on the gas cylinder.

Close the panel valve to the gas.

Close the panel valve to the pump and turn off the pump.

Slowly open the panel valve to the gas and bring the gas up to the desired pressure.

Close the valve on the cell.

Remove the cell from the panel and put the vacuum flange protector on the cell.

Replace the blank-off disk on the cell port of the panel.

You may leave the vacuum pump line connected if it will not be in your way.

Carefully replace the cell on its post on the optical bench. For consistency orient the cell so that the valve knob is on the side opposite the spectrometer.

V.3. Setting Up the Computer

Turn on the computer. The password is "Viburnum". Double click on the icon for the Hamamatsu application (named H1189ver0200) that appears on the Desk-

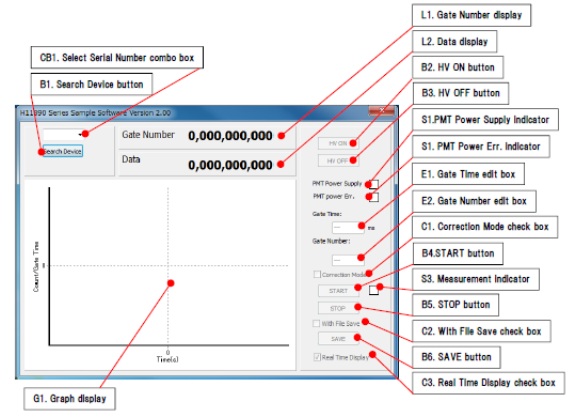


FIG. 3. Labels for the different parts of the Hamamatsu application.

top. The following application image, figure 3 (without the annotation) should appear on the screen. Click on the Search Device button B1. The serial number of our photodetector appears in CB1.

In the Gate Time box E1 enter the counting time in milliseconds for each point in the spectrum. This will almost always be between 1000 and 5000. Click on the HV ON button B2. The HV Power Supply indicator will come on as green. It is important to understand that the high voltage can be applied to the PMT even when one is not running a measurement. The HV Power Error Indicator lights up red when excessive light is detected but stays white during normal operation. Click the START button B4. The Gate Number readout L1 will begin to indicate which data point you are taking: 1, 10, 2,523 etc. and the Data readout L2 will show how many counts were recorded in the current data point. At the same time a plot of the data will begin to appear on the graph. This is a good time to check for stray light. When the room lights are on there will be a count rate of 100 - 200 counts per second due to light entering the input slit. When a dark cloth is draped over the input slit housing the count rate should drop to the PMT's dark count of less than 10 counts per second. If this is not the case check to make sure a permanent black cloth is draped over the output slit and photodetector area.

The graphic display has a quirk that can be annoying at times. After it has been running for a while it will stop displaying the newest data when the graph reaches the right side of the display. Data is still being recorded as can be seen in the Data window but the graph does not advance. After a delay of 10 seconds or more the graphic display comes to life again displaying the most recent data in the left half of the display and writing the new data into the right half. This is generally not a problem when one is taking data but is inconvenient when one is watching the display while trying to adjust some element of the system.

Click on the STOP button.

Click on the HV Off button.

V.4. Aligning the Laser Beam with the Scattering Cell

Put on a pair of laser goggles. Keep them on except for those few times when you must view some aspect of the laser light, for example when checking beam alignment by looking at reflected light and when you are looking at the scattered beam through the microscope.

Turn on the laser using the key on the front of the power supply. It will start at a low power of about 10 mW.

Open the aperture on the front of the laser.

Check to see that the beam elevator is set for full transmission.

Check to see that the beam passes cleanly through all the optical elements, in particular the apertures in the cell, and produces a clean spot at the beam stop. If there is a problem with the transmitted beam, check to see that the cell is seated properly on its mount with the knob on the 11 valve facing the microscope and that cell's mount is rotated so that the reflection from the input window is centered on the half-wave plate. Small adjustments of the beam through the cell apertures are most easily made by adjusting the angle of the 45 degree mirror. [Note: Be sure to do these adjustments at low power. If the beam at high power grazes an internal aperture it can cause material to ablate, material which will coat around in the gas and scatter brightly when it is in the laser beam. These bright spots are very intense when viewed in the microscope. They can also overload the phototube during the final alignment of the collection optics. One can only wait until the " settles out. That may take over night.]

V.5. Aligning the Input Slit to the Beam

Make sure the polarization of the beam entering the cell is vertical by looking at the stray reflected light with a marked polaroid sheet. If not, make it so by rotating the half wave plate.

Turn the laser power up to 2.0 watts.

Focus the microscope on the beam in the cell by using the micrometer on the microscope mount. Adjust the vertical position of the microscope so that the laser beam crosses the reticle scale at the line marked 50. If you are having difficulty seeing the reticle scale try shining a flashlight on the face of the scattering cell.

Close the aperture on the laser head. Turn on the slit illumination. Turn it up just to the point where you can see a clear image in the microscope. Too high a power could burn out the bulb.

Use the micrometers on the collection lens to bring the image of the slit into focus in the microscope at the same vertical position that the beam had. Adjust the

horizontal position of the slit image to be centered in the cell. Rotate the dove prism if necessary to make sure the image of the slit is horizontal, as was the laser beam. Note that the lines on the reticle scale may not be exactly horizontal. the slit illumination.

Experience has shown that this alignment process is close, but not necessarily optimum. The vertical position is pretty good and depends sharply on the micrometer setting. The forward and backward position of the lens is less critical because of the depth of focus of the collection lens. We will re-tune the alignment in the next step.

V.6. Measuring the Spectrum

Open the aperture on the laser.

Rotate the half wave plate by 45 degrees so that the electric field of the laser beam is horizontal in the cell, thus minimizing the amount of elastically scattered light that will be collected. The easy way to do this is to view the stray light or the light in the beam dump while holding the marked polaroid sheet with the easy axis vertical. Rotate the half wave plate to minimize the intensity of the viewed image.

Close the aperture on the laser. Set the DIRECTION knob on the spectrometer to OFF. Turn on the spectrometer by depressing the MAIN SWITCH button on the right end of the panel. You can confirm that it is on by seeing if it sweeps by setting the sweep speed to the 1000 $cm^1/minute$ and rotating the DIRECTION knob away from OFF for just a second. Don't leave the sweep on.

Fine tune the optical alignment by using the unshifted scattered light. Put a ND 2 (transmission of 10^2 neutral density filter in the filter holder following the Dove prism. Approach the unshifted line as follows to minimize the delay due to backlash in the drive mechanism of the spectrometer. Use the motor drive at about 1000 $cm^1/minute$ to sweep the spectrometer up to 19200 cm^1 . At a slower rate of 250 $cm^1/minute$ then at 50 $cm^1/minute$ sweep down to 18920 cm^1 and stop.

Open the laser aperture. Turn on the photodetector control application on the computer. Set the counting time to 1000 ms, turn on the high voltage, and click START. The counting rate should be only slightly higher than the dark count rate at this point because of the 10^2 filter and the fact that the spectrometer setting is above the frequency of the central line. Switch the sweep rate to 5 $cm^1/minute$ and turn the downward sweep on again. It will take several minutes before the wavenumber indicator begins to move again. When the central line is reached the count rate will peak somewhere around 6,000 counts per second. Stop the sweep. It does not matter if one is at the exact top of the line. We just want a high counting rate to make the optical alignment easier. Now in order adjust the vertical height of the collection lens, its position toward and away from the cell, and the rotation of the Dove prism. You may want to go back through these three adjustments to be sure the alignment is opti-

mum. When you are satisfied close the laser aperture and click STOP on the computer.

You are now ready to take data. Note that the figure of 6,000 counts per second is for N₂ at one atmosphere. Other gases at other pressures might require more than 10² of attenuation of the scattered light. You might first try a ND 3 filter (transmission of 10³). When a sweep is begun there are transient effects in the grating sweep mechanism that require time and/or excursion before a linear rate of $\text{cm}^1/\text{minute}$ is established. The following procedure seems to be adequate to obtain a linear rate in the region of the spectrum where analytic measurements are made. Use the motor drive at about 1000 $\text{cm}^1/\text{minute}$ to 4 sweep the spectrometer up to 19200 cm^1 . At a slower rate of 250 $\text{cm}^1/\text{minute}$ then at 50 $\text{cm}^1/\text{minute}$ sweep down to 18950 cm^1 and stop. On the computer application check the With File Save check box C2. This prepares the data to be saved to a file in the folder Junior Lab Raman Spectra 2018" (located on the desktop) at the end of the measurement. Do not check this box when making various adjustments because that will crowd the folder with unwanted files.

Remove the neutral density filter. Switch the sweep rate to 5 $\text{cm}^1/\text{minute}$ and turn the downward sweep on again. It will take several minutes before the counter begins to move. At that time click START on the computer. This begins the data file for your run which you will save later. You should to see the count rate go up and down as the spectrometer sweeps through the up-shifted portions of the rotational Raman spectrum. Due to the temperature dependent occupation of the rotational levels of the molecule, the down-shifted Raman peaks will be somewhat higher than the up shifted ones. Watch the count rate on the computer display carefully. When it begins to rise rapidly and go off scale, drop the 10² neutral density filter in the collection path again. This should give you a trace of the central line without over-driving the PMT. When the signal drops sufficiently, remove the filter and watch the down-shifted portion of the spectrum evolve. This is the portion of the spectrum that you will examine in detail. You will use the position of the central line to establish zero frequency shift and then assume that the sweep rate has become constant by that time.

Sweep through at least 20 of the peaks. Click STOP on the computer. Stop the sweep and make a note of the wavenumber setting on the spectrometer. Click SAVE on the computer. If you are satisfied with your results turn off the computer application and the laser. Download your data from the computer to a flash drive.

V.7. Processing the Data

The data generated by the Hamamatsu computer application is saved as a text file in the following format.

After 4 lines of identifying information each line has the format of "counter gate number" followed by a single

```
H11890
GateTime 1000
GateNumber 0
SN 30060074
1 17
2 6
3 10
4 15
5 11
6 14
7 21
...
```

space followed by the "counts" accumulated during that gate. It is not as simple as the above figure might lead one to believe. The "counter gate number" can grow to 3 or 4 digits so the single spaces will not be in a single vertical line. You are free to analyze this data any way you choose. However most students will want to use Microsoft Excel so I will point out how to accomplish that.

When the file is opened by Excel a window will appear asking what original data type best describes your data. Choose "Delimited". There is also an opportunity to exclude the first four lines if you wish. You can also do that by hand later. Click Next. The window then switches and asks for the type of delimiter. Choose "Space". Click Next again. In the final window choose the Column data format as "General" and hit Finish. The counter gate number and counts will be in separate columns, ready for you to process and plot.

V.8. Analysis

Data

You should record a clean spectrum of N₂ and of O₂ at 1 atmosphere. You should record spectra of CO₂ at 1 atmosphere and at 3 atmospheres (2 atmospheres "gauge"). In each case display the data as a plot of counts per second verses frequency shift (downward) in wavenumbers. In the case of N₂ and O₂ you may want to use a 3 point average – corresponding to a 3 second integration time – to smooth out some of the fluctuations.

Analysis

Use the rigid rotator approximation to deal with these linear molecules. It neglects the fact that as the molecule rotates more rapidly it stretches out and its moment of inertia increases. This is only a small effect in these experiments. In the rigid rotator approximation the downward shift of each line from the elastic scattering is given by

$$\Delta\tilde{\nu}(L) = (4L + 6)B_e$$

where L is the rotational angular momentum of the initial state involved in the transition and $B_e \equiv k_B \Theta_R / ch$ is the “rotational constant” for the molecule expressed in wavenumbers¹.

For N_2 and O_2 make a plot of $\Delta\tilde{\nu}(L)$ verses L and from it determine the relevant B_e . The scatter of the points about a straight line will come from both statistical error and from non-linearities in the sweep of the spectrometer.

On your plots of the spectra show curves for the expected heights of the even L peaks and odd L peaks taking into account the statistical occupation of the initial L state and its degeneracy. For each molecule does the the measured ratio of the amplitudes of the two curves match the theory?

Although CO_2 is not a homonuclear diatomic molecule, it can be treated as such. The carbon at the center only serves to increase the molecule’s length, it does not contribute to the rotational angular momentum. Thus the spectrum should have all the features exhibited by an $I = 0$ molecule without the complications of electronic wave function parity and spin found in O_2 . Confirm this using the 1 atmosphere data and determine the appropriate B_e .

The CO_2 spectrum at 3 atmospheres looks different because collisions between the molecules broaden the individual lines. This is most easily seen by the filling in of the troughs between the lines. The trough filling occurred to some extent in the 1 atmosphere spectrum, but that was due primarily due the smaller shift between the lines (than was the case for O_2) causing an overlap between the tails of the instrumental profile. If you look carefully you may also be able to discern that the individual lines in the 3 atmosphere spectrum are broader than in the 1 atmosphere case.

You should be able to use the CO_2 spectra to determine how many collisions it takes to disrupt the rotational motion of the molecule. This will be a semi-quantitative analysis, but it should be instructive.

A Poisson Random Process describes a series of discrete events occurring randomly in time at a uniform rate r events per second. In any vanishing small increment of time dt the probability of having an event is $r dt$. The probability of finding n events in the finite time interval t is

$$p(n; t) = \frac{1}{n!} (rt)^n \exp(-rt)$$

¹ A comment about notation. Different authors use different notations for the various angular momenta encountered in the study of diatomic molecules. I follow here the notation used in the accompanying notes Indistinguishable Particle Effects in Rotational Raman Scattering.

The spin angular momentum of a single nucleus is \vec{I} and its magnitude is indexed by the letter I . The rotational angular momentum of the molecule is \vec{L} and its magnitude is indexed by the letter L . The total spin angular momentum of the electrons is \vec{S} and its magnitude is indexed by the letter S . $\vec{L} + \vec{S} \equiv \vec{J}$, a quantity which is relevant to the study of O_2 .

The mean number of counts in the interval is $\langle n \rangle = rt$, the variance

$\text{Var}(n) \equiv \langle (n - \langle n \rangle)^2 \rangle = \langle n \rangle$, and the standard deviation $\sigma \equiv \sqrt{\text{Var}(n)} = \sqrt{\langle n \rangle}$. Note that the probability can be written more simply in terms of the mean.

$$p(n; t) = \frac{1}{n!} \langle n \rangle^n \exp(-\langle n \rangle)$$

The probability density for the waiting time Δt_1 between one event and the next is given by

$$p(\Delta t_1) = r \exp(-r\Delta t_1)$$

Now imagine one has a signal at a fixed frequency ν_0 with a phase ϕ . If the phase ϕ is constant, the spectrum of this signal – the spectral power density to be precise – is a delta function at $\nu = \nu_0$. Now imagine that the phase of the signal is reset at random at a series of times described by a Poisson random process with a rate r . It can be shown that the spectrum is no longer monochromatic. Rather, it is a Lorentzian line centered at $\nu = \nu_0$ with a half width at half height $\Delta\nu_{hwhh} = r/\pi$:

$$S(\nu) = \frac{1}{\pi} \frac{(r/\pi)}{(\nu - \nu_0)^2 + (r/\pi)^2}$$

Thus if we assume that the L value of a given rotating molecule changes randomly at a rate r we would expect the intrinsic line shape of each rotational line to be a Lorentzian of width $\Delta\nu_{hwhh} = r/\pi$ or $\Delta\tilde{\nu}_{hwhh} = r/c\pi$. The measured line shape would be the convolution of the intrinsic line shape with the instrumental profile of the spectrometer.

At the high resolution we are using, the instrumental profile of the spectrometer is not represented by any analytic function. However, it does share one important feature with a Gaussian: it falls off rapidly in the tails. In fact, the spectrometer was designed with this goal in mind since it is that feature which allows it to resolve weak lines which are close to strong ones. It will be convenient in what follows to approximate the instrumental profile by a Gaussian.

The line shape resulting from the convolution of a Gaussian and a Lorentzian is a non-analytic function known as a Voigt function. It is described quite nicely in Wikipedia at wikipedia.org/wiki/Voigt_profile. That article gives the following approximation for the ratio of the full width at half height of the Voigt function to that of the Gaussian f_V/f_G in terms of the full width of the Lorentzian to that of the Gaussian f_L/f_G :

$$(f_V/f_G) = 0.5346(f_L/f_G) + \sqrt{1 + 0.2166(f_L/f_G)^2}$$

We want to go the other way and determine f_L/f_G from f_V/f_G . The simplest way to do that is to graph the above function with f_L/f_G on the horizontal axis and f_V/f_G on the vertical axis. We will be interested in the region where $0 \leq f_L/f_G \leq 1$.

Go to your 1 atmosphere trace and expand the region around the highest peak. Taking the base line to be the dark count (which will be almost negligible on this scale) and not the valley in the trace, measure the full width at half height of the 3 tallest peaks. [This is a reasonable approach since the tails of the overlapping lines fall off relatively rapidly.] Take an average of these values as the full width of the instrumental profile. Why not just measure the width of the central line? You only go through that once. [You could if you want go back over all the central lines you have swept through and average those widths.]

Now do the same thing on the 3 atmosphere trace and take that average as the full width of the convolved line, the Voigt function. From these two values determine full width at half height f_L , in wave numbers, of the intrinsic line shape at 3 atmospheres. This width is due to collisions between the molecules so will be proportional to the density. Check to see that our neglect of the intrinsic broadening at 1 atmosphere was justifiable. At 3 atmospheres, what is the mean time $1/r$ between changes in L ?

The mean free time between molecular collisions is inversely proportional to the density n and the collision cross-section σ .

$$\tau = \frac{1}{n\sigma} \sqrt{\frac{2m}{\pi k_B T}}$$

A collision cross-section can be found from the viscosity. This cross-section is relevant to molecular transport phenomena. It applies to collisions which change the linear momentum of the molecule – magnitude or direction – in a significant way.

$$\eta = \frac{1}{\sigma} \sqrt{\frac{8mk_B T}{9\pi}}$$

The viscosity of CO₂ at T = 300 kelvin is 1.48×10^{-4} gram cm⁻¹ sec⁻¹. What is the collision cross-section σ ? What is the mean time between collisions τ at 3 atmospheres? How does τ compare with $1/r$? Is this reasonable?

CO₂ was specifically chosen for this part of the experiment because it is known that it is more sensitive to collision broadening than N₂ and O₂. The magnitude of the broadening in terms of f_L per atmosphere is 3 times larger for CO₂ than it is for N₂ or O₂. On the other hand, the transport cross-section discussed above is roughly similar for the 3 molecules.

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- [1] K. N. J. Ferraro and C. Brown, “Introductory Raman Spectroscopy,” (Elsevier Science, 2002).
 - [2] T. Greytak, “8.044 Lecture Notes,” (2013), <https://web.mit.edu/8.13/8.13a/references-spring/raman/Greytak.notes.Raman.pdf>.
 - [3] A. Weber, “Raman Spectroscopy of Gases and Liquids,” (1979), https://web.mit.edu/8.13/8.13a/references-spring/raman/RamanSpec_GasesAndLiquids_Weber1979.pdf.

VI. APPENDIX

VI.1. Detailed optical Chain

A Laser

The laser, a Coherent “Verdi G2”, is an optically pumped solid state laser operating at 532.3 nm ($\leftrightarrow 5.632 \times 10^{14}$ Hz $\leftrightarrow 1.879 \times 10^4$ cm⁻¹) and delivering between 10 mw and 2.5 watts. When taking data, we use a power of 2.0 watts. The laser beam is vertically polarized and has a full width at the $1/e^2$ point (intensity) of 2.1 mm. Sometimes, when the laser has been on at 2.0 watts for a long time a weaker line will appear about 3.5 cm⁻¹ higher than the main line.

B Laser power supply

The power is selected by rotating the large knob on the front of the power supply. When the laser is turned on, it always automatically resets to 10 mw.

C Chilled water unit

A closed cycle unit, not requiring connection to an external supply of water, circulating water at a set temperature through an aluminum channel plate on which the laser head is mounted. We use a water temperature of 20 degrees C.

D Beam elevator

A mirror tower which raises the the level of the beam to 31.3 cm above the optical table surface, the height of the center of the slits on the spectrometer.

The 10 mw lower level of the laser power is usually low enough for most purposes. However, if lower power levels are necessary one can decrease the intensity of the beam by about 10^{-2} by switching the lower 45 degree mirror from a high reflector to a thick uncoated glass window. Although one uses the beam from the front surface of this window, the internal reflection from the back surface also makes it up to the 31.3 cm level. Since that beam is displaced from the desired one, it can be eliminated from the optical chain by an aperture. When the window is used instead of the mirror, the beam

transmitted through the window is intercepted by a beam stop at table level.

E Beam expander

A pair of short focal length lenses separated by the sum of their focal lengths expands the beam diameter to about 4 mm. The larger diameter beam is less likely to damage the half-wave plate further along the chain.

F Aperture

An iris diaphragm used to clean the beam profile.

G Mirror

A high reflectance dielectric mirror used to turn the beam by 45 degrees.

H Half waveplate

A mounted zero order $1/2$ waveplate at 532 nm from ThorLabs (WPH05M-532). Used to rotate the polarization of the beam in the direction of the scattered light, thereby reducing by about a factor of 4 (determined by the solid angle accepted by the Collection lens, N) the light collected from the dipolar elastic scattering while having little effect on the amount of depolarized light collected from the rotational Raman scattering.

I Beam focusing lens

The focal length of 30 cm was chosen to produce a diffraction limited focal region of diameter $40\ \mu$ and length $6\ \text{mm}$. The collection optics produce an image of the spectrometer slit in the scattering region which is reduced by a factor of 3. Thus a $150\ \mu$ by $1\ \text{cm}$ slit has an image size of $50\ \mu$ by $3.3\ \text{mm}$, well matched to the beam.

J Aperture

An iris diaphragm used to clean the beam profile.

K Scattering cell

A copper cell that was once used in a Raman scattering experiment in superfluid helium. Among the changes, the indium “O” rings have been replaced by neoprene ones.

L Microscope

By moving the microscope forward and back, the graduated reticule in the focal plane of the microscope can be focused on the laser beam in the gas. Then the position of the collection lens (N) can be adjusted to place the image of the input slit of the spectrometer at the same location.

M Beam stop

N Collection lens

A 50 mm f/1.9 camera lens on a mount permitting translation in three directions: parallel to the beam, toward the spectrometer, and vertically. The last two are the primary adjustments used to maximize amplitude of the collected signal.

O Dove prism

By rotating this prism about its long axis the image of the vertical input slit can be made horizontal in the scattering cell. This transformation is most efficient when the image is at infinity. Thus the collected light is made as parallel as possible at this point by placing the laser beam at the focal point of the collection lens (N) and the slit at the focal point of the input slit lens (Q).

P Filter holder

Filters are used to reduce the light sent to the phototube when the system is bring aligned and when one is sweeping through the unshifted line due the the elastically scattered light.

Q Input slit lens

An achromat with a focal length of 150 mm.

R Spectrometer

A Spex model 1401 double monochrometer. Two separate but simultaneously driven monochrometers separated by a third, internal slit. The geometry is designed to reduce the tails of the instrumental profile that arise from light scattering and reflection within the spectrometer. We are operating with $150\ \mu$ width input and output slits and a $300\ \mu$ width internal slit (the slit widths are twice the reading on the associated micrometers). In this configuration at 532 nm the instrumental profile has a full width at half height of about $1.7\ \text{cm}^{-1}$ and the line appears at $18892\ \text{cm}^{-1}$ when sweeping downward. Don't worry about the absolute value, which is not very accurate. We measure shifts from the position of this line, and these shifts are accurate.

S Input slit power supply

Powers the light that illuminates the input slit when trying to align its image with the laser beam. **REMEMBER TO TURN OFF THIS LIGHT BEFORE TURNING ON THE PHOTODETECTOR.**

T Output slit lens

This lens places a reduced image of the output slit on the 8 mm active diameter of the photocathode of the photomultiplier tube in the photodetector.

U Photodetector

A model H11890-210 Photon Counting Head from Hamamatsu. We try to restrict the total photo count to less than 10^4 counts per second to preserve the sensitivity of the photocathode. **OPERATION ABOVE 10^5 COUNTS PER SECOND MAY PERMENATALY DAMAGE THE TUBE.**

Optical Chain for Raman Scattering

