THE RAMAN EFFECT

PURPOSE:

To learn optical detection techniques.

To measure the Raman spectrum of some simple organic liquids.

To use Raman scattering to determine the composition of an unknown liquid mixture.

APPARATUS: Continuum Minilite 10 Hz pulsed YAG laser (355 nm), YAG laser goggles, quartz sample tubes, phototransistor trigger, Instruments SA H20 Monochrometer, Rutgers P1100 Monochrometer Driver (scanning motor and control box), Hamamatsu R928 photomultiplier, high voltage power supply, Stanford Research Systems (SRS) Fast Preamplifier model SR240, SRS Gated Integrator and Boxcar Averager model SR250, Ortec 401A power supply and NIM bin, Two Tektronix 100 MHz Oscilloscopes model 2235, USB Flash Drive.

BACKGROUND: **Introduction:** Rayleigh scattering of light is a familiar phenomenon that is responsible for the blue color of the sky. Light from the sun strikes air molecules and is scattered in all directions without losing energy or changing frequency. The blue color arises because the strength of the scattering depends strongly on the fourth power of the frequency so that blue light is much more strongly scattered than yellow or red.

> *Questions: The frequency of violet light is even greater than that of blue. Why isn't the sky violet? Why is the sun yellow at noon, but red at sunset?*

In 1928 C.V. Raman discovered another (much weaker) type of light scattering in which the frequency changes when the light is scattered. The frequency shift Δv occurs when some of the energy of the scattered photon is taken up by a molecule, which is excited into vibrational motion. This effect is shown in Figure 1. Most of the molecules are initially in the ground state (labeled 0 in the figure) but because of thermal agitation some molecules will be in an excited state (labeled 1). The scattering process can be thought of as the incoming photon raising the molecule to a virtual (i.e., non-existent) excited state.
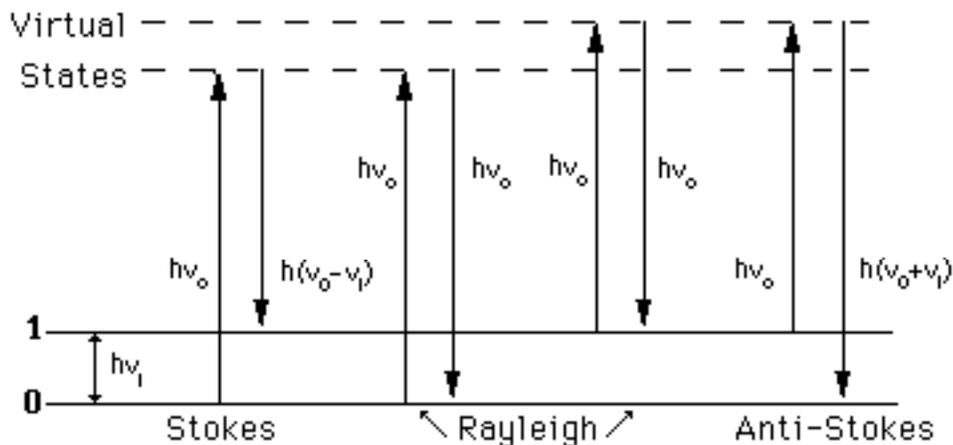
Figure 1: Raman and Rayleigh Scattering of Light

But, since the molecule cannot remain in this virtual level, it must immediately fall back down to a lower level with the emission of a photon. If the molecule falls into the same level as it started from, there is no frequency shift in the emitted photon and there is have Rayleigh scattering.

If, on the other hand, the molecule falls into a different level, the energy of the emitted photon must differ from that of the incoming photon in order to conserve total energy. In this case, the emitted photon has a different frequency from that of the initial photon. This process is called Raman scattering. The frequency can decrease (giving rise to Stokes lines in the spectrum) or increase (anti-Stokes lines), depending on whether the molecule starts in the ground state or an excited state. Since the initial population of the excited states is usually very small, the anti-Stokes lines are much weaker than the Stokes lines and sometimes cannot be observed. (The number of molecules in each excited state obeys Boltzmann statistics, so the higher levels are less likely to be populated. Since large Raman shifts must result from higher excited states, large Raman shifts happen less frequently. Therefore, Stokes lines with small Raman shifts are the most likely lines to be observed.)

Units: Spectroscopists, and especially chemists, frequently use wave numbers $\nu*$ (expressed in units of inverse centimeters) to measure frequency. A wave number is defined as $\nu* = \nu/c = 1/\lambda$, where c is the speed of light in cm/s and λ is the wavelength in cm. The wave number gives the number of wavelengths of light that will fit into one centimeter.

Notice from Fig. 1 that the Raman shift $\Delta\nu = \nu_o - (\nu_o \pm \nu_1) = \pm \nu_1$ does not depend on the frequency ν_o of the incident light; the shift only depends on the excitation energy of the excited state. Therefore, in reporting Raman spectra, only $\Delta\nu*$ is recorded. The spectrometer you will use sweeps the wavelength linearly with time and is calibrated in nm. It is straightforward to calculate $\Delta\nu*$ from the wavelength λ_0 of the incident photon and λ_1 of the Raman scattered photon measured in nm (see Appendix C):

$$\Delta\nu* = [1/\lambda_0 - 1/\lambda_1]10^7 = [(\lambda_1 - \lambda_0)/\lambda_0 \lambda_1]10^7 \qquad (cm^{-1}) \quad (1)$$

Interpretation of Raman Spectra: The atoms of a molecule can vibrate in many ways-these are called the normal modes of vibration. The normal modes have different excitation energies so the Raman spectrum will consist of more than one line. The number of normal modes is easily deduced; if the number of nuclei in the molecule is N, then the total number of degrees of freedom (i.e., the number of coordinates required to specify the positions of all of the nuclei) is 3N. Of these, three account for translation of the molecule as a whole and three more for its rotation. This leaves 3N-6 coordinates to account for the relative positions of the nuclei relative to each other, i.e., for internal motions. This is the number of normal modes. (However, this calculation only puts an upper limit on the number of lines in the Raman spectrum. Some normal modes may be degenerate, i.e., have the same energy. Others, due to their symmetry, may be Raman

inactive, i.e., unable to Raman scatter a photon. Still others may not produce a line intense enough to be resolved from the background noise.)

For a simple molecule like carbon tetrachloride (CCl_4), N = 5 and there are 9 classical normal modes. However, only six Raman lines can be observed: $\Delta v* = 218, 314, 459, 762, 790$, and 1539 cm^{-1}. (Note that the 762 cm^{-1} and 790 cm^{-1} lines may become blurred together and that the 1539 cm^{-1} line is very weak.) The strongest line at 459 cm^{-1} corresponds to a symmetric stretching of the four Cl ions along their bonds to the C. If the resolution of the spectrometer were better it would show a splitting caused by a slight difference in excitation energy depending upon whether the molecule has 1, 2, 3, or 4 atoms of the heavier ^{37}Cl isotope rather than ^{35}Cl.

Description of the modes of a particular molecule and application of selection rules to predict the Raman spectrum require knowledge of group theory beyond the scope of this experiment. However, the basic idea is that when light strikes a molecule it sets the electron cloud in oscillation. This oscillating polarization then reradiates the energy as scattered light. In order for the vibration of the nuclei to interact with this oscillating (accelerated) charge polarization and produce a Raman shift, it is necessary that some component of the electron cloud polarization have the same symmetry as the normal mode transition. We shall not attempt to interpret individual lines but, rather, treat the Raman spectrum as a characteristic pattern which can be used to identify unknown substances, or whose relative intensity can give a quantitative measure of the composition of mixtures of liquids.
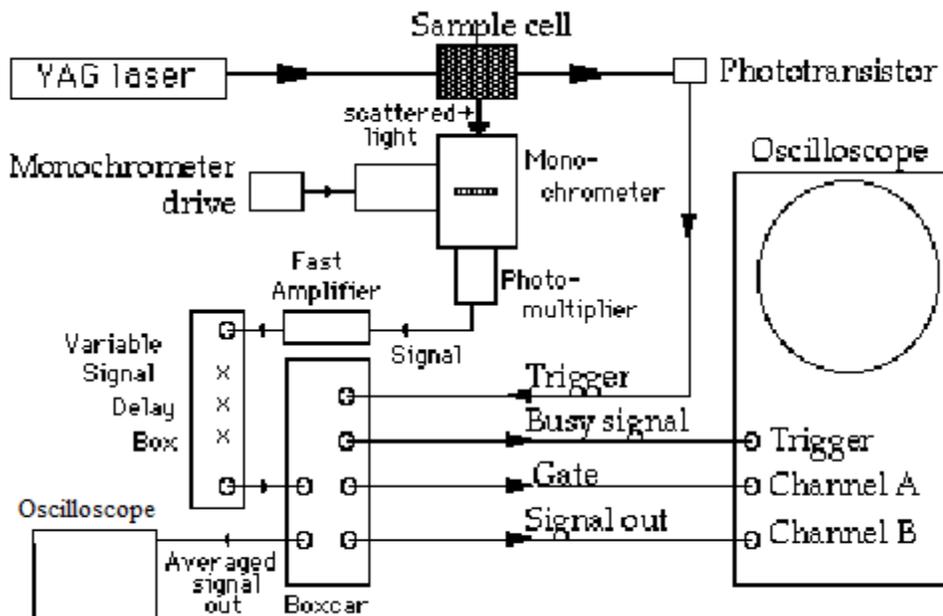

Figure 2: Block Diagram of the Raman spectrometer

EXPERIMENTAL SETUP: Raman scattering is an extremely weak process. Only about 10^{-7} of the incident photons are scattered as compared to 10^{-4} in Rayleigh

scattering. (Despite this weakness, Raman discovered the scattering using sunlight as the source and his eyes as the detector!) To get quantitative results in this experiment we will have to use some rather sophisticated light detection apparatus. Figure 2 gives a block diagram of the equipment. We will now discuss the components in detail:

1. **YAG laser:** The light source is a pulsed laser whose operation is discussed in Appendix A. The intensity of Raman scattering increases as the fourth power of the frequency, so to get a large signal, we want to use the highest frequency light source possible. The YAG laser puts out ~ 5 ns wide pulses with an ultraviolet wavelength of 355 nm at a pulse rate of 10 per second. The pulse energy is 4.5 mJ, which translates into a peak power of 0.9 MW. The laser pulse contains some residual 1064 nm infrared light as well. Both of these wavelengths are invisible to the human eye. **Although this might seem to be a rather small amount of energy, it can damage the eyes and is especially dangerous since the beam is invisible. Be sure to wear goggles whenever the laser is operating.** Note that the laser has a shutter which must be open for the experiment to work. Keep it closed for safety reasons when the laser is not in use.

2. **Sample Cell:** One of the strengths of Raman scattering as an analytical tool is that no special sample preparation is required. The liquid (or solid dissolved in a solvent) is placed in a 1 cm thick quartz sample cell. The only requirement for the sample is that it must be transparent to the incident beam and not fluoresce. Make sure when positioning the cell that the label on the cell (or any other obstruction) is not blocking the light!! Because of the danger to your eyes from stray laser light, the path from the laser output to the sample cell is enclosed and the sample cell is covered with a light shield. **Never attempt to operate the laser without having the sample shield in place.**

3. **Photogate Trigger:** Since the signal is weak and the laser is pulsed, we can use pulsed electronics to detect the signal. The laser has a 5 ns jitter (variation in the starting time of the pulses) after the flashlamp fires. In order to eliminate the effects of this jitter on the detection process, a phototransistor is placed in the beam path after it passes through the sample cell. When a pulse strikes the phototransistor, it generates a voltage pulse (trigger) that is used to synchronize the detection electronics with the laser.

4. **Monochrometer:** The scattered light from the sample cell is a mixture of all the Raman lines, plus the intense Rayleigh scattered light. In order to measure the spectrum, the light is resolved into its components with a grating monochrometer, pictured in Figure 3. The diffraction grating is mounted on a motor-driven gear mechanism so that the wavelength reaching the exit slit varies linearly with time. Operation of this motor is described in more detail below. The grating has a spectral range of 3-850 nm. It is calibrated to ± 1 nm and has a linear dispersion of 4 nm/mm (i.e., if the exit slit is 1 mm wide, it will pass a 4 nm wide band of light). The entrance and exit slits are ~ 0.1 mm wide, and thus the bandpass is 0.4 nm.
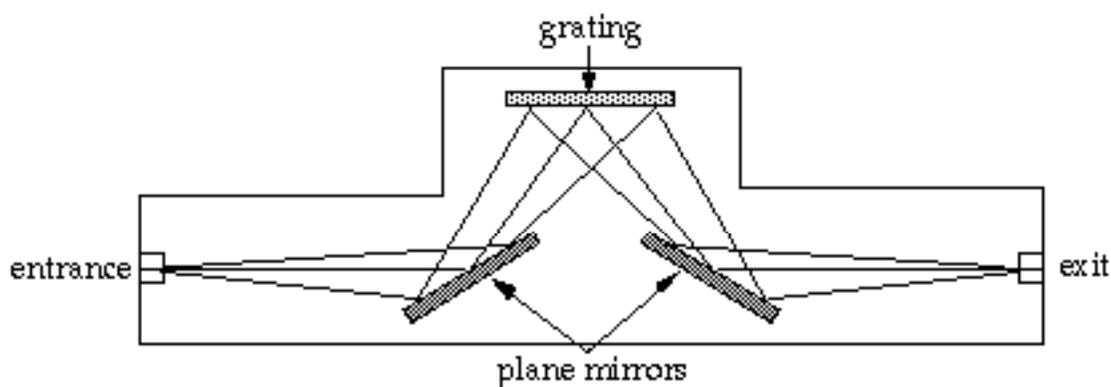
Figure 3: The Grating Monochrometer

The widths of the entrance and exit slits to the monochrometer are fixed (~ 0.1 mm) but the height (8 mm max) can be varied using the "fish-tail" slides located at the each end of the spectrometer. Pushing them all the way in gives maximum height and transmitted light, but reduces the resolution. There is a trade-off between resolution and signal-to-noise and the length of time it takes to perform the experiment (see below).

5. **Monochrometer Drive:** The monochrometer drive has two sets of speeds: fast return speeds and slow operation speeds used during data acquisition. To operate in the fast return speeds the Fast Return switch is set to either INC (increase) or DEC (decrease). Once an initial wavelength is set (either by using the fast return settings or by manually turning the knob on the monochrometer) the drive needs to be in the slow operation speeds. Do this by setting the Fast Return switch to the center position. From here the operation speed is controlled by the speed control to the right. Although the labeled speeds no longer match the actual calibrations, the speeds are sufficiently low enough for data taking, and the three settings still correspond to the highest, middle, and lowest speeds. The Pause button to the far right of the switch area is used to temporarily suspend the motor from running, and the Reset button is used to start the motor again after the Pause button is disengaged. When the motor is running you may note that the wavelength display stops moving. This is caused when a gear ceases to catch within the monochrometer. There is no consistent fix for this problem. The user must adjust the wavelength using the manual knob or fast return speeds on the drive until the motor catches, and then begin taking the spectra again. This lab is an excellent opportunity to work on becoming a more patient person.

6. **Photomultiplier (PM):** The light from the monochrometer is detected with a Hamamatsu phototube, which has a quantum efficiency in excess of 5% over the range 150 to 700 nm (i.e. it detects more than 5% of the photons striking it). The PM is highly sensitive and must be protected from ambient light at all times when the accelerating voltage (800 to 1000 V) is applied to the tube. The tube is equipped with a shutter to be closed whenever the high voltage is on if there is a possibility of ambient light reaching the tube. **Be sure that the high voltage is turned off or the shutter is closed whenever you remove the sample shield to change samples. To avoid damaging the boxcar**

with a voltage pulse from the PM, always turn the high voltage power supply down to zero before turning it off or on.

    7. **Boxcar Integrator:** The output of the PM consists of 5 ns wide, negative pulses, occurring at a rate of 10 pps (pulses per second) and partially obscured by considerable noise generated in the phototube. To obtain a signal with adequate signal-to-noise ratio, we will use two techniques:

The first is signal averaging (or integrating); the PM signal will be integrated over P pulses. Since the desired Raman signal from the PM will always be negative, the integrated signal after P pulses will be P times larger than that of a single pulse. The phototube noise on the other hand will fluctuate randomly with both positive and negative polarity. Thus the integrated noise will partially cancel out. Calculation shows that if P pulses are integrated the signal-to-noise will improve by $\sqrt{P}$. For this experiment you will integrate over 10 to 30 pulses for a S/N gain of 3 to 5.5.

A much more significant improvement in the S/N will be achieved by using a boxcar integrator, an integrating circuit that is gated (turned on) only during the time period when a gate pulse is present. The Raman signal is present for only a small fraction of the time (.000005% of the time for a 5 ns pulse repeated at a 10 pps rate). During the time between pulses there is no useful signal from the PM; if we integrate during this time, we only add noise. Thus by using a boxcar integrator gated to coincide with the PM signal we can integrate only during the short time when the desired signal is present and ignore all the intervening noise.

    8. **Oscilloscope:** An oscilloscope in Single Sequence mode is the best way to record the spectra. In Single Sequence mode, the scope will record data for a pre-determined amount of time and then stop. When the Single Sequence button is pressed, the oscilloscope will arm itself for a few seconds and then wait for a trigger signal to arrive. However, the scope misses lots of data if the trigger output of the boxcar integrator is used as an external trigger for the oscilloscope. (This is because the scope takes a break in between triggers.) Instead, it is possible to force the oscilloscope to take data for the whole time by pressing the Force Trigger button. Nothing will appear on the screen until the data has been recorded (this takes about eight minutes). When the measurement is done, use the Save/Recall button to save the spectra onto a USB flash drive as a .CSV file (this can be opened in Microsoft Excel). There should be a flash drive in the room. (The scope can also be used to view a small range of wavelengths if the trigger is set to auto and the Run/Stop button is used, rather than the Single Sequence button.)

OTHER CONSIDERATIONS:

Coaxial cables: Signals are carried from one part of the spectrometer to another using coaxial cables which confine the signals and protect them from stray electric and magnetic fields. A coaxial cable consists of a thin inner conductor and a cylindrical, coaxial outer conductor that is usually made of braided wire and is flexible. A coaxial cable can be completely characterized by two parameters -- the inductance per unit length

L and the capacitance per unit length C. From L and C you can calculate v, the speed of propagation of a signal on the cable, and R_o, the characteristic resistance of the cable:

$$v = 1/\sqrt{(LC)} \tag{2}$$

$$R_o = \sqrt{(L/C)}. \tag{3}$$

For the cable most commonly used in a research lab (RG58u), a handbook gives $C = 93.5 \times 10^{-12}$ F/m and $R_o = 50$ ohms. Substituting these values into Eqs. 2 and 3 we find that $v = 2.14 \times 10^8$ m/s, about 70% of the speed of light. This gives a transmission delay of 4.7 ns/m.

When using coaxial cables it is important to avoid reflections at the end of the cable. If a cable is terminated with a resistance R, the ratio of the incoming voltage V_i to the reflected voltage V_r is given by

$$V_r/V_i = [R - R_o]/[R + R_o]. \tag{4}$$

The total voltage across the terminating resistance is $V = V_i + V_r$. Three cases are of interest:
1. $R = 0$: Then $V_i = - V_r$ and $V = 0$, as you would expect for a short circuit.
2. $R = \infty$: Then $V_i = + V_r$ and $V = 2 V_i$.
3. $R = R_o$: Then $V_i = 0$ and $V = V_i$.

When $R = R_o = 50$ ohms, the cable is properly terminated and there is no reflected signal. Proper termination is also important for maintaining the lineshape for sharply rising pulses; if the termination is not proper, the rise and fall times for a square pulse will be slowed and the pulse will be broadened.

Timing: The measurement process is initiated by the photogate trigger pulse traveling from the phototransistor to the boxcar. There are a number of sources of delay in the system: the PM cannot respond instantly to the laser pulse, the phototransistor and other electronic circuits do not respond instantly, and there is a propagation delay of about 5 ns/m in the coax cable connecting the PM to the input amplifier. We also intentionally delay the amplified signal by about 30 ns so that when we observe the signal on the oscilloscope, it does not fall at the edge of the screen. We compensate for these delays using an adjustable delay in the boxcar between the time the boxcar receives the trigger pulse and when it generates the gate pulse that initiates the integration. Adjustment of the timing is simple; the gate signal and the delayed PM signal are observed on one of the oscilloscopes and the boxcar delay is adjusted so that the gate pulse coincides with the PM pulse. The width of the gate can also be adjusted to improve the S/N. It should be set narrow enough that it only covers the time when the pulse from the photomultiplier is present but not so narrow that it excludes too much signal. The S/N is sufficiently large that neither the gate pulse delay setting nor the gate-width is critical.

Resolution: The resolution of a spectrometer measures how close in wavelength two spectral features can be before the spectrometer will no longer be able to resolve them as separate features. We saw in the discussion of the monochrometer that the bandpass is ~0.4 nm. Thus we cannot expect to resolve features much smaller than 0.4 nm. But there is another possible limit on the resolution: In order to measure the wavelength dependence of the Raman scattering, the monochrometer grating is rotated so that the wavelength reaching the PM increases linearly with time. The boxcar is the continual average of the signal received from the last P pulses. Thus if P = 100 and the laser pulse rate is 10 pps, the boxcar averaging time is 100/10 = 10 s. In order to avoid distorting the spectrum, the rate at which the wavelength is swept must be slow enough that the spectrum does not change appreciably in 10 s. Thus the resolution depends on the interplay of sweep speed and the number of samples averaged. If, for the example considered above, the monochrometer is swept at its slowest rate of ~2.5 nm/min, then the spectrometer will not be able to resolve features closer than about two or three times 2.5(10)/60 = 0.42 nm. This exceeds the 0.4 nm bandpass and thus degrades the resolution of the spectrometer. In practice, the number of samples averaged should be kept at 30 or less.

PROCEDURE: Because of the safety hazard, the laser beam is entirely enclosed and no adjustments are needed. However, it is wise to take precautions against accidental exposure. **Put on the laser safety goggles.**

A. Remove the sample shield, insert the CCl_4 sample, and **replace the shield.** Check that the shutter protecting the PM is open.

B. Turn the high voltage power supply to "standby". The supply is a vacuum tube unit and needs to warm up for about a minute before being turned to "on". Turn on the SRS power supply, the oscilloscope, and the phototransistor. Be sure that the corridor door is closed; otherwise the interlock will prevent the laser from firing. On the laser power supply turn the key to the "on" position, turn the three-position knob to "start" and press the green power button. The red Interlock LED should go out and the green Emission LED should come on. Turn the three-position knob to 10 Hz. After about 10 s the laser will begin firing. You can recognize when this happens by the clicking sound and the flashing of the green trigger LED on the boxcar. The system is now operating.

C. Set the monochrometer to 355 nm to observe the very strong Rayleigh scattering. The oscilloscope should be set up as shown in Fig. 2. Be sure that the scope inputs are properly terminated with 50-ohm resistors.

    1. First observe the gate pulse on channel A. It should be reasonably square provided the coaxial cable is properly terminated. [Remove the 50-ohm resistor and observe the effect on the signal.] Observe how the gate pulse changes as you change the gate delay and gate width settings on the boxcar.

    2. Now observe the PM signal on channel B. Be sure that the delay box following the amplifier is set to at least 16 ns delay so that the Raman signal does not fall at the edge of the screen. You will see a 5 ns negative superimposed on considerable noise. Notice the oscillatory nature of the noise. This is due to "ringing" within the phototube

and reflections of pulses back and forth through the system. Notice how the signal changes with and without the 50-ohm termination at the oscilloscope.

3. Sweep the monochrometer a few nm off the 355 nm Rayleigh line. Observe how the Raman signal disappears, while the noise remains unchanged.

4. Return to 355 nm and adjust the gate pulse width and delay so that the Raman signal is centered on the gate. You are now ready to record a Raman spectrum.

5. Move the monochrometer below the Rayleigh line. Turn on the oscilloscope and use the boxcar sensitivity to adjust the gain of the signal you observe. (The Rayleigh signal is extremely large compared to the Raman lines and the spectrum will move off the set scale when you use adequate sensitivity to observe the Raman spectrum.) Turn the monochrometer to sweep and record the signal. Pick one Raman line and optimize the signal by adjusting the number of samples averaged, the gate width and delay, and the sweep rate.

D. It takes either ~8 or ~16 minutes to record a spectrum (depending on if you need to do multiple runs with oscilloscope). Perform the following experiments:

1. Record the Raman spectra of carbon tetrachloride (CCl_4) and acetone ((CH_3)$_2CO$) and compare the Raman shifts with the accepted values given in the atlas of Raman spectra (see Readings). Sweep both above and below the 355 nm line to observe the Stokes and anti-Stokes lines.

2. The atlas of Raman spectra shows that the 459 cm^{-1} CCl_4 line is split into at least three components due to differing numbers of ^{35}Cl and ^{37}Cl ions in the various CCl_4 molecules, as discussed above. Likewise, there are closely spaced lines at 762 and 790 cm^{-1}. Attempt to resolve the splittings of these two spectral features by setting the spectrometer for maximum resolution (slow sweep speed, reduced number of samples averaged, reduced slit height). With these settings measure the width (FWHM) of the 218 and 314 cm^{-1} lines for CCl_4. These lines are not split and their measured width reflects the resolution of the spectrometer. In your report, calculate and plot the lineshape for two Gaussian lines with the same FWHM separated by a small distance. Determine the relationship of resolution to linewidth. That is, from your simulation determine how close the two lines can be (expressed in units of FWHM) and still be clearly resolved as two lines.

3. Use Raman spectroscopy and the atlas of Raman spectra to determine the composition of the unknown liquid sample.

4. Organic solvents are a frequent contaminant of ground water. Raman spectroscopy can be used to measure the degree of contamination. Measure the Raman spectrum of the sample marked H_2O+Acetone to determine the percent of acetone. Compare the signal heights of the strongest Raman line in the pure acetone sample with that of the unknown. The two spectra must be taken under identical settings (except for boxcar sensitivity, which must be reduced for the pure acetone sample to obtain an on-scale reading). Water has a very sparse Raman spectrum with a broad shoulder on the 355 nm line, a weak, broad line at ~ 1640 cm^{-1} (377 nm), a strong, broad line at ~ 3400 cm^{-1} (407 nm).

5. The Raman shift is predicted to be independent of the wavelength of the exciting light, although the intensity increases as λ^{-4}. In addition to the 355 nm light in each pulse the YAG laser also concurrently emits some, much less intense light at 532 nm. Attempt to verify this prediction by searching for Raman scattering from the 532 nm pulse in

CCl_4. The signal will be much weaker than for 355 nm scattering and you will need to use maximum spectrometer sensitivity. (Do not attempt to do a general search; calculate where you expect the strongest CCl_4 line to fall and do a careful, high sensitivity search in that region.)

READINGS:

1. DMS Raman/IR Atlas, vols. 1 and 2, ed. by W. Meier, Verlag Chemie 1974. On the reference shelf in the Chemistry Library [QC454.R36 S37]
2. Durig and Sullivan: "Infrared and Raman Spectroscopy" in <u>Determination of Chemical Composition and Molecular Structure--Part A</u> ed. by Rossiter and Hamilton, pp 2-9, 16-21.
3. Straughan: "Infrared and Raman Spectroscopy" in <u>Spectroscopy</u> ed. by Straughan and Walker, pp l38-9, 225-250.3.

TROUBLESHOOTING:

Problem: the wavelength stops changing during a scan. This may be caused by slippage between the shaft and the gear in the motor-driven unit. To correct this tighten the set screw.
If this fails contact Dr. Lu, Hsu-Chang   x3897   room W230.

APPENDIX A: The Nd:YAG Laser. The laser that you will use in this experiment generates very narrow (5 ns), high power (0.8 mW) pulses of ultraviolet light (355 nm) at a pulse rate of up to 20 pulses/s. It works as follows: the lasing medium is a man-made rod shaped single crystal of yttrium aluminum garnet (YAG) doped with a small amount of neodymium. (Garnets are naturally occurring, semi-precious gem stones composed of magnesium aluminum silicate. YAG has the same crystal structure, but with the magnesium replaced with the rare earth yttrium.) The laser resonator is formed by placing the YAG rod between highly reflecting mirrors that reflect photons back and forth through the YAG.
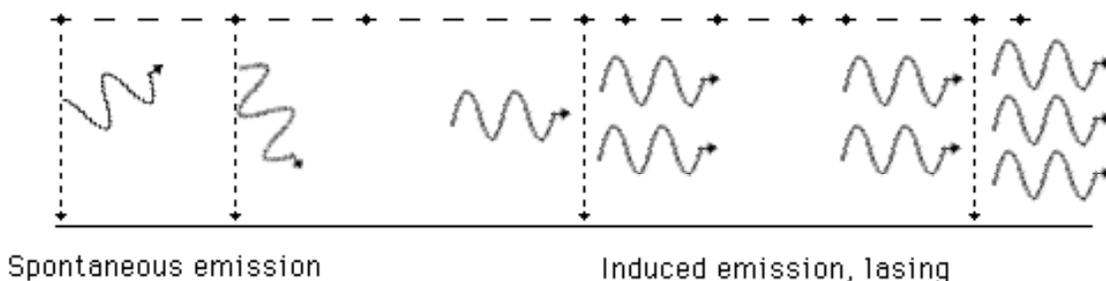

Spontaneous emission   Induced emission, lasing

Figure A1. Principle of Operation of a Laser

The YAG is optically pumped by a brief (~ 0.1 ms), intense flash of light from a flashtube wrapped around the rod. The light excites the Nd electrons to a higher metastable electronic state, which de-excites only slowly by spontaneous emission of

photons. After being pumped for a short while (a few μs) the population of the metastable state becomes large enough that the rate of spontaneous emission of photons exceeds the loss of photons from the YAG. Then the photons begin to stimulate de-excitation of the metastable state (induced or stimulated emission) and the YAG begins to lase, Fig. A1. If this were allowed to happen, the laser output would not be very intense

because the flashlamp has not had time to build up a large number of excited Nd ions and the pulse length would be almost as long as the flash of pumping light. To make an intense, narrow pulse the laser is "Q-switched": The Q, or quality factor, of a resonator is a number proportional to the ratio of the energy stored in the resonator to the energy lost per cycle; a high Q resonator has very low loses. In order to lase, a laser resonator needs to be high Q. To narrow the pulse a Q-switch is introduced into the laser cavity to block spontaneously emitted photons from reentering the YAG until the optical pump has produced a maximum number of excited Nd ions. The switch is then suddenly opened, and the stored energy is released in a very short, intense laser pulse.

The Q-switch works as follows: a vertical polarizer and quarter-wave plate (QWP) are included in the laser cavity. The QWP is adjusted so that it rotates the phase of light passing through it by 45^0. Then when a photon (having passed through the vertical polarizer) passes through the QWP, is reflected by the end mirror, and again passes through the QWP, its phase is rotated by a total of 90^0, and it blocked by the polarizer from reentering the YAG, making lasing impossible. After the population of excited Nd ions reaches a maximum (about 100 μs after the flashlamp starts) a very high voltage pulse is applied to electrodes on either side of the QWP. The potential changes the speed of light through the crystal and (for the proper amplitude pulse) which changes the phase of light traveling through the QWP by an additional 90^0. (This is called the Pockels effect and the device is called a Pockels cell.) These photons can then pass through the vertical polarizer and reenter the YAG to induce lasing. A short, intense laser pulse results.

However, there is one complication. The lasing occurs at a wavelength of 1064 nm, which lies in the infrared. In order to generate a laser pulse at higher frequency, a technique called harmonic generation is used, which converts the 1064 nm photons into 532 nm (second harmonic) or 355 nm (third harmonic) photons. 532 nm photons are efficiently generated when the intense infrared beam strikes a specially chosen crystal that responds non-linearly to the intense electric field generated by the laser beam. The 355 nm beam is generated in a second non-linear crystal that combines 532 and 1064 nm photons.

APPENDIX B: Conversion of Raman wavelength to Raman shift (355nm)

λ (nm)	Raman Shift (cm^1)	λ (nm)	Raman Shift (cm^1)
355	0	405	3478
356	79	406	3538
357	158	407	3599

358	236	408	3659
359	314	409	3719
360	391	410	3779
361	468	411	3838
362	545	412	3897
363	621	413	3956
364	696	414	4014
365	772	415	4073
366	847	416	4131
367	921	417	4188
368	995	418	4246
369	1069	419	4303
370	1142	420	4359
371	1215	421	4416
372	1287	422	4472
373	1359	423	4528
374	1431	424	4584
375	1502	425	4640
376	1573	426	4695
377	1644	427	4750
378	1714	428	4805
379	1784	429	4859
380	1853	430	4913
381	1922	431	4967
382	1991	432	5021
383	2059	433	5074
384	2127	434	5128
385	2195	435	5181
386	2262	436	5233
387	2329	437	5286
388	2396	438	5338
389	2462	439	5390
390	2528	440	5442
391	2594	441	5493
392	2659	442	5545
393	2724	443	5596
394	2788	444	5646
395	2853	445	5697
396	2916	446	5747
397	2980	447	5798
398	3043	448	5848
399	3106	449	5897
400	3169	450	5947
401	3231	451	5996
402	3293	452	6045
403	3355	453	6094

404   3417   454   6143