EXPERIMENT #22

Laser Raman Spectroscopy: Vibrational Spectrum of CCl$_4$

Introduction

Determine the vibrational frequencies of carbon tetrachloride using inelastic light scattering (Raman scattering). With Raman scattering, energy shifts of the scattered radiation are used to determine the normal-mode vibrational frequencies of CCl$_4$. In addition, by varying the polarization of the incident light, the aspects of the symmetry of the vibrational modes can be determined. From the vibrational frequencies and symmetry, it can be deduced which vibrational modes the frequencies correspond to. Using a valence force model, this information can be used to to determine the force constants acting on the C-Cl bond. Finally, by determining the ratio of the Stokes to anti-Stokes scattering, the temperature of the sample can be determined.
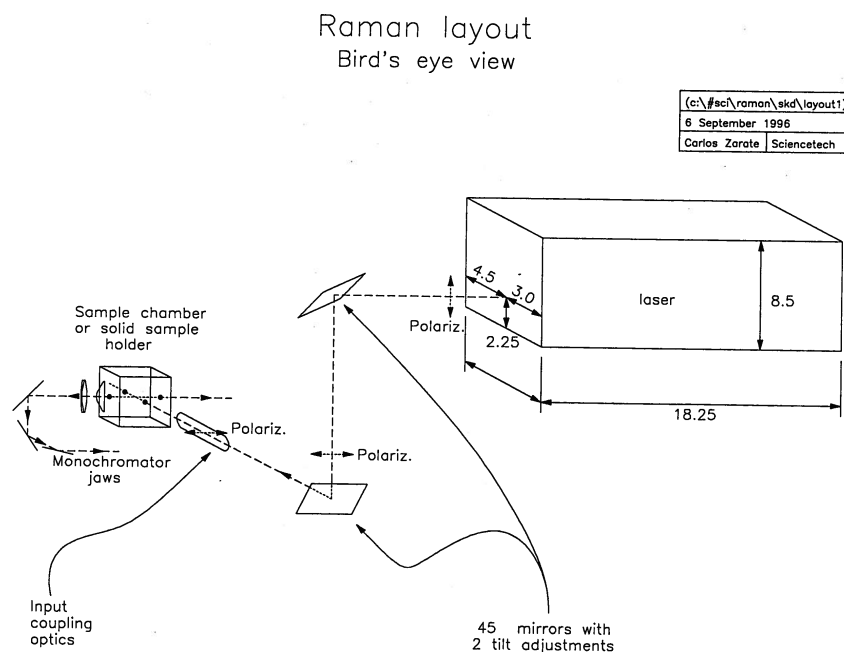
Theory and Background

Background theory on Raman scattering in molecular systems is given in reference 1, sections 1.1 to 1.9. Additional reference material is given in ref. 2 and 3 and appendix A.

Apparatus

This experiment utilizes an argon ion laser as source, a 0.5 m double monochromator to disperse the scattered light, and a photomultiplier as the detector.

Laser: The argon ion laser uses the 488.0 nm laser line and produces light that is linearly polarized with the electric field vector in the vertical direction ($\pm 5^o$). However, before reaching the sample, the light is deflected first downwards and then to the left by two mirrors located in the black mirror column. The first of these reflections rotates the polarization from vertical to horizontal, giving a polarization parallel to the scattering plane. By convention, this polarization is referred to as *p*-like (for parallel). By inserting a half-wave plate into the path of the incident light, the polarization can be rotated 90° to vertical, giving a polarization perpendicular to the scattering plane. By convention, this polarization is referred to as *s*-like (for senkrecht, the German word for perpendicular).

Raman layout
Bird's eye view

Sample chamber
or solid sample
holder

laser

4.5
3.0
Polariz.
2.25
8.5

18.25

Polariz.

Monochromator
jaws

Polariz.

Input
coupling
optics

45 mirrors with
2 tilt adjustments

Figure 1: Layout of Laser relative to the sample chamber. Two mirrors deflect the light downward and to the left, rotating the linear polarization from vertical to horizontal. In our specific experiment, an attenuator and slot to place a polarizer is located between the 2nd 45 degree mirror and the sample chamber.

Monochromator: The spectrometer is a 0.5 m Czerny-Turner double monochromator (Scienetech 9040DA), shown in figure 2. The double monochromator is fitted with two 1800 lines/mm holographically ruled diffraction gratings, which disperse the scattered light from the sample. The gratings rotate in unison and are driven by computer-controlled stepper motors. In addition to the gratings, the spectrometer includes entrance, intermediate and exit slits, as well as several concave and plane mirrors. The spectral resolution of the monochromator is determined the line spacing of the gratings, the geometry of the diffractrometer and size of the entrance and exit slits. In this experiment, the gratings and geometry are fixed, but the entrance and exit slits can be varied to achieve a different spectral resolution.

Note, the monochromator is designed to reject stray light, especially that at the laser wavelength, and so allow relatively weak Raman signals to be detected.
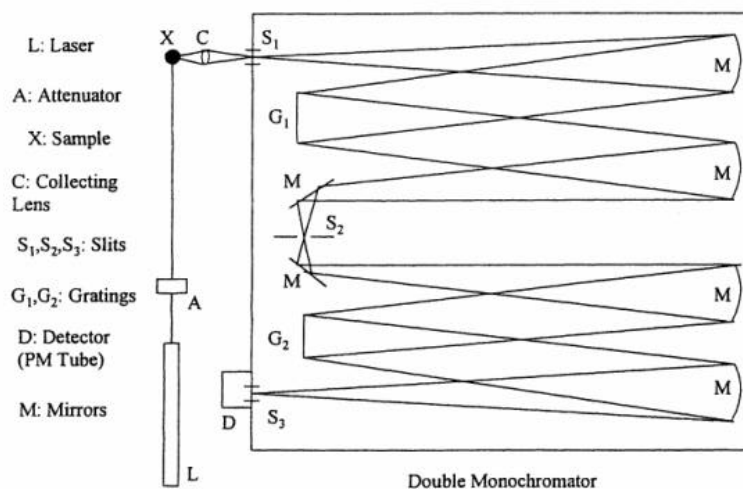
Figure 2: Layout of Double Monochromator. The gratings G_1 and G_2 are rotated by computer-controlled stepper motors during a scan while all other components remain fixed.

Detector: Positioned at the exit slit is a photomultiplier tube detector (Hamamatsu R4220). A photomultiplier tube (PMT) is composed of a photosensitive cathode followed by high-voltage dynodes that multiply electrons via secondary emission onto an anode. The resulting charge can be read out of the electronics. In principle a PMT can be used as a single photon sensitive detector, with a pulse of charge resulting from each detected photon. In this experiment, the PMT is not operated in single photon counting mode. Rather, the measurement electronics integrate over several pulses to produce a voltage pulse that is proportional to the number of incident photons. The gain and the time constant of the electronics can be varied to produce a large signal and reduce noise.

Additional components:
Additional optics: The system has additional optics after the sample stage to collect a large solid angle of scattered light and focus it onto the monochromator entrance slit.

Automatic attenuator: The automatic attenuator is controlled by the computer and makes use of the energy calibration (grating motor position is calibrated to photon energy) to actuate a relay the blanks off the beam when the photon energy is at $\pm$ 20 cm^{-1} of the laser wavenumber. This is necessary to protect the photomultiplier from the strong Rayleigh signals. Note, the attenuator makes a loud "clack" when actuated.

Procedure

Safety issues:

1. The laser beam is directed within transparent tubes to prevent injuries to eyes, hands, etc. Do NOT remove these tubes! Call a demonstrator if you think the beam is misaligned or

if there is any other problem. When changing samples, first put the shutter in the beam and remove it only when the procedure is completed. NEVER look directly at the laser beam or at a strongly scattering sample! Use common sense! If you are not sure, ASK!

2. CCl_4 is a toxic substance and can cause liver and/or kidney damage if ingested or inhaled. The prescribed short-term exposure limit is 20 ppm CCl_4 vapour in air (~125 mg/m^3). In order to reach this limit in a typical laboratory room of 750 m^3 volume, 100 g of liquid CCl^4 would have to evaporate into the atmosphere. Since CCl_4, has a moderately low vapour pressure and is used in small quantities in this experiment, the level of hazard in this experiment should be minimal if reasonable care is taken in handling the CCl_4. Contact the instructor immediately if CCl_4 is spilled during the experiment.

1. Place the cuvette containing CCl_4 in the sample compartment. Replace cap on sample cell.
2. IMPORTANT! Switch on the attenuator box. The automatic attenuator is activated to protect the photomultiplier from –20 to +20 cm^{-1}. Note, even with the automatic attenuator, the attenuated laser peak appears weakly near 0 cm^{-1}. The
3. Turn on the laser:
   a. After it starts, adjust to minimum power.
   b. The laser beam will strike the sample obliquely, so that the directly reflected beam is not collected by the entrance optics. Only radiation scattered near 90° will enter the monochromator.
4. Turn on the detector:
   a. Turn on the high voltage to the photomultiplier. Adjust its value to ~ 1100 V.
   b. Switch to photomultiplier current output and adjust to give a small positive value, if necessary. Use Gain = 10, Time Constant 0.1 s.
5. Computer control of scans:
   a. Start the SCISPEC 2.21 software
   b. To setup a scan, go to Setup:Scan Mode:Energy in the drop-down menu. Use the following scan parameters for CCl_4.
      - Start Energy: –850 cm^{-1}
      - Stop Energy: +400 cm^{-1}
      - Step Size: 1.0 cm^{-1}
      - Dwell Time: 500 msec
      - Signal Average 500
      - Scan Average 1
      - Single Sample Scan.
   c. To acquire a scan, go to: Acquire:Sample in the dropdown menu. (During the scan, click screen to give automatic scaling of intensities.)
   d. Save the file to disk.
6. Insert the half-wave plate (polarization rotator) in the incident beam and rescan the spectrum.

Shut-down Procedure

(1)   Turn off the laser. (The cooling fans will run for a few minutes, then shut down.)
(2)   Turn off the high voltage to the photomultiplier.
(3)   Turn off the automatic attenuator.
(4)   Click File → Exit → Exit Windows.

(5)   Turn off computer and monitor.
(6)   Place the two samples in their stand-by location

Analysis and Discussion

1. Determine the peak energies and depolarization ratios of fundamentals of CCl_4. Determine the uncertainty of the peak positions and depolarization ratios.

2. Assign the fundamentals of CCl_4 to the modes depicted in figure 3. To assign the modes, use the fact that the stretching motions are expected to occur at higher frequencies than the bending motions. The depolarization ratios can be used to determine with of the two high-frequency bands should be assigned to v_1. To decide on the v_2 and v_4 assignments, use the fact that the only infrared band observed below 600 cm^{-1} is a feature near 300 cm^{-1} (explain this reasoning from the differences between infrared and Raman spectroscopy).
    The v_3 vibration will be observed as a doublet due to a phenomena called Fermi resonance splitting, a process that can occur if an overtone or combination energy level happens to fall near the energy level of a fundamental vibration and if both levels have the same symmetry. The v_3 frequency can be taken as the mean of the doublet peaks. From your values of v_1, v_2 and v_4 determine which combination band is involved in the Fermi-resonance with v_3.
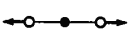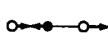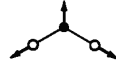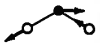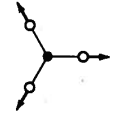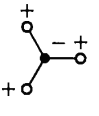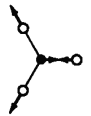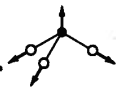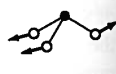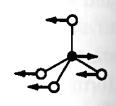
3. Tabulate the Stokes and anti-Stokes frequencies and intensity ratios I_{AS}/I_S. The intensity ratio of the Stokes to anti-Stokes peaks is predicted to be:
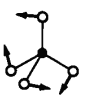
$$\frac{I_{AS}}{I_S} = \left(\frac{v_0 + v_i}{v_0 - v_i}\right)^4 \exp\left(\frac{-hv_i}{k_B T}\right). \qquad (1)$$

    where v_i is the vibrational frequency, v_0 is laser frequency. Using eqn. 1, determine the vibrational temperature characterizing the Boltzmann distribution. Does the vibrational temperature that you deduce agree with the ambient temperature?

TABLE 1 Normal modes of vibration for several molecular types

TYPE	POINT GROUP	VIBRATIONAL MODES,[a] SYMMETRIES, INFRARED-RAMAN ACTIVITIES, AND RAMAN POLARIZATIONS[b]			
B—A—B	$D_{\infty h}$	ν_1 Σ_g^+ (Rp)	ν_{2x} ν_{2y} Π_u (IR)		ν_3 Σ_u^+ (IR)
A with B, B (C_{2v} bent)	C_{2v}	ν_1 A_1 (IR, Rp)	ν_2 A_1(IR, Rp)		ν_3 B_1 (IR, Rdp)
B, A—B, B	D_{3h}	ν_1 A_1' (Rp)	ν_2 A_2'' (IR)	ν_3 E' (IR, Rdp)	ν_4 E' (IR, Rdp)
A with B, B, B (C_{3v})	C_{3v}	ν_1 A_1 (IR, Rp)	ν_2 A_1 (IR, Rp)	ν_3 E (IR, Rdp)	ν_4 E (IR, Rdp)
B, A with B, B, B (T_d)	T_d	ν_1 A_1 (Rp)	ν_2 E (Rdp)	ν_3 F_2 (IR, Rdp)	ν_4 F_2 (IR, Rdp)

[a] Only one of two E or three F modes in the respective degenerate sets is shown for the AB_3 and AB_4 cases. Each mode of a degenerate set oscillates at the same frequency, and the description of the nuclear motion associated with each component of a degenerate mode is somewhat arbitrary.

[b] Rp indicates an allowed Raman band that is polarized; Rdp indicates an allowed depolarized Raman band.

Figure 3: Vibrational modes for different types of molecules. Figure taken from ref. 2.

4. Test the valence force and central force models (see Appendix A). Determine the valence force constants k and k_δ/l^2 using eqn.'s (3) and (4) and check against eqn.'s (5) and (6), comparing RHS and LHS of these equations. Similarly determine the values of k_1, k_2 and k' in the central force model and check your results by comparing the LHS and RHS of eqn. (10). Comment on which model best describes your measurements and whether your data allows you to distinguish the models.

5. Consider isotope shifts for CCl_4. The natural abundance of $^{35}Cl:^{37}Cl$ is 75.5:24.5. Calculate the relative intensities and frequencies you expect for the different isotope components of the ν_1 mode and compare these with your observations.

References

1. *Introductory Raman Spectroscopy, 2nd edition. J. R. Ferraro, K. Nakamoto and C. W. Brown, Amsterdam ; Boston : Academic Press, 2003. (available as ebook.)*
2. *Experiments in Physical Chemistry, 6th edition.* D. P. Shoemaker, C. W. Garland and J. W. Nibler. New York: McGraw-Hill, 1996.
3. Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra. G. Herzberg, Van Nostrand: Princeton, New Jersey, 1968. (pg. 159-183)

Appendix A: Force Models of CCl_4 (adapted from ref. 3)

Valence force model

In the simplest harmonic oscillator model, the valence force model, the molecule is modelled as if there is a strong restoring force (springs) in the line along the valence bonds connecting the C and each Cl atom that depends on the distance between the two atoms in the bond. In addition, there is a restoring force opposing a change in the angle between two valence bonds connecting one atom with two others. The potential energy of CCl_4 in this model can be written as

$$U = \frac{1}{2}k\left(r_1^2 + r_2^2 + r_3^2 + r_4^2\right) + \frac{1}{2}k_\delta\left(\delta_{12}^2 + \delta_{13}^2 + \delta_{14}^2 + \delta_{23}^2 + \delta_{24}^2 + \delta_{34}^2\right), \qquad (2)$$

where r_i is the change in the length of the C-Cl bond i from its equilibrium value l and δ_{ij} s the change in the angle between bonds i and j. From classical mechanics, one obtains the following relations between the vibrational frequencies and the force constants k and k_δ/l^2:

$$4\pi^2 v_1^2 = \frac{k}{m_{Cl}}, \qquad (3)$$

$$4\pi^2 v_2^2 = \left(\frac{3}{m_{Cl}}\right)\frac{k_\delta}{l^2}, \qquad (4)$$

$$4\pi^2\left(v_3^2 + v_4^2\right) = \left(1 + \frac{3m_{Cl}}{4m_C}\right)\frac{k}{m_{Cl}} + \left(1 + \frac{8m_{Cl}}{3m_C}\right)\left(\frac{2}{m_{Cl}}\right)\frac{k_\delta}{l^2}, \qquad (5)$$

$$16\pi^2 v_3^2 v_4^2 = \left(1 + \frac{4m_{Cl}}{m_C}\right)\left(\frac{2}{m_{Cl}}\right)\frac{k_\delta}{l^2}\frac{k}{m_{Cl}}. \qquad (6)$$

where $v_i = c\omega_i$ is the frequency of the scattered light from the laser frequency, where ω_i is the frequency expressed in wavenumbers (cm^{-1}), $l = 1.77$Å is the bond length in CCl_4; and m_{Cl} and m_C should be expressed in grams using $1.660531(1)\times10^{-24}$ gr/amu.

since there are 2 force constants and 4 frequencies, the problem is over constrained. This allows one to test the validity of the model by determining k and k_δ from both (3) and (4) and from (5) and (6).

Central force model

In the central force model, it is assumed that each atom exerts a force on every other atom along lines connecting the centers of the atoms. Each force is treated as harmonic (obeying Hooke's law) but the forces are not necessarily zero at equilibrium (only the net force is zero at equilibrium). In this model the forces between Cl atoms is $F_{Cl-Cl} = a - k_1 Q_{ij}$, where Q_{ij} is the displacement from the equilibrium distance t between Cl atoms i and j, and the force between C and Cl atoms is $F_{C-Cl} = -b - k_2 R_i$, where R_i is the displacement distance of the C from Cl atom i. At equilibrium ($R_i = 0$ and $Q_{ij} = 0$), the net force must be zero and it follows from the forces that $b = \sqrt{6}a$. From the forces and the relation between a and b, the potential energy of CCl$_4$ in the central force model is:

$$V = -a \sum_{ij} Q_{ij} + \sqrt{6}a \sum_i R_i + \frac{1}{2} k_1 \sum_{ij} Q_{ij}^2 + \frac{1}{2} k_2 \sum_{ij} R_i^2 \qquad (7)$$

Solving equation (7) for the normal modes leads to the flowing set of equations:

$$4\pi^2 v_1^2 = \frac{k_2}{m_{Cl}} + 4 \frac{k_1}{m_{Cl}}, \qquad (8)$$

$$4\pi^2 v_2^2 = \frac{k_1}{m_{Cl}} - \frac{k'}{m_{Cl}}, \qquad (9)$$

$$4\pi^2 \left(v_3^2 + v_4^2 \right) = \frac{2k_1}{m_{Cl}} + \frac{4m_{Cl} + 3m_C}{3m_C m_{Cl}} k_2 - \frac{2\left(3m_C + 16m_{Cl}\right)}{3m_C m_{Cl}} k' \quad (10)$$

$$16\pi^4 v_3^2 v_4^2 = \frac{2\left(4m_{Cl} + m_C\right)}{3m_C m_{Cl}^2} \left(k_1 k_2 - 8k_1 k' - 5k_2 k' - 8k'^2\right). \quad (11)$$

where $k' = -a/t$. Combining (7), (8) and (9) gives

$$4\pi^2 \left(v_3^2 + v_4^2 \right) - \frac{4m_{Cl} + 3m_C}{3m_C} 4\pi^2 v_1^2 - \frac{2\left(3m_C + 16m_{Cl}\right)}{3m_C} 4\pi^2 v_2^2 = -\frac{4\left(m_C + 4m_{Cl}\right)}{m_C m_{Cl}} k_1, \quad (12)$$

which can be used to determine k_1.