

Raman Spectroscopy: Polarizing Filters

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Vibrational modes of Carbon Tetrachloride (CCl_4) and quartz molecules were investigated using depolarization ratios for Raman spectra. It was found that all three of the CCl_4 modes visible in the spectrum were symmetric. Sources indicated that two other vibrational modes are present in CCl_4 that were not found in this data. The only vibrational mode visible in the quartz spectrum was found to be symmetric, for which no comparable data could be found.

I. INTRODUCTION

One way to examine the molecular structure of a substance is to irradiate it with a monochromatic laser and measure the frequencies of the scattered photons [1]. Raman scattering, so called because it was first used by C. V. Raman in 1928,^{1 2} gives the experimenter information about the rotational, vibrational, and electronic levels of the molecules in the substance [2]. One particularly interesting application of Raman spectroscopy involves using polarizing filters to find symmetric or non-symmetric normal modes of the molecules in a sample [3].

This experiment examines the scattering properties of Quartz (SiO_2) and Carbon Tetrachloride (CCl_4) using Raman spectroscopy. After collecting the initial spectrum for both samples, a polarizing filter was placed between the sample and the detector, and separate spectra were taken. Comparing these polarized spectra provides information about the normal modes of CCl_4 and quartz molecules.

II. THEORY AND EXPERIMENTAL DESIGN

A Raman spectrum is created by irradiating a sample with a laser and detecting the scattered light with a spectrometer. An overview of Raman and Rayleigh scattering (A) and of the depolarization ratio (B) will give the reader the tools necessary to analyze the collected spectra taken by the methods outlined (C).

A. Raman and Rayleigh Scattering

In Raman scattering, light excites a molecule from the ground state to a “virtual” energy state, and then when this molecule relaxes to the ground state (or another vibrational state) it emits a photon. A Raman spectrum can pick up three different kinds of energy transitions:

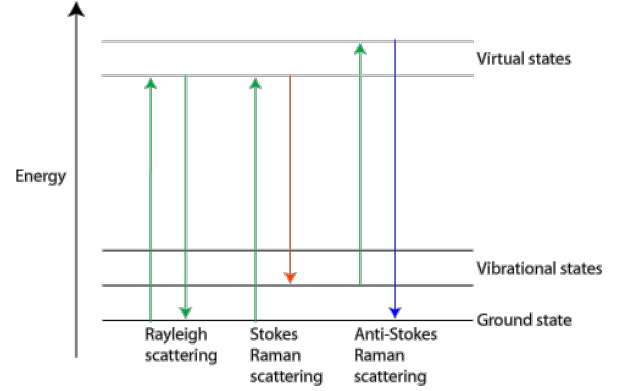


FIG. 1: Energy transitions for Rayleigh and Raman scattering. Adapted from http://www.doitpoms.ac.uk/tlplib/raman/raman_scattering.php

Rayleigh scattering, anti-Stokes scattering, and (most importantly) Stokes scattering [4]. These last two types of scattering are more broadly referred to as Raman scattering.

An incoming photon imparts energy equal to

$$E = h\nu_{\text{laser}} \quad (1)$$

on a molecule, where h is Planck’s constant and ν is the frequency of the light (in this case, the laser). The left-most arrow in Fig. (1) shows the molecule jumping from the ground state to the virtual state of energy $E = h\nu$, after interacting with the photon. In Rayleigh scattering the molecule drops back to the ground state (downwards green arrow), so energy is thus conserved in this elastic collision between the photon and the molecule. This means that the photon released is of the exact same frequency as the original incident photon and

$$\nu_{\text{Rayleigh}} = \nu_{\text{laser}} \quad (2)$$

In Stokes scattering there is the exact same jump to energy $E = h\nu$ caused by the photon, but this time when the molecule relaxes it drops down to the first vibrational state (downwards red arrow), not the ground state. If the difference in energy between the ground state and the first vibrational state is given by ΔE , then the frequency of the emitted photon is

¹ A feat that won Raman the Nobel prize in 1930.

² Though Raman and his student K. S. Krishnan were the first to use it, the technique was predicted by Adolf Smekal in 1923. Also in 1928, it was discovered independently by Grigory Landsberg and Leonid Mandelstam.

$$\nu_{\text{Stokes}} = \frac{h\nu_{\text{laser}} - \Delta E}{h}. \quad (3)$$

Finally, anti-Stokes scattering has to do with the (relatively few) molecules that already start out in the first vibrational state. From here the photon boosts the molecule to the virtual state $E = h\nu + \Delta E$ (where ΔE refers to the difference in energy in from the ground state and the first vibrational state). So when it drops down to the ground state (downwards blue arrow), the molecule emits a photon of frequency

$$\nu_{\text{antiStokes}} = \frac{h\nu_{\text{laser}} + \Delta E}{h}. \quad (4)$$

Rayleigh scattering creates a photon of identical frequency of the incoming photon, Stokes emission creates a photon of frequency less than the incoming photon, and anti-Stokes emission creates a photon of greater frequency than the incoming photon. By measuring the counts of photons at each frequency across a range of frequencies, one creates a spectrum with peaks corresponding to points of Rayleigh and Raman scattering. Because most molecules start out in the ground state and the most probable relaxation is all the way to the ground state, the tallest peak (greatest number of photons) is usually the Rayleigh peak, followed by the Stokes emission peaks, and finally the anti-Stokes emission peaks.

B. Depolarization

All of the photons coming from the laser are polarized in the same direction. After the photons interact with the sample, their polarizations may change. One way to measure how much their polarizations change is with the depolarization ratio, ρ , defined as

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad (5)$$

where I_{\parallel} is the intensity of the light (proportional to photon count) of parallel polarization and I_{\perp} is the intensity of the light that is perpendicular to the original laser.

It turns out that the depolarization ratio is affected by the symmetry of the vibrations that cause scattering. A depolarization ratio of less than 0.75 is called a polarized band, and means that the vibrational mode of the molecule is totally symmetric. A depolarization ratio of 0.75, or a depolarized band, means that the vibrational mode is not symmetric [4].

For CCl_4 , a tetrahedral molecule, there are two major symmetrical vibrational modes: symmetric stretch and symmetric bend. The two major non-symmetrical vibrational modes are: asymmetric stretch and asymmetric bend.

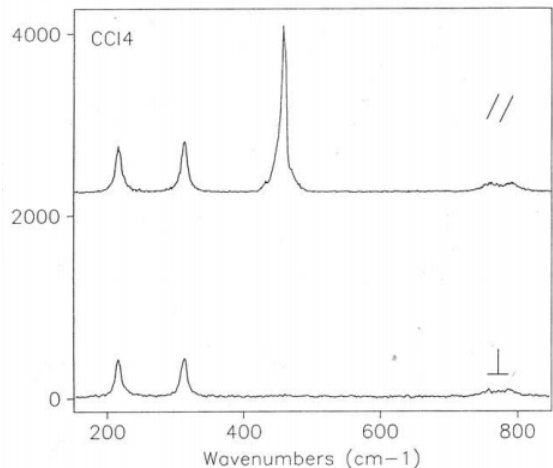


FIG. 2: Strommen's Raman spectrum for CCl_4 for parallel (//) and perpendicular (\perp) orientations of the polarizing filters. Spectrum was taken with a laser of $\lambda_0 = 4880$, a 100-mW power, and 2 cm^{-1} resolution. Adapted from Strommen (J. Chem. Educ., vol 69, p. 804. 1992).

It is worth mentioning the experiment carried out by D.P. Strommen (after which this investigation is modeled), in which the depolarization ratios of the Stokes peaks of CCl_4 were analyzed. A plot of the intensity of scattered light as a function of the wavenumber for parallel and perpendicular orientations of the polarizing filter, is shown in Fig. (2). The peaks at 218 cm^{-1} and 314 cm^{-1} seem to change very little in terms of overall height despite a 90 degree rotation, and the spectrum shows that these have depolarization ratios of about 0.75. The third peak at 459 cm^{-1} clearly has a depolarization ratio much less than 0.75. Finally, between $760\text{-}792 \text{ cm}^{-1}$, there is a tiny, fourth and final peak [5][6].³ Thus for CCl_4 , there are three clear peaks and one small one. The first two represent non-symmetric vibrational modes, the third one represents a symmetric vibrational mode, and Strommen does not indicate what his results were for the fourth peak.

C. Experimental Design

Spectra were taken of CCl_4 and quartz with an added polarization filter at varying angles.

The experimental setup is shown in Fig.(3). An Argon INNOVA 90C Series Ion laser produced a (blue) laser beam of wavelength $\lambda_0 = 4880 \text{ \AA}$. The photons were redirected by a mirror aimed at the sample, either a cu-

³ This final peak may not be incredibly obvious in these two spectra, but other sources (including the original spectra recorded by Raman and Krishanan for CCl_4) confirm its existence.

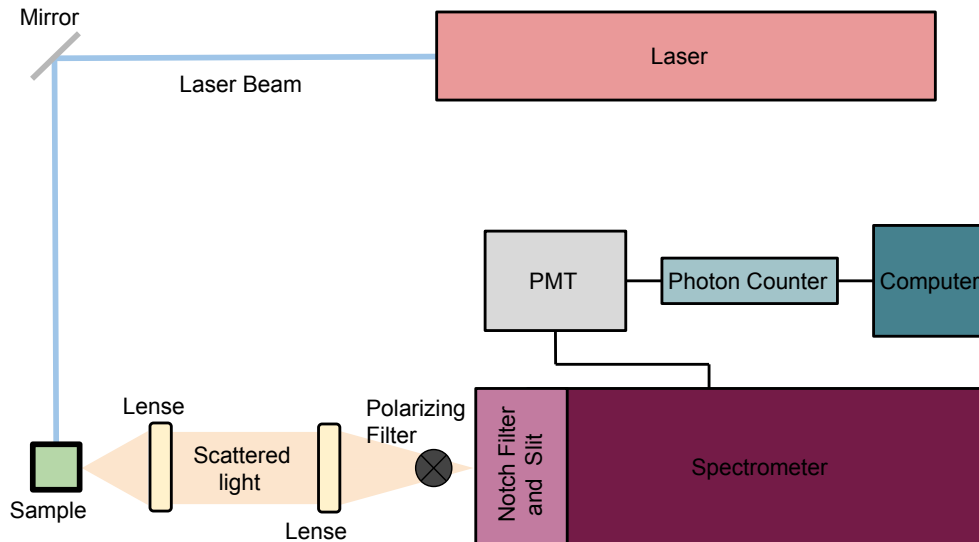


FIG. 3: A diagram of the experimental setup.

vette of CCl_4 or a quartz crystal. The quartz crystal was placed in exactly the same position for every trial to prevent crystal orientation from affecting the spectra (though no effects were found even when this variable was examined). From the sample, scattered light is collected and carried by two lenses, set up at a 90° with respect to the laser beam hitting the sample. This setup up is the most basic (no beam splitters or other devices required), and is effective because it allows an optimum number of photons through [7]. The photons then passes through the polarization filter, and then to the spectrometer. At the mouth of the spectrometer is the notch filter which blocks the very specific wavelength of $\lambda_0 = 4880 \text{ \AA}$. This means that the data will not have a Rayleigh scattering peak, because all of the photons of this wavelength are blocked before entering the spectrometer. An adjustable slit is also found at the mouth of the detector. This slit is controlled by turret dials, and controls the max resolution as well as the intensity of the light (which in turn affects the time needed to take a spectrum). Every millimeter affects the spectrum resolution by 8 \AA .

Once inside the spectrometer's body, the light is reflected off of a mirror towards a grating. The grating only reflects light of a very specific wavelength towards a photomultiplier tube, which converts the photons into an electrons which is then multiplied many times over. The current from the PMT is directed towards a photon counter. Everytime the voltage exceeds a setpoint, the photon counter counts one photon. This information is transferred to LabVIEW program, which collects the data.

The spectrometer counts the photons for one wavelength, which is controlled by the diffraction grating. After counting the photons for one wavelength, it switches

to the next wavelength, eventually cycling through all of the values in the spectrum. Spectra were taken from 4880 \AA (the wavelength of the laser), until 5400 \AA (after which no noticable peaks could be found). Taking data below 4880 \AA would have turned up anti-Stokes peaks, which are much trickier to interpret.

Even though the depolarization ratio only requires that one take measurements with the polarizing filter at 0° and 90° , it was decided that spectra would also be taken at 45° and (for quartz only) 60° , out of curiosity.⁴

III. DATA ANALYSIS

The data collected in LabVIEW showed the photon counts as a function of wavelength. The wavelength was converted to wavenumber, by taking its inverse. Taking the difference between the wavenumber of each data point and the wavenumber corresponding to the wavelength of the laser ($\lambda_0 = 4880 \text{ \AA}$ with wavenumber $\nu_0 = 20,492 \text{ cm}^{-1}$) provides the experimenter the Raman shift. This allows for a standard comparison of peaks; the peak is found a specific wavenumber from the laser's peak. The y axis shows the photon counts, which is proportional to intensity.

The Raman spectrum for CCl_4 (with 0° and 90° polarizing filters) is shown in Fig. (4). A Raman spectrum for quartz (again with both polarizing filter orientations) is shown in Fig. (5). It should be noted that the quartz

⁴ Plots including these polarizations can be found on the attached Mathematica Notebook.

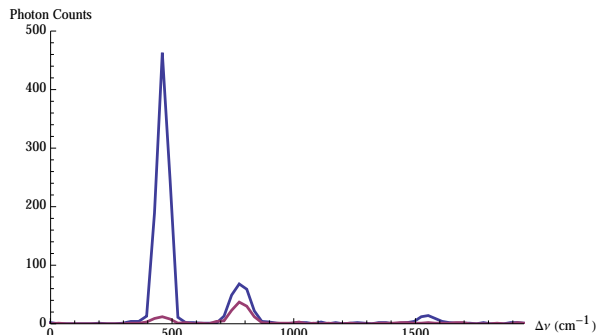


FIG. 4: Raman spectrum for CCl_4 excited by laser of wavelength $\lambda_0 = 4880 \text{ \AA}$ which corresponds to a wavenumber of $\nu_0 = 20,492 \text{ cm}^{-1}$. The x-axis shows $\Delta\nu = \nu - \nu_0$, which represents a shift of ν_0 so the numbers correspond to the Raman shift. The polarization was at 0° for the purple line and 90° for the pink line.

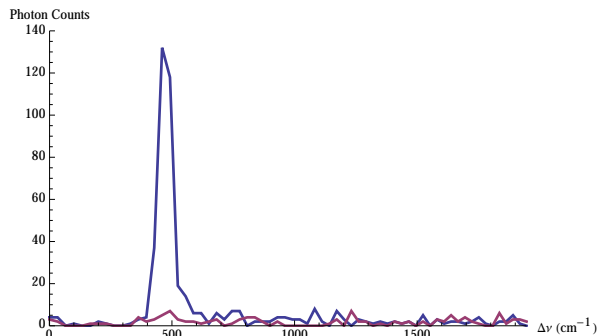


FIG. 5: Raman spectrum for quartz excited by laser of wavelength $\lambda_0 = 4880 \text{ \AA}$ which corresponds to a wavevector of $\nu_0 = 20,492 \text{ cm}^{-1}$. The x-axis shows $\Delta\nu = \nu - \nu_0$, which represents a shift of ν_0 so the numbers correspond to the Raman shift. The polarization was at 0° for the purple line and 90° for the pink line.

spectra look much noisier because the y-axis is scaled differently; both samples had about the same amount of noise.

The depolarization ratios were computed by two methods to ensure consistency. The first method involved comparing the intensities at the highest peak (which was at the same wavelengths in every case). The second method involved averaging the data for the entire peak, not just the highest point. Reassuringly, both methods found similar results. The depolarization ratios for CCl_4 are shown in Table I and for quartz in Table II.

For CCl_4 , all peaks had a depolarization ratio less than 0.75, which indicates that all three vibrational modes found on this spectrum are symmetric. It should be noted however, that the Raman spectrum collected in this investigation (Fig. (4)) varied considerably from the spectrum found in other sources. Comparing against the experiment carried out by Strommen discussed in II.B and shown in Fig. (2), we see that both spectra have a large peak at 459 cm^{-1} and a small peak at $762\text{-}790$

TABLE I: Depolarization ratios for the three peaks in the CCl_4 spectrum, calculated with two different methods.

	Peak 1	Peak 2	Peak 3
Tallest Point Ratio	0.03	0.54	0.14
Mean Peak Ratio	0.09	0.49	0.22
Average of Both Methods	0.06	0.54	0.18

TABLE II: Depolarization ratios for the only peak in the quartz spectrum, calculated with two different methods.

	Peak 1
Tallest Point Ratio	0.05
Mean Peak Ratio	0.08
Average of Both Methods	0.07

cm^{-1} , the former which behaves as expected under a 90° rotation of the polarization filter. The spectra in this investigation, however, are missing two crucial peaks at 314 and 218 cm^{-1} . Strommen shows these peaks to indicate non-symmetric vibrational modes, because their depolarization ratios are at about 0.75. Our spectrometer did not even pick up little blips at these wavenumbers, despite scanning the relevant ranges.

For quartz, the lone peak had a depolarization ratio less than 0.75, so the vibrational mode was again symmetric.

IV. CONCLUSION

The data collected for CCl_4 found one peak at 459 cm^{-1} and another at $762\text{-}790 \text{ cm}^{-1}$. The depolarization ratio of the former peak was 0.06 and of the latter peak was 0.53; both were less than 0.75 indicating symmetric molecular vibrational modes. The other peak was so far out (1550 cm^{-1}), that it usually is not reported on most Raman spectra. It's depolarization ratio of 0.18 also implied a symmetric vibrational mode.

The spectrometer only recorded two of the four expected peaks for a CCl_4 Raman spectrum. Despite scanning the appropriate ranges across multiple laboratory sessions, adjusting the slit width, and adjusting the resolution (in LabVIEW), no trace of these peaks could be found. Thus, it is unknown what could have caused the omission of the peaks, or what could be done to find them.

In quartz, the one peak had a depolarization ratio of 0.07, so it is another symmetric molecular vibrational mode. However, it is expected that these Raman spectra are also incomplete; possibly missing peaks at the range less than 450 cm^{-1} for the same reason the CCl_4 spectra were missing peaks at this range. This shouldn't be reason to discount the peak that was found.

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