

Using Laser Raman Spectroscopy to Measure the Vibrational Modes of Carbon Tetrachloride and Cyclo-Octasulfur

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Abstract

Here we measure the Raman scattering intensity spectra for light polarised perpendicular and parallel to the scattering plane for samples of Carbon Tetrachloride and Cyclo-Octasulfur. Wavenumber shift values for vibrational modes of the molecules were found close to but not within uncertainties of known values, and depolarisation ratios were calculated. The vibrational temperature of the Carbon Tetrachloride was calculated to be $305.8 \pm 0.6 K$, and it was found that the central force model is a better fit for Carbon Tetrachloride molecules than the valence force model.

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1 Introduction

In 1928 Sir C.V. Raman and K.S. Krishnan demonstrated the inelastic scattering of light from a fluid, work that would later earn Raman a Nobel prize.

The scattering technique which now bears his name was first performed using filtered sunlight and photographic plates, though modern technologies have made the method more accessible with the development of lasers and charge-coupled devices. A spectrum of the scattering intensities at different wavelengths can be used to identify a material by comparing it to spectral libraries. This technique is more versatile than IR spectroscopy, as it can be used on solids, liquids and gases, including samples within glass containers or where the substance is in solution, as infrared wavelengths would be absorbed by glass and water.[1]

Interpretation of a Raman spectrum can provide information on the vibrational modes of polyatomic molecules, such as their frequencies and energies.[2] This experiment will aim to use a double monochromator and 488.0nm Argon laser to record the Raman spectra for Carbon Tetrachloride (CCl_4) and Cyclo-Octasulfur (S_8) with two perpendicular polarisations, in order to find their vibrational mode frequencies and test two atomic force models. The peak intensities will also be used to estimate the temperature of the samples from the spectra.

2 Theory

Light incident on a material will be elastically scattered in all directions, which is called Rayleigh scattering and is responsible for the blue skies and red sunsets on Earth. This occurs because the oscillating electric field of the EM wave induces an electric dipole moment in the particle,

$$P = \alpha E \tag{1}$$

proportional to the electric field and the polarisability α of the particle. If the polarisability at the equilibrium position of the particle changes with small displacements, the dipole will also scatter light inelastically, with wavelengths above or below that of the incident light by an amount dependent on the frequency of a vibrational mode of the molecule. When the scattering intensity of monochromatic light is plotted for a range of wavelengths, these high intensity regions are called Stokes and Anti-Stokes lines and correspond to frequencies of $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ respectively, where ν_0 is the frequency of the light source and ν_m is the frequency of the vibrational mode.[2] Compared to Rayleigh scattering the intensity of the light scattered this way is very low, so lasers are typically used as a monochromatic and high intensity light source.

Polyatomic molecules consisting of N atoms will have $3N$ degrees of freedom, however in 3D space 3 of these correspond to translations and 3 more for rotations, leaving $3N - 6$ internal degrees of freedom corresponding to vibrational modes.[2]

The frequency ν , wavelength λ and wavenumber $\tilde{\nu}$ of the scattered light are all related by

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \quad (2)$$

where c is the speed of light constant. In Raman spectra it is conventional to consider the wavelength of light as a relative wavenumber or wavenumber shift, which is the difference in wavenumber from that of the source light. These shift values will be negative for Stokes lines and positive for Anti-Stokes lines, but should be of the same magnitude for each.

The symmetry of a normal vibration will affect how intensely it will scatter light polarised parallel to the scattering plane (P-polarised) compared to perpendicular polarised light (S-polarised). A quantity called the depolarisation ratio, ρ , is given by the ratio of the intensity of a Stokes line with S polarised light to the intensity of the corresponding line with P polarised light,

$$\rho = \frac{I_S}{I_P} \quad (3)$$

3 Experimental Details

The apparatus used in the experiment was set up as shown in Figures 1 & 2, with the 488.0nm Argon laser being reflected by two mirrors at 45 degrees to give a horizontally polarised beam, which strikes the sample obliquely and sends scattered light of various wavelengths into the double monochromator spectrometer, which would select a specific wavelength and output a voltage from a photomultiplier proportional to the number of incident photons with that frequency. The spectrometer was controlled by software on a computer, which was able to take voltage readings for different wavelengths automatically, stepping through the desired range. The sample was contained within an opaque box, with a lid that was kept on whilst the sample was being analysed. This served to prevent most of the light from outside of the experiment from getting into the monochromator. The monochromator input was positioned such that only light scattered by 90 degrees would enter it. An automatic attenuator between the mirrors and the sample box would shut off the laser at wavelengths close to that of the laser, to avoid measuring the

very strong Rayleigh scattering from the samples, which could damage the detector. A shutter plate was placed after the mirrors whilst samples were being changed, so that the laser would not reach the sample chamber when it was open. A 100:1 attenuator plate after the mirrors was used for the Sulfur sample to reduce the laser intensity incident on it, as it scatters very strongly. After reflecting off the second mirror, the light would be horizontally polarised (s-polarised), so to measure the Raman spectra for vertically polarised (p-polarised) light, a rotator plate was inserted just after the mirrors.

Raman spectra were recorded for both polarisations for each of two samples, one of solid Cyclo-Octasulfur (S8) and one of liquid Carbon Tetrachloride (CCl₄).

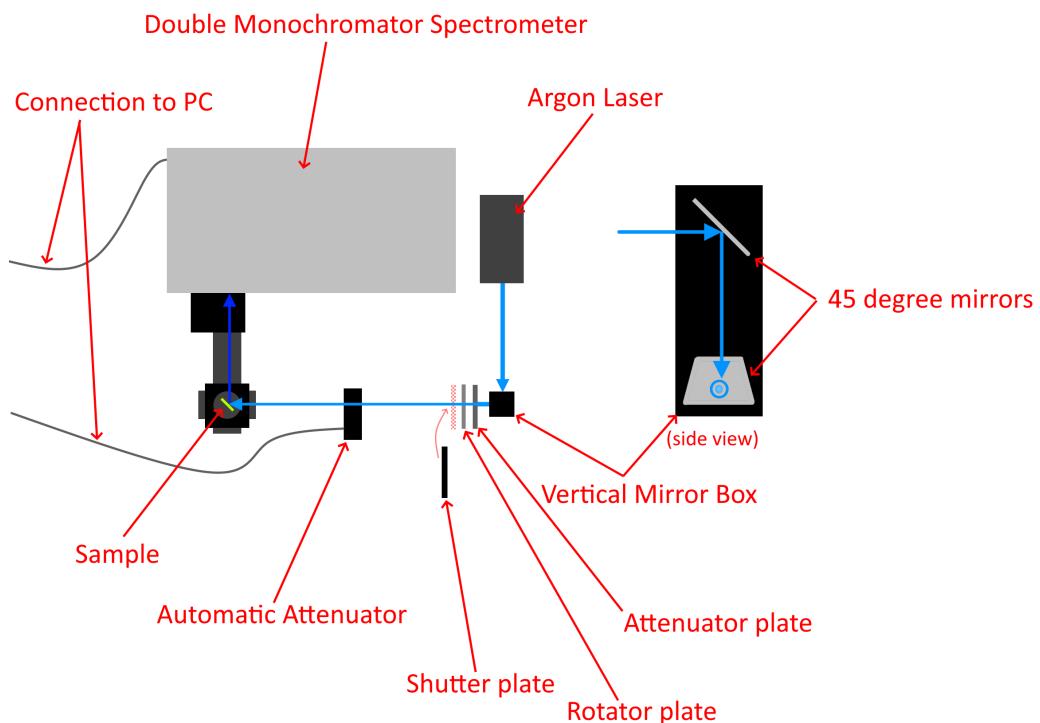


Figure 1: Schematic of experimental apparatus.

Mode	Known Shift Value	S-spectrum	P-spectrum
ν_1	475	477.4 ± 0.5	476.4 ± 0.5
ν_{10}	437	440.0 ± 0.5	441.0 ± 0.5
ν_{11}	248	251.264 ± 0	251.264 ± 0
ν_2	218	223.1 ± 0.5	222.1 ± 0.5
ν_8	152	155.5 ± 0.5	156.5 ± 0.5
ν_9	86	85.4 ± 0.5	86.5 ± 0.5

Table 1: Raman shift values (in cm^{-1}) for the vibrational modes of S8 measured with S and P polarised light, and compared to their known values.

4 Experimental Results and Discussion

The Raman spectra shown in Figures 3 and 4 were obtained for the S8 sample, showing 6 clear peaks, some quite large but others much smaller. Performing a peak search on the data yielded the intensities of the Stokes lines as well as their wavenumber shifts, shown in Table 1. These values are close to the expected values, however not within uncertainties. From these peak intensities the depolarisation ratios of the vibrational modes were calculated, shown in Figure 5, with all values within a range of 0.2 around 1. This means that there was very little dependence on the light polarisation for all of the modes, and so they are all non-totally symmetric.

Spectra were also obtained for the CCl₄ sample (Figure 6), which with S-polarised light showed a doublet peak at low frequencies, and three other more intense Stokes lines. It also shows two comparatively weaker Anti-stokes lines on the opposite side of the central large peak at the laser frequency due to Rayleigh scattering. Within roughly 20cm^{-1} of the Rayleigh peak the automatic attenuator engaged as intended, resulting in the sharp cut-offs either side, but the Rayleigh peak was still intense enough to be detected at its most intense, demonstrating that the attenuator was indeed necessary. By considering the expected ratio of intensities of Anti-Stokes and Stokes lines,

$$\frac{I_{AS}}{I_S} = \left(\frac{\nu_0 + \nu_i}{\nu_0 - \nu_i} \right)^4 \exp \left(\frac{-h\nu_i}{k_B T} \right) \quad (4)$$

the vibrational temperature for the CCl₄ sample was found to be $305.8 \pm 0.6\text{K}$, or $32.7 \pm 0.6^\circ\text{C}$, close to the ambient temperature but slightly higher. As the sample was kept in a box with no cooling or airflow, and was exposed to the laser beam for several continuous minutes, it is likely it was heated a

Vibrational Mode	Known Value	S-spectrum	P-spectrum	Mean
ν_3	776	778.8±0.6	779.4±0.6	779.1±0.6
ν_1	459	464±1	466±1	465±1
ν_4	314	318.8±0.1	318.5±0.1	318.6±0.1
ν_2	217	223.1±0.8	221.4±0.8	222.3±0.8

Table 2: Raman shift values (in cm^{-1}) for the vibrational modes of CCl_4 measured with S and P polarised light, and compared to their known values.

few degrees above the ambient temperature, which was already above normal room temperature due to the continuous heat output of the laser and it's power supply.

An unexpected very thin sharp peak was detected at a shift of -735.6cm^{-1} , just to the right of the doublet, however upon repeating that small section of the spectrum no such peaks were found, and it was not detected for P-polarised light either, so it is likely due to electrical signal noise or some fault with the equipment.

A spectrum was also measured for the negative wavenumber shifts of CCl_4 with P-polarised light (Figure 7), which showed a doublet and two singlet peaks at the same positions as with S-polarisation. It also showed a very weak peak at a shift of -465.8cm^{-1} , which is close to the shift of the much larger peak on the S-spectrum. It corresponds to a very small depolarisation ratio, shown in Figure 8 in the middle of the ratios of the other peaks, which were all very close to 1. This suggests that the corresponding vibrational mode of the CCl_4 molecule is totally symmetric, and thus will be the ν_1 mode, where all 4 Chlorine atoms oscillate in sync along the axes of their bonds with the central Carbon atom.

From the mean of the measured vibrational mode wavenumber shifts for CCl_4 with S and P polarised light, shown in Table 2, values were found for the force constants of both the valence force and central force models (Table 3). We were able to insert these values into equations that were not used to find them, in order to test their validity. Comparing left- and right-hand sides of the equations, they were of the same order of magnitude in all cases, however they differed by 39.5% and 48.2% for the valence force model equations, and only 6.1% for the central force equation. Therefore the central force model

Force Model	Constant	Obtained Value (N/m) [6 s.f.]
Valence	k	451.692
	k_δ/l^2	34.4437
Central	k_1	82.2063
	k_2	122.866
	k'	-21.1247

Table 3: Force constants obtained for two different force models for CCl₄, calculated using the measured vibrational mode frequencies.

fits our measurements significantly better, and is likely the more appropriate model for CCl₄.

5 Conclusions

We were able to measure Raman scattering peaks at wavenumber shifts close to the expected values, however not within uncertainties. The values obtained were consistently of greater magnitude than the known values, suggesting there may have been some systematic error due to that apparatus. Additionally, for the CCl₄ S-polarised spectrum, the Rayleigh scattering peak was found to be at a shift of -3.4cm^{-1} , supporting this explanation. This could be investigated by performing the experiment without the automatic attenuator, but with a strong attenuating plate to protect the detector, and observing at what wavenumber shift the Rayleigh peak is detected. This could then be used to calibrate the machine, or offset the measurements accordingly.

We calculated depolarisation ratios for the peaks of CCl₄ and S8 spectra, with a low ratio value corresponding to the ν_1 totally symmetric mode of CCl₄, as expected. Comparison of the peak intensities of the corresponding Stokes and Anti-Stokes lines in the S-polarised CCl₄ spectrum allowed a vibrational temperature of $305.8 \pm 0.6\text{K}$ to be calculated for the CCl₄ sample, which is close to what would be expected for the ambient temperature in a warm room and with a laser beam incident on the sample for many minutes. It should be possible to do the same calculation for S8 as well, if either side of the Rayleigh peak were to be measured. It might be good to verify that the same vibrational temperature is obtained for non-totally symmetric modes with P-polarised light, and a temperature probe could be used to measure the actual temperature of the room and the sample for comparison.

The measured vibrational mode frequencies of CCl₄ were used to calculate the force constants for two harmonic oscillator models, and using these we showed that the central force model is the best fit for CCl₄ molecules.

References

- [1] Vandenabeele P. *Practical Raman spectroscopy an introduction*. Chichester: Wiley; 2013.
- [2] Ferraro J R, Nakamoto K, Brown C W. *Introductory Raman spectroscopy*. 2nd ed. Amsterdam ; Boston: Academic Press; 2003.

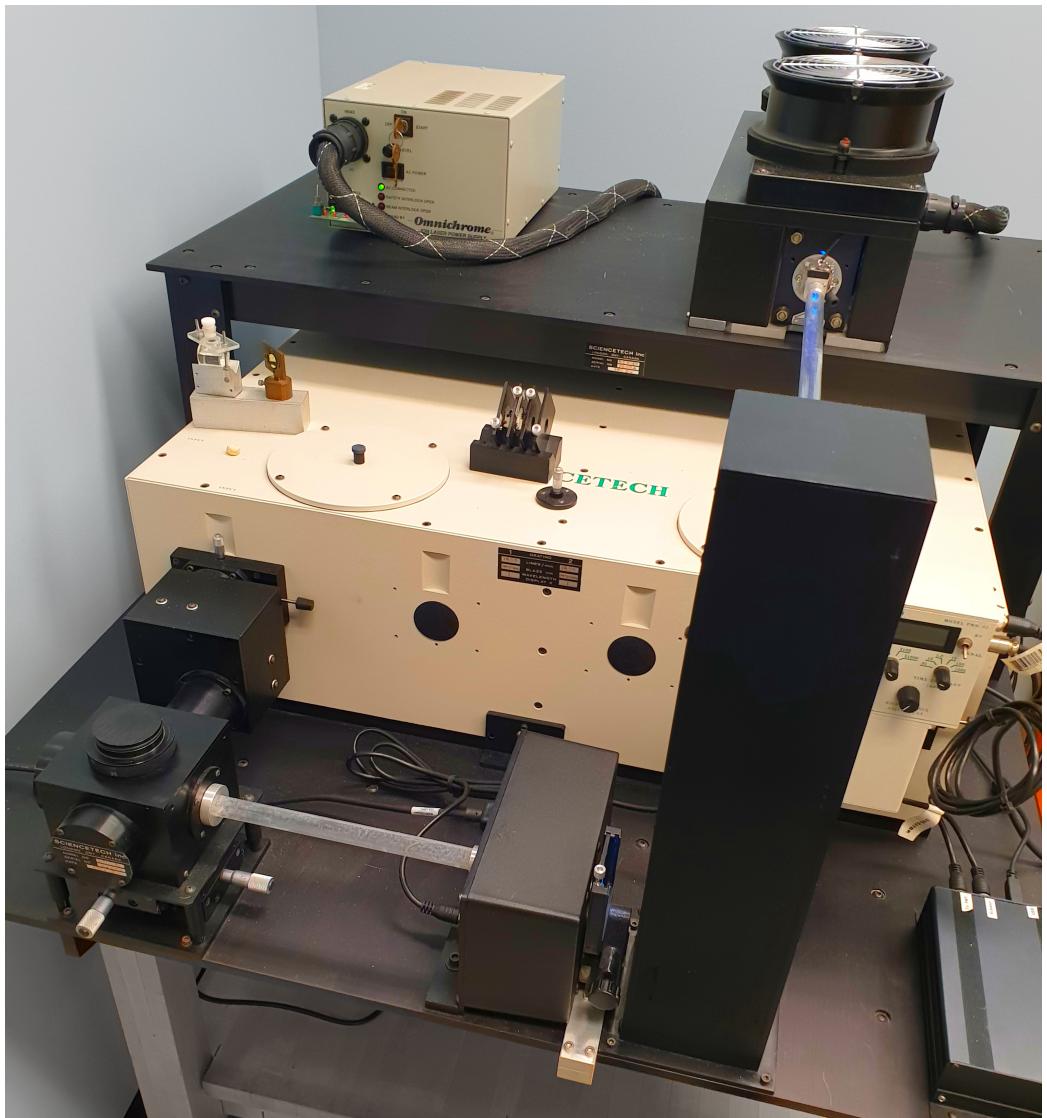


Figure 2: A photo of the setup used.

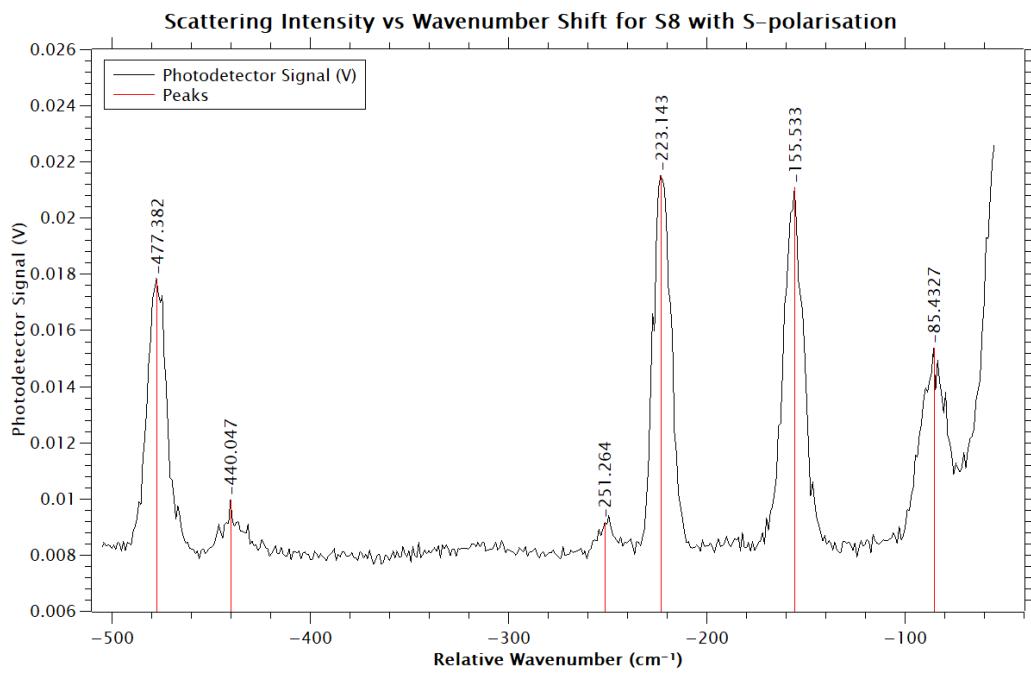


Figure 3: Raman spectrum for S8 using S-polarised light.

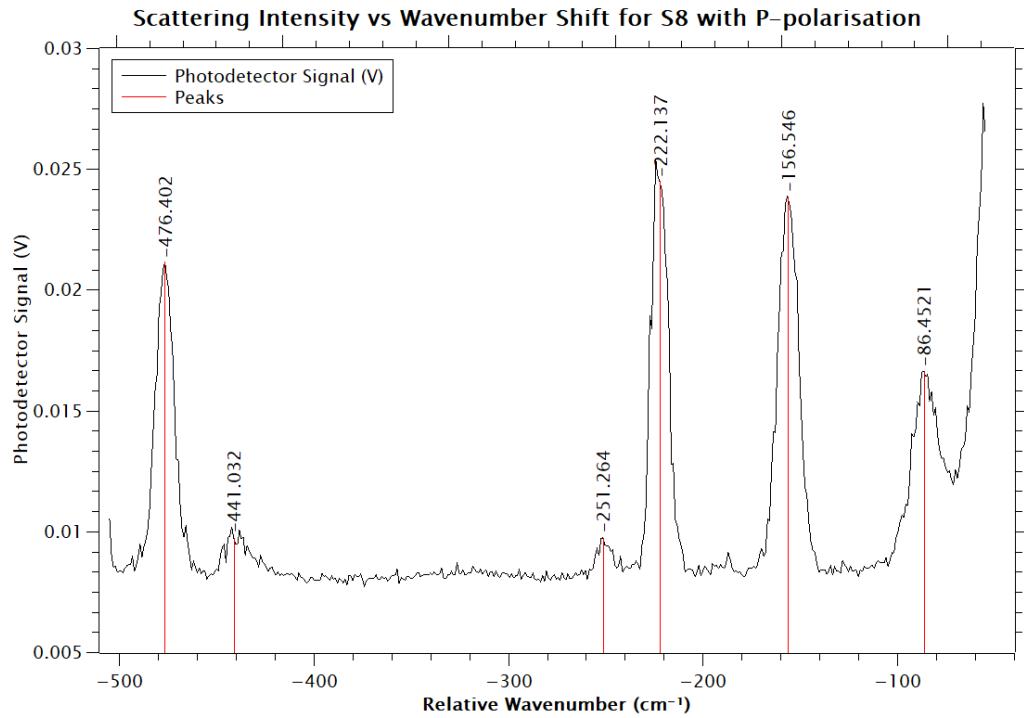


Figure 4: Raman spectrum for S8 using P-polarised light.

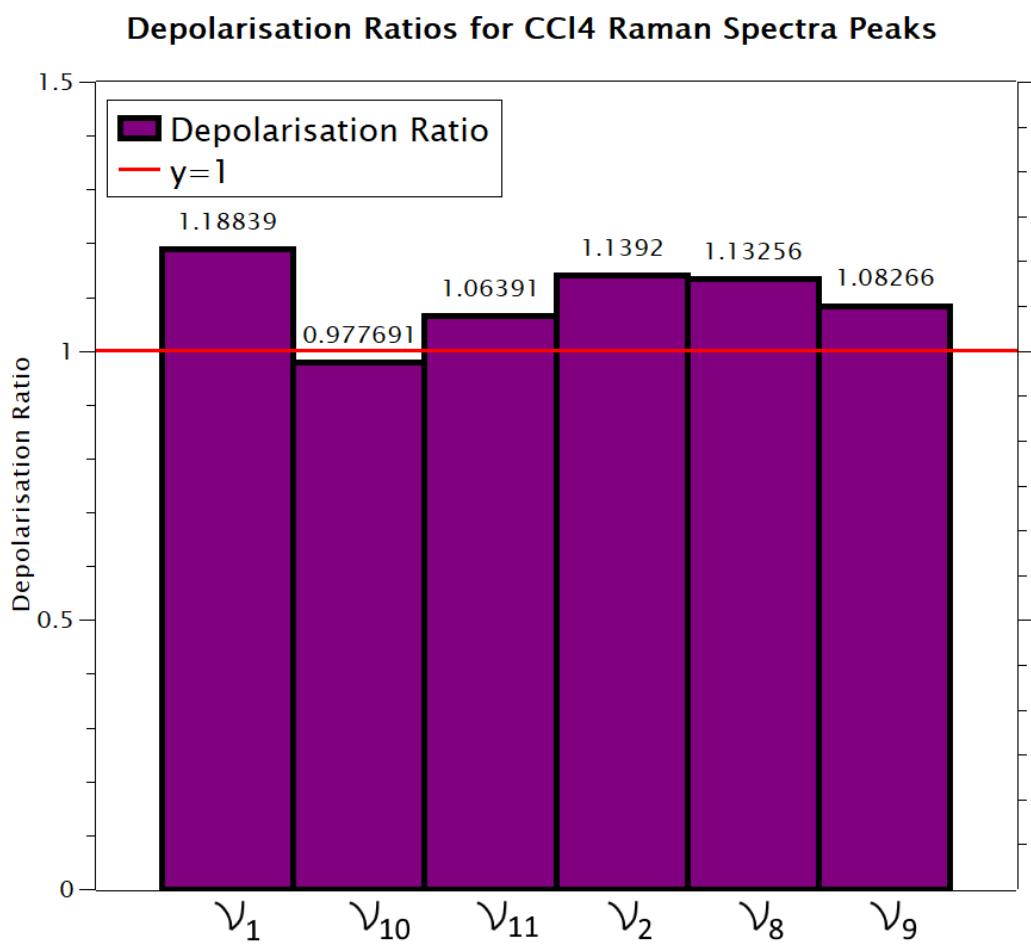


Figure 5: Depolarisation ratios for the Stokes lines of S8, decreasing in energy from left to right.

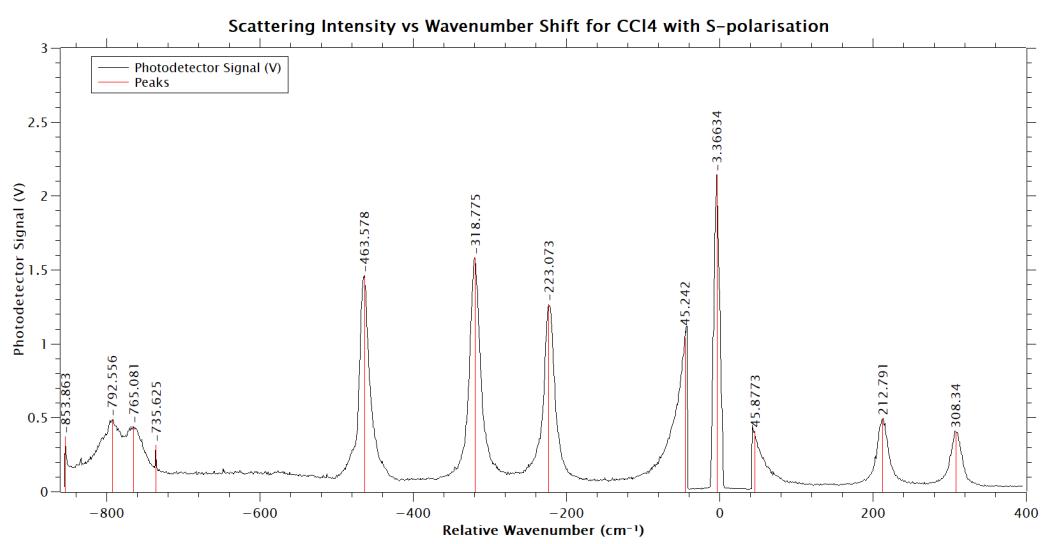


Figure 6: Raman spectrum for CCl₄ using S-polarised light.

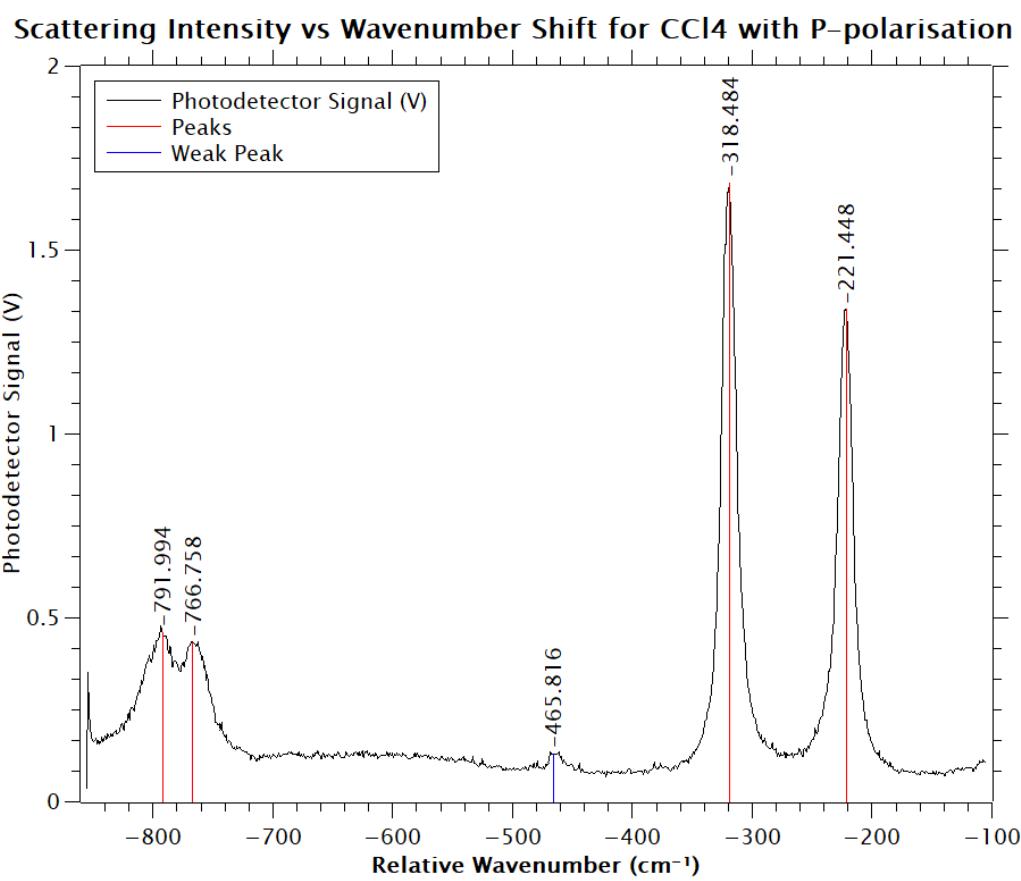


Figure 7: Raman spectrum for CCl₄ using P-polarised light.

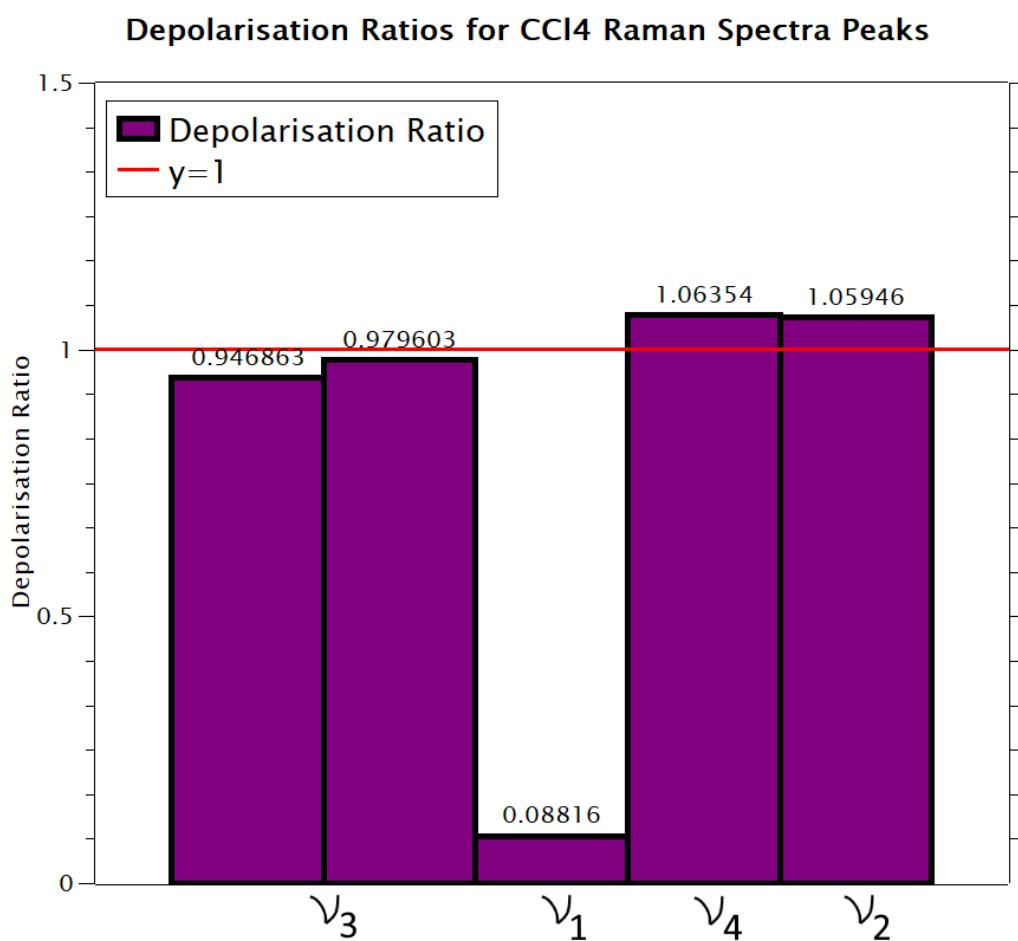


Figure 8: Depolarisation ratios for the Stokes lines of CCl₄, decreasing in energy from left to right, and showing both peaks of the doublet separately.