

Practical Physical Chemistry 3 – Marking and Feedback Form

Exp. 12: IR and Raman Spectroscopy.

Date: 26/12/20

Name: Christopher Davies

Date:

Markers:

/ 50

Results and Analysis

/ 20

All relevant experimental data presented together with all important parameters of the measurements. Deviations from standard procedure given. Quality of data. Data analysis performed correctly. Data given with correct units. Realistic error calculations (if appropriate).

Abstract and Discussion

/ 20

The abstract gives the main results and states the principal conclusions in a short, precise and concise manner. Results correctly placed into the context of the experiment. Comparison to literature values. Critical assessment and interpretation based on analysis. Honest conclusions.

Structure and Presentation

/ 10

Clear and logical structure. Clear scientific English, use of correct grammar and spelling. Clearly formatted figures and tables in appropriate size with figure captions and table titles. Scientific formatting of values, errors, units, etc. Report had an appropriate length.

Other comments

Experiment 12: IR/Raman Spectroscopy

C. Davies

(Dated: 26 December 2020)

Raman and IR spectroscopy were used to identify three unknown dichloroethene (DCE) isomers. Using a computational simulation package and symmetry arguments, samples A, B and C were determined to be 1,2-cis-DCE, 1,2-trans-DCE and 1,1-DCE respectively. The Raman and IR spectra of Sodium sulphite and nitrate were obtained and group theory was used to assign the symmetry of their respective vibrational modes.

I. PART 1

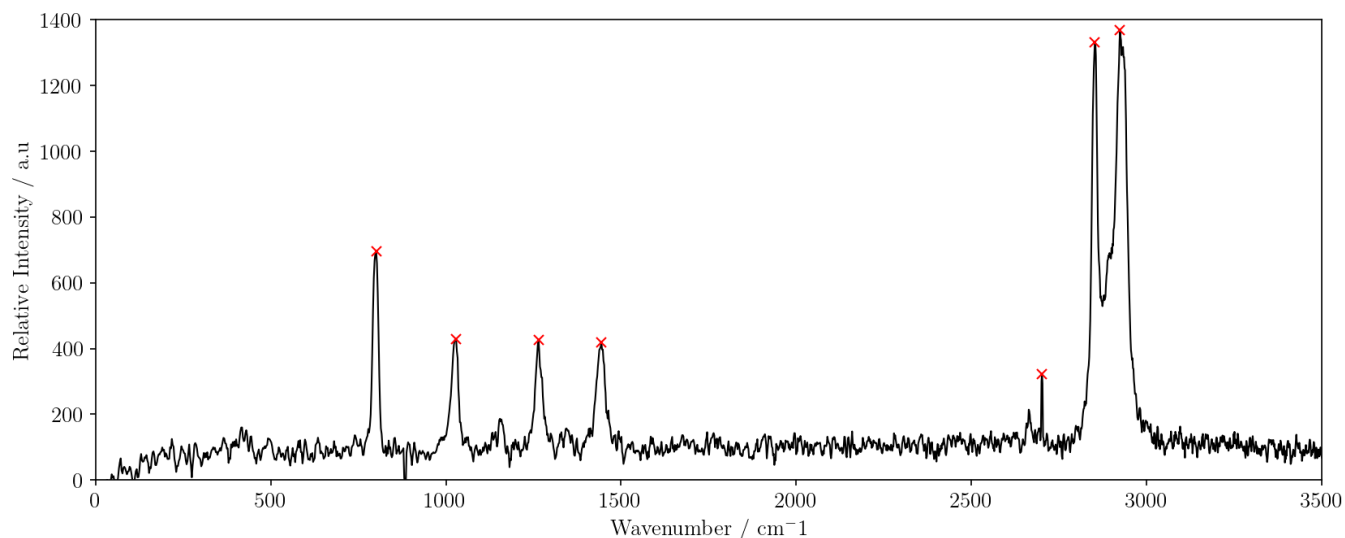


FIG. 1. Raman spectrum of cyclohexane with points used for calibration marked (red).

The Raman spectrum for cyclohexane (Fig.1) was obtained to check the calibration of the spectrometer. While it is expected for there to be small percentage error in each reading, the average difference of 0.3 cm^{-1} suggests that the calibration is off as an average difference of zero should be seen. Each subsequent Raman value will be adjusted by this. While data acquisition was done by a member of the department, it is assumed that the integration time and number of scans taken were optimised when the data was taken to compromise between signal to noise ratio and integration time (as noise adds as a function of \sqrt{N} over successive measurements). Another important practical aspect is to retake the baseline when changing the integration time as changing integration time changes the intensity of the dark current. It is also assumed that the spectrometer was allowed to warm up as the power output of a laser stabilises as gases thermally expand within the laser¹. Peak widths in Raman are sensitive to many factors. Rezaev² finds that for cyclohexane, a reduction in temperature reduces the peak width due to changes in the chaotic reorganisation of molecules. Reducing the temperature would therefore increase the resolution of this experiment. It is also found that reducing temperature increases Raman intensity for cyclohexane and, along with the reduction in thermal noise in the dark current, would lead to an increase in signal to noise

TABLE I. Comparison of recorded Raman spectrum (Fig.1) and literature values⁴

Recorded peak / cm^{-1}	Literature peak / cm^{-1}	Difference / cm^{-1}
801.0	801.3	0.3
1029.2	1028.3	-0.9
1264.4	1066.4	2.0
1444.0	1444.4	0.4
2663.7	2664.4	0.7
2852.4	2852.4	0.0
2924.3	2923.8	-0.5

ratio. Changing the laser itself might lead to a reduction in peak width if the distribution of the first laser is large. Another consideration is that molecules fluoresce at certain frequencies and it is often useful to change the Raman laser frequency to try to reduce this, reducing noise. Due to their liquid state, lines will be broader as the molecules experience greater intermolecular forces which affect vibrational modes. Where possible a baseline correction algorithm based on the work of Zhang et al.³ was used to clean up IR and Raman signals for easier comparison with the 'clean' computed spectrum.

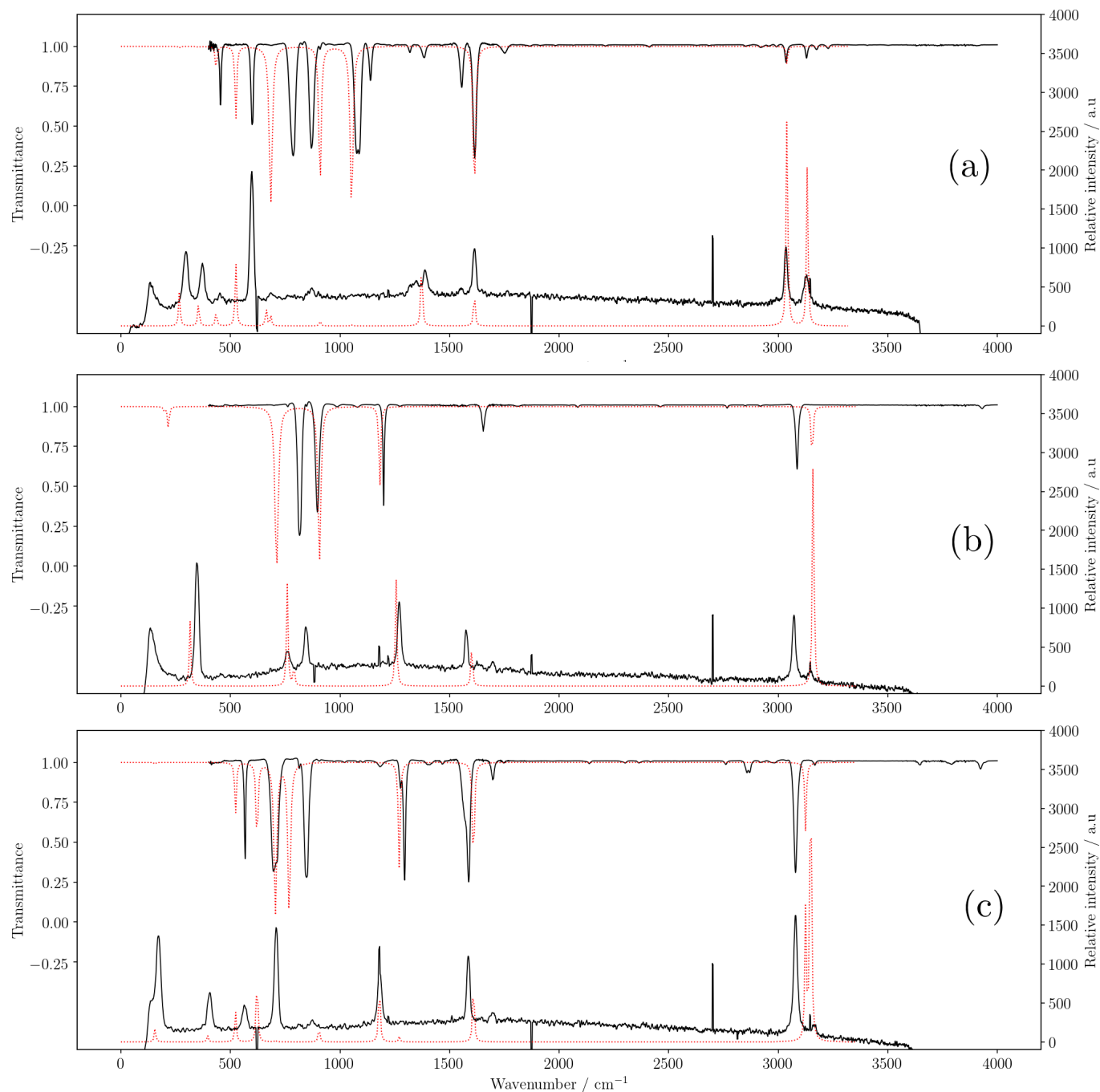


FIG. 2. Recorded IR and Raman spectra (black) against calculated spectra (red) for 1,1-DCE (a), 1,2-cis-DCE (b) and 1,2-trans-DCE (c).

II. PART 2

The effects of molecular symmetry on the IR and Raman spectra for the three unknown samples was used to determine the trans isomer. 1,1-dichloroethene and cis-dichloroethene both belong to the C_{2v} point group whereas trans-dichloroethene has C_{2h} symmetry. The selection rule for a vibrational mode to be IR active is that the electric dipole (μ) must change between the final and initial states (Eq.1).

For IR absorbance, the fundamental transition from a totally symmetric (of A_1 symmetry) ground state wavefunction (ψ_i) to an excited state (ψ_f) is only allowed if the integral (Eq.2) is non-zero. The A_1 symmetry of the ground state means that the product $\psi_f \otimes \mu$ must also have the same A_1 symmetry. A vibrational mode is Raman active if the polarizability tensor (α) changes as the molecule vibrates through a coordinate Q giving Eq.3.

$$\frac{d\mu}{dr} \neq 0 \quad (1)$$

$$\int \psi_f \mu \psi_i d\tau \quad (2)$$

$$\frac{d\alpha}{dQ} \neq 0 \quad (3)$$

$$\int \psi_f \alpha_{mn} \psi_i d\tau \quad (4)$$

By comparing equations 2 and 4 it can be seen that as that ψ_i and α both have gerade symmetry and μ has ungerade symmetry, IR transitions must be ungerade while Raman transitions must be gerade. This leads to a mutual exclusion when a point group has an inversion element. The C_{2v} point group has an inversion element meaning that a vibrational mode cannot be both IR and Raman active. Fig.2 (c) shows no agreement between IR and Raman modes and so suggests that this compound is trans-dichloroethene. GaussView, a computational package, was used to predict the IR and Raman modes for the three isomers. Having determined trans-dichloroethene, the generated spectra were shifted (discussed later) and Fig.2 (a) was determined to be 1,1-dichloroethene and Fig.2 (b) the cis-dichloroethene isomer. In each IR spectrum a small absorption at around 2350 cm^{-1} can be assigned to a CO_2 stretch.

TABLE II. Assigned symmetry of Raman active vibrational modes recorded compared with comparison to computed values for different DCE isomers.

Isomer	Calculated peak / cm^{-1}	Recorded peak / cm^{-1}	Symmetry assignment
1,1-DCE	281.0	297.2	A1
	373.1	372.7	B2
	1444.9	1388.5	A1
	1698.0	1615.7	A1
	3200.6	3035.7	A1
	3298.1	3131.5	B2
Cis-DCE	162.3	172.9	A1
	412.1	406.2	B2
	544.9	562.8	B2
	1676.2	1695.2	A1
	3255.3	3079.5	B2
Trans-DCE	328.7	345.7	A_g
	790.9	843.5	B_g
	1307.9	1270.6	A_g
	1668.5	1575.0	A_g
	3291.7	3072.6	A_g

TABLE III. Assigned symmetry of IR active vibrational modes recorded compared with comparison to computed values for different DCE isomers.

Isomer	Calculated peak / cm^{-1}	Recorded peak / cm^{-1}	Symmetry assignment
1,1-DCE	3200.6	3036	A1
	1698.0	1615	A1
	1108.2	1087	B2
	956.6	908	B1
Cis-DCE	3255.3	3079	B2
	1676.1	1697	A1
	1323.3	1295	B2
	799.9	783	B2
	734.4	712	B1
	647.2	700	A1
Trans-DCE	740.5	763	B_u
	943.9	983	A_u
	1230.8	1199	B_u
	3286.3	3086	B_u

It can be seen in tables II and III that no modes for trans-DCE are both IR and Raman active (due to the inversion element in its point group) and that all the Raman modes have gerade symmetry and all the IR modes have ungerade symmetry as discussed earlier.

III. PART 3

The point groups of the sulphite and nitrate anions can be determined by using VSEPR to predict their shapes. The nitrate anion is trigonal planar whereas the extra lone pair on Sulphur causes the sulphite anion to be trigonal pyramidal. This places them in D_{3h} and C_{3v} respectively. For a non-linear N atom compound we expect $3N-6$ vibrational modes leading to 6 expected vibrational modes for each compound. Applying the symmetry elements from the D_{3h} point group on the three axes for each atom in the nitrate anion we find:

E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
12	0	-2	4	-2	2

By use of the reduction formula, $\Gamma_{tot} = A'_1 + A'_2 + 3E' + 2A''_2 + E''$, we obtain the 12 expected degrees of freedom. The character table is then used to remove rotations and translations to give $\Gamma_{vib} = A'_1 + 2E' + A''_2$ which agrees with our earlier answer of 6 degrees of freedom. Due to the nitrate anion having three bonds we expect 3 stretches and 3 bends. By placing an axis along each bond we find $\Gamma_{stretch} = A'_1 + E'$ and $\Gamma_{bend} = A''_2 + E'$. The group table can now be used to assign IR activity (linear coordinate functions) and Raman activity (quadratic coordinate functions). Bends are expected to be at lower energies than the stretches. This process was then repeated for the sulphite anion and the spectra were assigned mode symmetry.

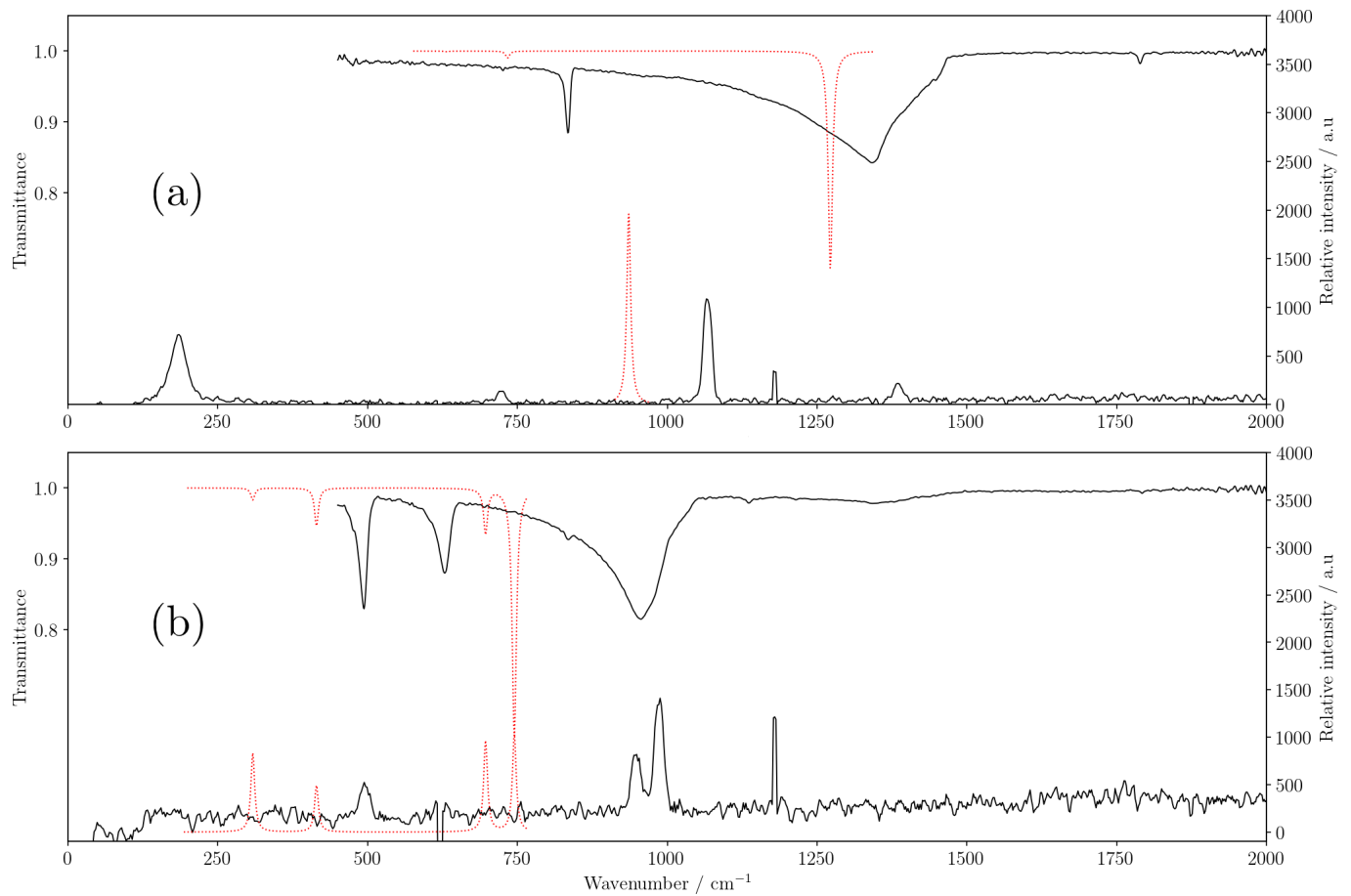


FIG. 3. Recorded IR and Raman spectra (black) against calculated spectra (red) for Sodium nitrate (a) and Sodium sulphite (b).

TABLE IV. Assigned symmetry of Raman active vibrational modes recorded compared with comparison to computed values for two Sodium salts.

Sodium anion	Calculated peak / cm^{-1}	Recorded peak / cm^{-1}	Symmetry assignment
Nitrate	974.7	1065.6	A ₁ '
Sulphite	431.8	494.6	A ₁
	725.8	944.8	A ₁
	775.8	988.3	Degenerate E

TABLE V. Assigned symmetry of IR active vibrational modes recorded compared with comparison to computed values for two Sodium salts.

Sodium anion	Calculated peak / cm^{-1}	Recorded peak / cm^{-1}	Symmetry assignment
Nitrate	764.1	834	A ₂ ''
	1325.2	1342	E'
Sulphite	321.2	494	Degenerate E
	431.8	629	A ₁
	725.8	853	A ₁
	775.8	956	Degenerate E

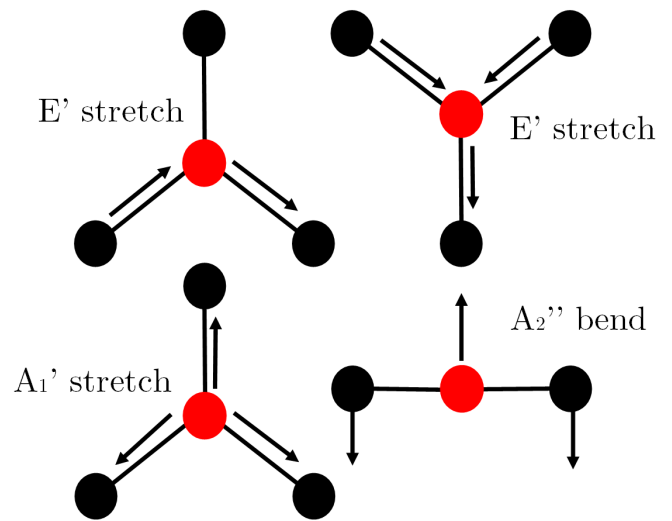


FIG. 4. 4 of the 6 total vibrational modes for the nitrate anion.

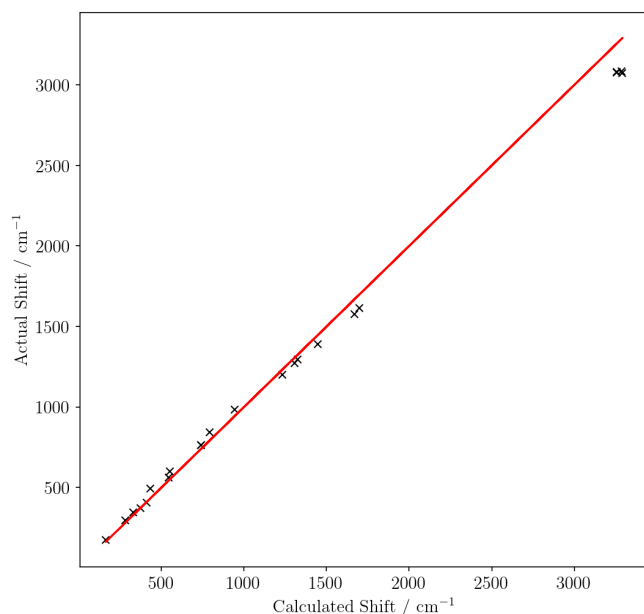


FIG. 5. Comparison of recorded and calculated shifts with the line $y=x$ added (red)

IV. FURTHER NOTES

Fig.5 shows the difference in GaussView calculated wavenumber and the observed wavenumber. It was found that the wavenumber was overcalculated by around 4% and had to be scaled by this amount for each graph and measurement. Three potential reasons for the overestimation are the use of a finite basis set⁵, the harmonic approximation of the bond⁶ and the approximate calculations used to model intermolec-

ular forces and their effect upon vibrational spectra. It can be seen in Fig.5 that the higher the wavenumber, the greater the overestimation of the shift. A variable scaling function would be much better suited than the solution detailed above but is beyond the scope of this report. A baseline correction had to be applied to the Raman data due to fluorescence. The red-shifted Stokes Raman scattered light is in the same region of the spectrum as the sample's fluorescence emission resulting in a raised baseline and decreased signal to noise ratio. Changing the laser wavelength would help with this issue. The choice of a laser frequency is also affected by the compromise between higher excitation efficiency and therefore better signal to noise ratio at higher frequency and lower laser cost at lower frequency. Particle size also has an effect upon Raman spectra and a possible modification to the experiment to reduce peak width of the solid samples would be to finely grind the sample³.

¹"Sam's laser faq - helium-neon lasers 2020," <https://www.repairfaq.org/sam/laserhen.htm#henhlopw>, accessed: 19/12/20.

²N. Razaev, *Molecular motions in liquids: proceedings of the 24. Annual Meeting of the Societe de Chimie Physique Paris-Orsay, 2-6 July 1972. Jointly spons. by the Associazione Italiana di Chimica Fisica ...* (Reidel, 1974) pp. 309–318.

³P. K. Duy, S. Chun, and H. Chung, "Characterization of raman scattering in solid samples with different particle sizes and elucidation on the trends of particle size-dependent intensity variations in relation to changes in the sizes of laser illumination and detection area," *Analytical Chemistry* **89**, 11937–11943 (2017).

⁴"McCreery group | raman materials," <https://www.chem.ualberta.ca/~mccreery/ramanmaterials.html#cyclohexane>, accessed: 19/12/20.

⁵"Basis sets | gaussian.com," <https://gaussian.com/basissets/>, accessed: 19/12/20.

⁶"Vibrational analysis in gaussian | gaussian.com," <https://gaussian.com/vib/>, accessed: 19/12/20.

⁷Z.-M. Zhang, S. Chen, and Y.-Z. Liang, "Baseline correction using adaptive iteratively reweighted penalized least squares," *The Analyst* **135**, 1138 (2010).