Practical Physical Chemistry 3 – Marking and Feedback Form

Exp. 12: IR and Raman Spectroscopy.

Date: 4/10/19	**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

[Do not delete this Section Break]

Christopher Davies
4/11/19

Three unknown isomers of dichloroethene (a,b and c) were determined from IR and Raman spectra using group theory and a computational simulation package. These were found to be 1,1-dichloroethene, *cis*-dichloroethene and *trans*-dichloroethene respectively. The IR and Raman spectra of $NaNO_3$ and Na_2SO_3 were measured and group theory arguments were used to assign symmetry species to vibrational modes.
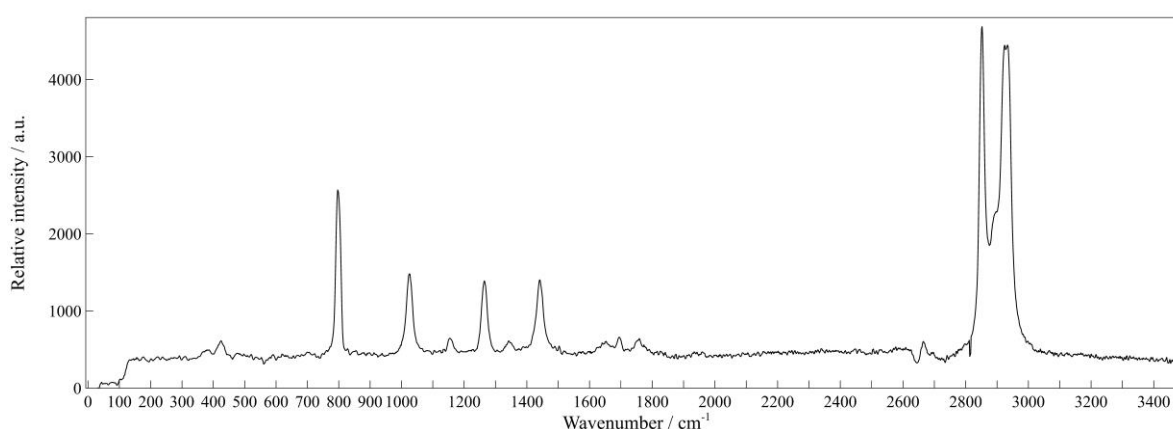
Results, Analysis and Discussion

Part 1

Figure 1:Raman spectrum for cyclohexane

Table 1: Comparison between recorded Raman wavenumber peak and literature values[1]

Recorded peak wavenumber / cm^{-1}	Literature peak wavenumber/ cm^{-1}	Difference / cm^{-1}
425.4	426.3	0.9
796.5	801.3	4.8
1154.5	1157.6	3.1
1264.4	1266.4	2
1442.0	1444.4	2.4
2852.4	2852.9	0.5
2924.3	2923.8	-0.5
2934.9	2938.3	3.4

The Raman spectrum for cyclohexane (figure 1) was taken to assess the calibration of the spectrometer. Integration time and number of scans taken were optimised to compromise between a low signal to noise ratio and a reasonable measurement time. The spectrometer was allowed to warm up, allowing the power output of the laser to stabilise due to thermal expansion of gasses within the laser[2]. Each time integration time was changed, a new dark signal needed to be taken. Each pixel in a Raman spectrometer accumulates noise in a predictable fashion due to thermal processes able to generate electrons in detector pixels. Changing integration time therefore changes the intensity of dark current and so a new dark signal must be taken.

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[1] Chem.ualberta.ca. (2019). *McCreery Group | Raman Materials*. [online] Available at: https://www.chem.ualberta.ca/~mccreery/ramanmaterials.html#cyclohexane [Accessed 3 Nov. 2019].

[2] Repairfaq.org. (2019). *Sam's Laser FAQ - Helium-Neon Lasers*. [online] Available at: https://www.repairfaq.org/sam/laserhen.htm#henhlopw [Accessed 3 Nov. 2019].

By comparing the measured values to literature, the maximum percentage error was found to be 0.02% - 0.6%. The resolution of the spectrometer was set to 4 cm^{-1}: readings were taken at approximately 2 cm^{-1} intervals. A higher resolution was not used as, compared to a gas, the molecules in a liquid sample experience greater intermolecular interactions leading to actual peak widths to broaden making a higher resolution ineffective. Taking both the spectrometer resolution and the percentage error into account, the spectrometer was accurate.
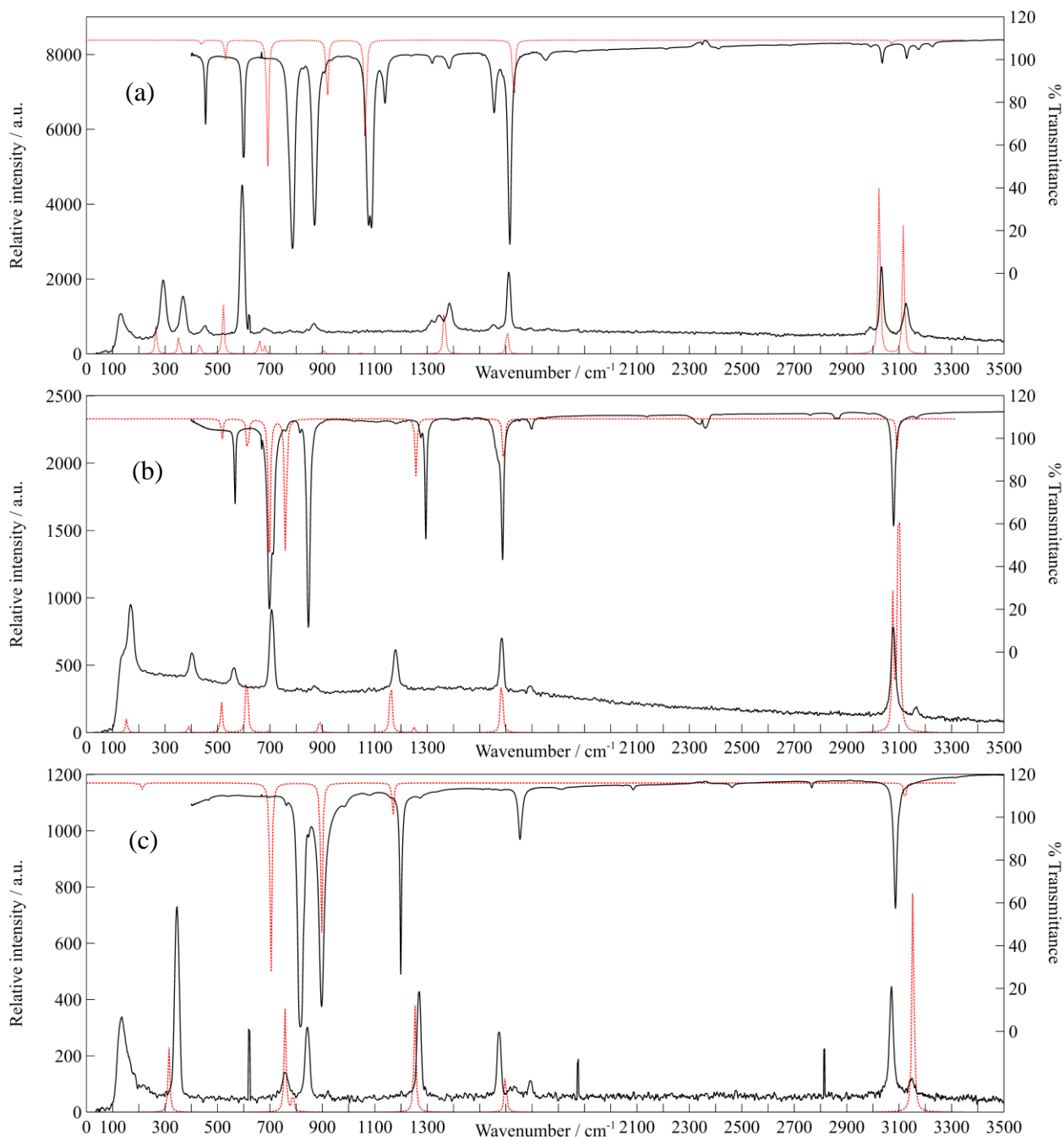
Part 2

Figure 2: Measured Raman (bottom) and IR spectra (top) for compounds a,b,c. Red traces are adjusted GaussView predicted spectra overlaid onto respective measured spectrum.

The first approach to identifying the three isomers was to consider molecular symmetry and its effect on IR and Raman spectra[3]. 1,1-dichloroethene and *cis*-dichloroethene both have C_{2v} symmetry. *Trans*-dichloroethene has C_{2h} symmetry. For a vibrational mode to be IR active, the electronic dipole of the molecule (**μ**) must change. This gives the selection rule below:

Equation 1:
$$\frac{d\mu}{dr} \neq 0$$

For fundamental transitions, the ground state wavefunction is totally symmetric and therefore has A_1 symmetry. For the total transition dipole-moment integral to be non-zero, it is required that the product of initial wavefunction (φ_i), dipole moment function (**μ**) and final wavefunction (φ_f) is totally symmetric. Hence the product $\boldsymbol{\mu} \otimes \varphi_f$ must have A_1 symmetry too. Both must therefore have the same symmetry.

A vibrational mode is Raman active if its polarizability tensor (α) changes as a molecule vibrates through coordinate Q giving the selection rule:

Equation 2:
$$\frac{d\alpha}{dQ} \neq 0$$

In symmetry groups with an inversion element, IR and Raman modes become mutually exclusive. The overall parity for both transition integrals must be gerade for the integral to be non-zero.

Equation 3: $\int \varphi_f \, \boldsymbol{\mu} \, \varphi_i \, d\tau$
Equation 4: $\int \varphi_f \, \boldsymbol{\alpha_{mn}} \, \varphi_i \, d\tau$

φ_i has *gerade* symmetry in both equation 3 and 4. **μ** is *ungerade*. $\boldsymbol{\alpha_{mn}}$ is *gerade*. Hence for the overall integrals to be non-zero, IR transitions must be *ungerade* and Raman transitions *gerade*. This leads to the mutual exclusion principle. The C_{2h} point group has an inversion element, and it can be seen in figure 2 that graph C shares no vibrational modes in both IR and Raman suggesting that compound c is *trans*-dichloroethene.

GaussView (A computational chemistry package) was used to predict the relevant spectra for the three compounds. 1,1- (compound a) and *cis*-dichloroethene (compound b) were differentiated by the fitting of their respective Raman spectra. The fitting of the IR spectra then confirmed this. All calculated peak positions were fitted (this is discussed later).

Table 2: Peak assignment for sample a

Wavenumber(Raman)/ cm^{-1}	Assignment	Wavenumber(IR)/ cm^{-1}	Assignment
3077	A_1 CH bend	3090	B_1 CH stretch
3072	A_1 CH bend	828	B_1 CCl stretch

Table 3:Peak assignment for sample b

Wavenumber(Raman)/ cm^{-1}	Assignment	Wavenumber(IR)/ cm^{-1}	Assignment
3077	A_1 CH stretch	3073	A_1 CH stretch
1587	A_1 CC stretch	1585	A_1 CC stretch
1179	A_1 CH bend	1181	$A_1$1 CH bend

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[3] Bernath, P. (2005). *Spectra of atoms and molecules*. New York: Oxford University Press, pp.293-309.

Table 4: Peak assignment for sample c

Wavenumber(Raman)/ cm^{-1}	Assignment	Wavenumber(IR)/cm^{-1}	Assignment
1274	A$_g$ CH bend	3090	B$_u$ CH stretch
763	B$_g$ CH bend	828	B$_u$ CCl stretch

In each IR spectrum the small peak ~ 2350cm^{-1} can be assigned a to CO_2 stretch, and the peak in each Raman spectrum present ~ 1600cm^{-1} is indicative of a C=C stretch.
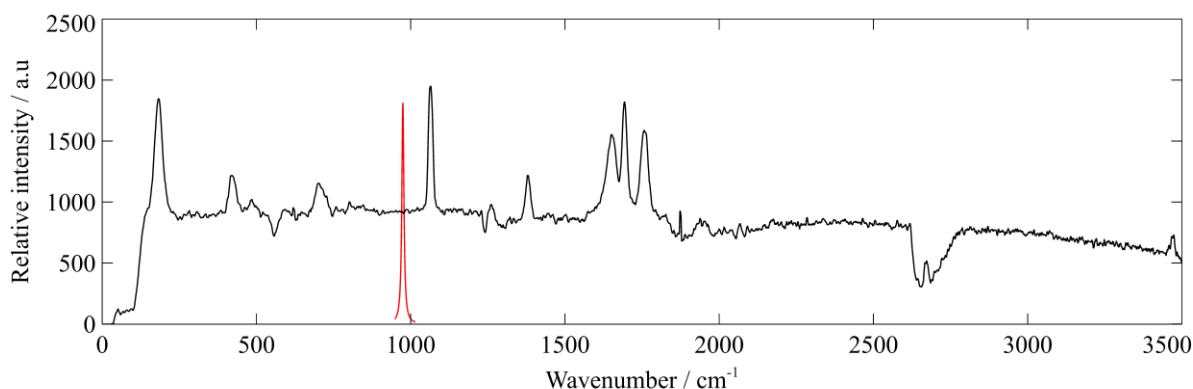
Part 3
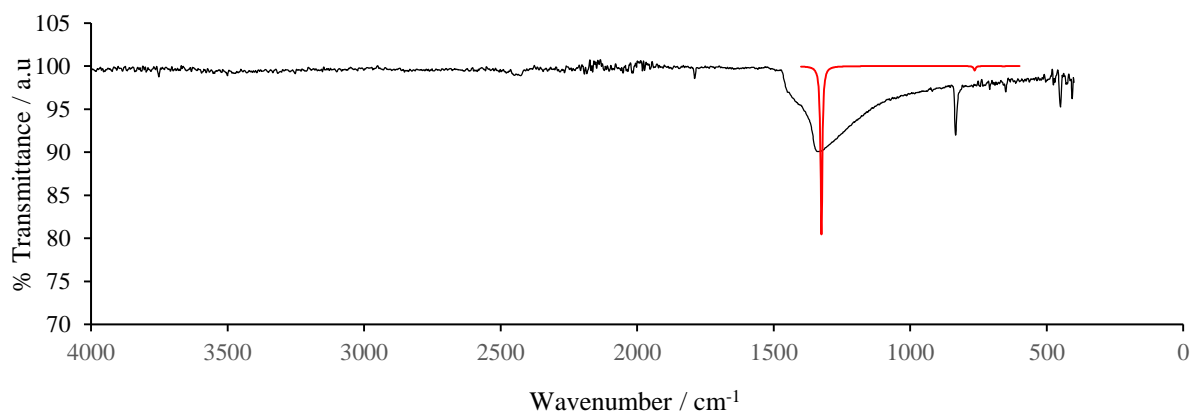

Figure 3: Raman spectrum of NaNO$_3$ (black) and calculated in red.

Figure 4: IR spectrum of NaNO$_3$ (black) and calculated in red.

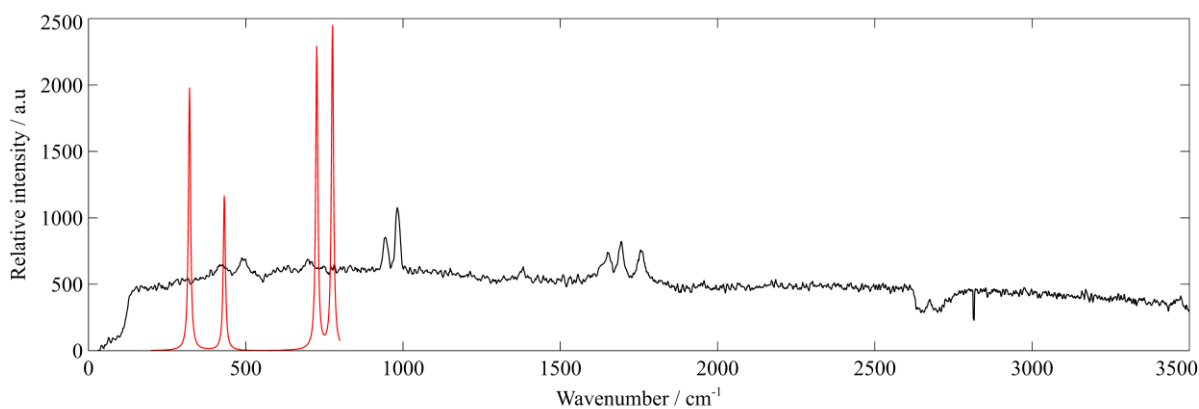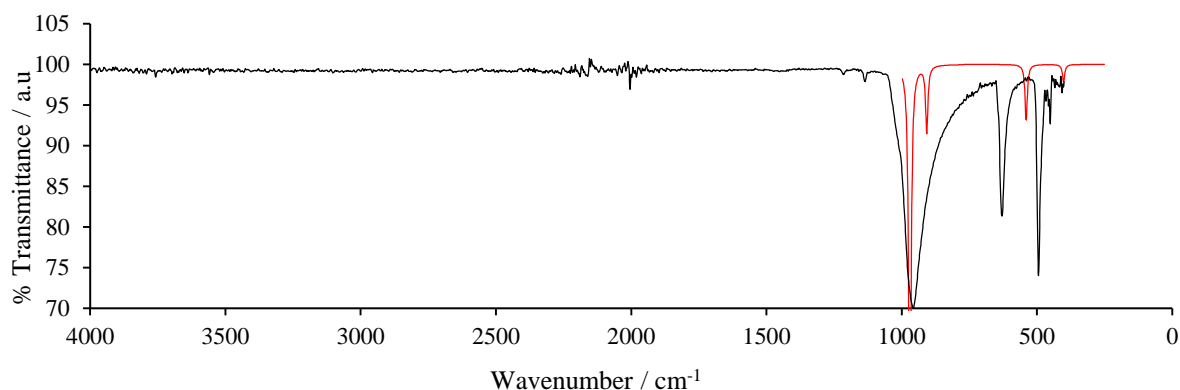Figure 5: Raman spectrum of Na$_2$SO$_3$ (black) and calculated in red.

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Figure 6: IR spectrum of Na_2SO_3 (black) and calculated in red.

VSEPR theory predicts that the nitrate anion adopts a trigonal planar configuration with point group D_{3h} whereas the extra lone pair on the sulphite anion causes it to adopt a trigonal pyramidal structure with a point group of C_{3v}. 3N-6 vibrational modes are expected, where N is the number of atoms. So, for both nitrate and sulphite, 6 vibrational modes are expected.
Using group theory for the nitrate anion:

Three axes on each atom gives the following when symmetry elements are applied:

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

And this can be reduced with the reduction formula to $\Gamma_{tot} = A_1' + A_2' + 3E' + 2A_2'' + E''$ agreeing with the 12 degrees of freedom expectd (3N). Using the character table, we find $\Gamma_{vib} = A1' + 2E' + A2''$ by removing rotations and translations (3N-6 vibrational modes). Due to NO_3^- having three bonds, this can be split into three stretches and three bends. By placing an axis along each bond we find $\Gamma_{stretch} = A_1' + E'$ and $\Gamma_{bend} = E' + A_2''$. Bends will be at lower energies than stretches and the group table is used to determine if a vibration is IR or Raman active (linear functions for IR vs quadratic functions for Raman). This procedure can be followed for the sulphite anion to assign the wavelengths to mode symmetry. Due to the poor correlation between results and calculation, the symmetry assignments have been shown with the GaussView calculated spectra (this discrepancy is discussed later).

Table 5: Calculated vibrational modes for the nitrate anion

	GaussView calculated wavenumber / cm^{-1}	Mode symmetry
Raman	658	E'
	974	A_1'
	1325	E'
FTIR	764	A_2''
	1325	E'

Table 6: Calculated vibrational modes for the sulphite anion

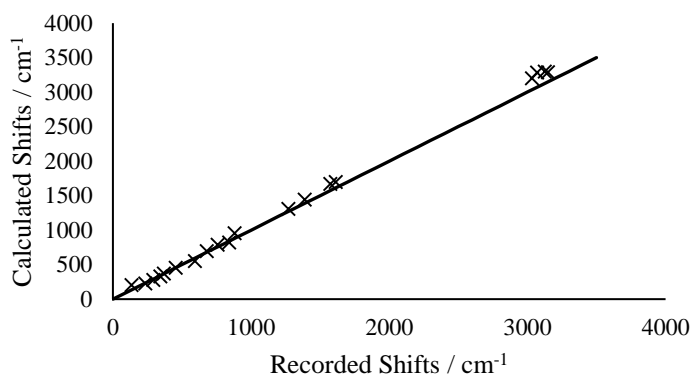|	GaussView calculated wavenumber / cm^{-1}	Mode symmetry
Raman	321	E
	431	A_1
	725	E
	775	E
FTIR	431	A_1
	725	E
	775	E

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General

Figure 7: comparison of recorded wavenumber with GaussView calculated wavenumber

By comparing actual wavenumber to the GaussView calculated wavenumber, it can be seen that at higher wavenumber, GaussView overestimates wavenumber due to the nature of the problem and the limited computing resources. Because of this, when fitting calculated data it was required to use scaling factors of between 2%-5% to achieve agreeing results. Two potential reasons for the overestimation are the use of a finite basis set[4] and harmonic approximation of the bond[5]. A potential way to reduce error would be use a variable scaling factor that increasing scaling with increasing wavenumber, instead of using a linear scaling factor.

The Raman spectra, especially *cis*-dichloroethene showed fluorescence. Red-shifted Stokes Raman scatterd light overlaps with fluorescence emission, resulting in raising of the baseline[6]. While this decreased the signal to noise ratio, it was still possible to resolve peaks.

Raman spectra are dependant upon the form of the powder analysed. As particle size increases, the distribution of Raman photons broadens[7]. One way to mitigate this error would have been to finely grind samples.

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[4] Gaussian.com. (2019). *Basis Sets | Gaussian.com*. [online] Available at: https://gaussian.com/basissets/ [Accessed 4 Nov. 2019].

[5] Gaussian.com. (2019). *Vibrational Analysis in Gaussian | Gaussian.com*. [online] Available at: https://gaussian.com/vib/ [Accessed 4 Nov. 2019].

[6] Wei, D., Chen, S. and Liu, Q. (2015). Review of Fluorescence Suppression Techniques in Raman Spectroscopy. *Applied Spectroscopy Reviews*, 50(5), pp.387-406.

[7] *Anal. Chem.* 2017, 89, 22, 11937-11943,Publication Date:October 23, 2017 https://doi.org/10.1021/acs.analchem.7b01400