



UC BERKELEY COLLEGE OF CHEMISTRY

CHEMISTRY 125

PHYSICAL CHEMISTRY LABORATORY

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# Raman Spectroscopy

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# 1 Spectra analysis

## 1.1 CCl<sub>4</sub>

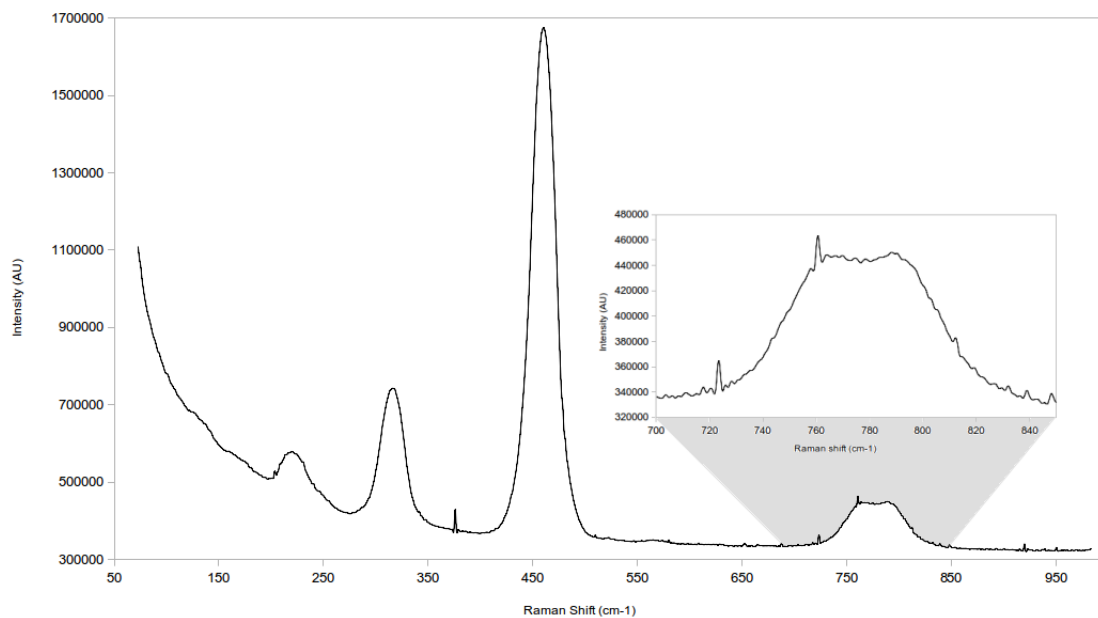


Figure 1: CCl<sub>4</sub> Raman spectrum, without baseline correction.

Shift (cm <sup>-1</sup> )		Error (cm <sup>-1</sup> )		Intensity (A. U.)		Properties	
Observed	Literature <sup>[1]</sup>	FWHM	CCD	Observed	Corrected	Symbol	Assignment
219.6	217.0	23.5	1.19	$5.79 \times 10^5$	$1.06 \times 10^5$	E	Deg. Deform.
315.9	313.5	20.9	1.19	$7.43 \times 10^5$	$3.27 \times 10^5$	F <sub>2</sub>	Deg. Deform.
460.6	458.7	22.4	1.19	$1.67 \times 10^6$	$1.32 \times 10^6$	A <sub>1</sub>	Sym. Str.
760.5	761.7	22.9	0.28	$4.63 \times 10^5$	$1.31 \times 10^5$	A <sub>1</sub> +F <sub>2</sub>	Deg. Str.
788.3	790.4	26.6	0.28	$4.50 \times 10^5$	$1.20 \times 10^5$	F <sub>2</sub>	Deg. Str.

Table 1: Assignment and error analysis of CCl<sub>4</sub> Raman spectrum. Data was collected with a 600gr/mm grating and a 655, 690, and 780nm window, with 5 accumulations of 10 sec. each.

## 1.2 CHCl<sub>3</sub><sup>1</sup>

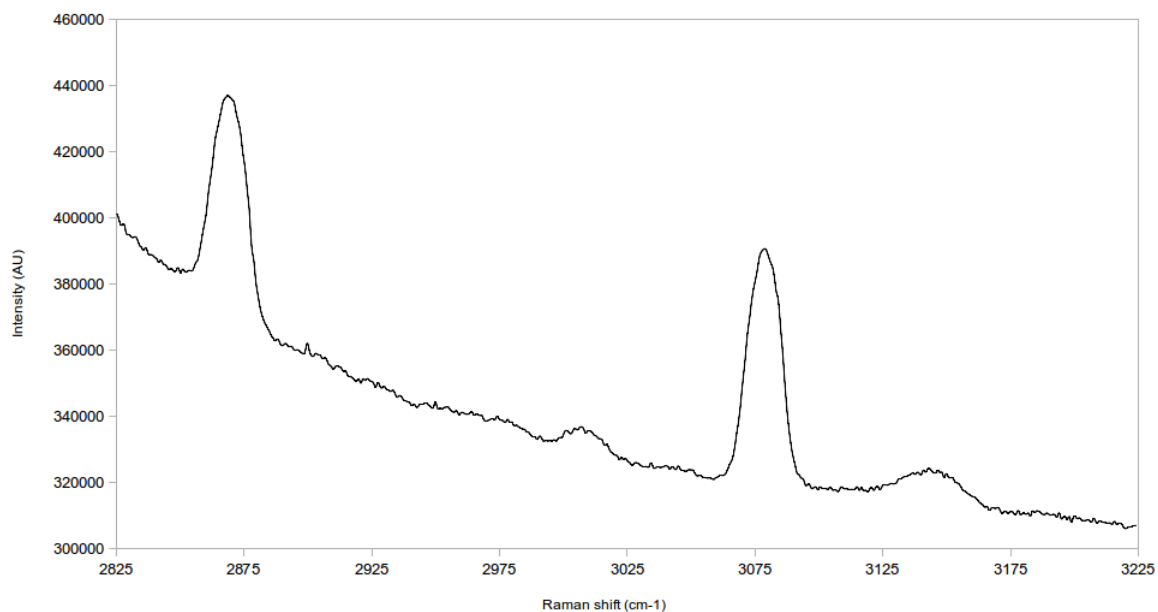


Figure 2: CHCl<sub>3</sub> Raman spectrum, without baseline correction.

Shift (cm <sup>-1</sup> )		Error (cm <sup>-1</sup> )		Intensity (A. U.)		Properties	
Observed	Literature <sup>[2]</sup>	FWHM	CCD	Observed	Corrected	Symbol	Assignment
264	261	11.4	1.12	$1.91 \times 10^5$	$1.36 \times 10^5$	E	C-Cl Deg. Deform.
366	363	13.3	1.12	$6.15 \times 10^5$	$6.01 \times 10^5$	A <sub>1</sub>	C-Cl Sym. Deform.
680.	672	18.5	1.12	$2.24 \times 10^6$	$2.03 \times 10^5$	A <sub>1</sub>	C-Cl Sym. Str.
743	760.	20.0	1.12	$3.31 \times 10^5$	$3.21 \times 10^5$	A <sub>1</sub>	C-Cl Deg. Str.
1201	1217	11.1	2.14	$5.10 \times 10^5$	$4.98 \times 10^5$	E	C-H Bend
3079	3030	12.7	0.53	$3.05 \times 10^5$	$3.90 \times 10^5$	A <sub>1</sub>	C-H Str.

Table 2: Assignment and error analysis of CHCl<sub>3</sub> Raman spectrum. Data was collected with both a 600gr/mm and an 1800 gr/mm grating and a 655, 690, and 780nm window, with 5 accumulations of 1 sec. each.

<sup>1</sup>Data for this molecule was incomplete. Supplementary material from Chung Jui Yu is also provided.

### 1.3 $\text{CDCl}_3^2$

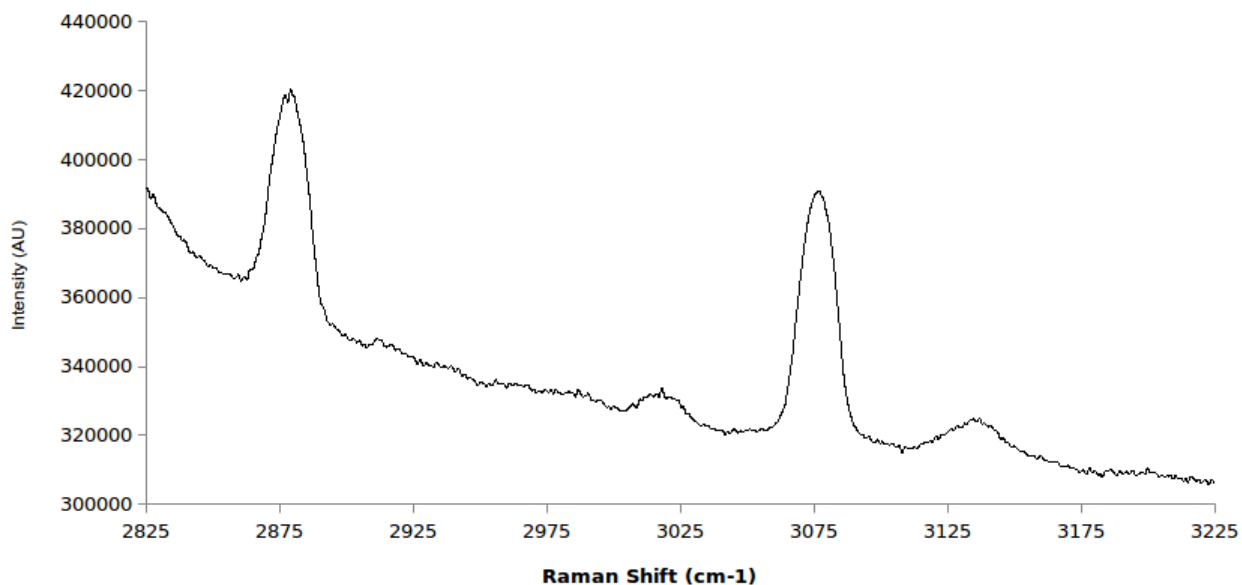


Figure 3:  $\text{CDCl}_3$  Raman spectrum, without baseline correction.

Shift ( $\text{cm}^{-1}$ )		Error ( $\text{cm}^{-1}$ )		Intensity (A. U.)		Properties	
Observed	Literature <sup>[3]</sup>	FWHM	CCD	Observed	Corrected	Symbol	Assignment
262	261	11.4	1.12	$1.91 \times 10^5$	$1.36 \times 10^5$	E	C-Cl Deg. Deform.
376	363	13.3	1.12	$6.15 \times 10^5$	$6.00 \times 10^5$	$A_1$	C-Cl Sym. Deform.
681	672	18.5	1.12	$2.23 \times 10^6$	$2.03 \times 10^5$	$A_1$	C-Cl Sym. Str.
743	760.	20.0	1.12	$3.30 \times 10^5$	$3.19 \times 10^5$	$A_1$	C-Cl Deg. Str.
1200.	1217	11.1	2.14	$5.10 \times 10^5$	$4.99 \times 10^5$	E	C-D Bend
3080.	3032	12.7	0.53	$3.03 \times 10^5$	$3.91 \times 10^5$	$A_1$	C-D Str.

Table 3: Assignment and error analysis of  $\text{CDCl}_3$  Raman spectrum. Data was collected with both a 600gr/mm and an 1800 gr/mm grating and a 655, 690, and 780nm window, with 5 accumulations of 1 sec. each.

<sup>2</sup>Data for this molecule was incomplete. Supplementary material from Chung Jui Yu is also provided.

## 1.4 CH<sub>2</sub>Cl<sub>2</sub>

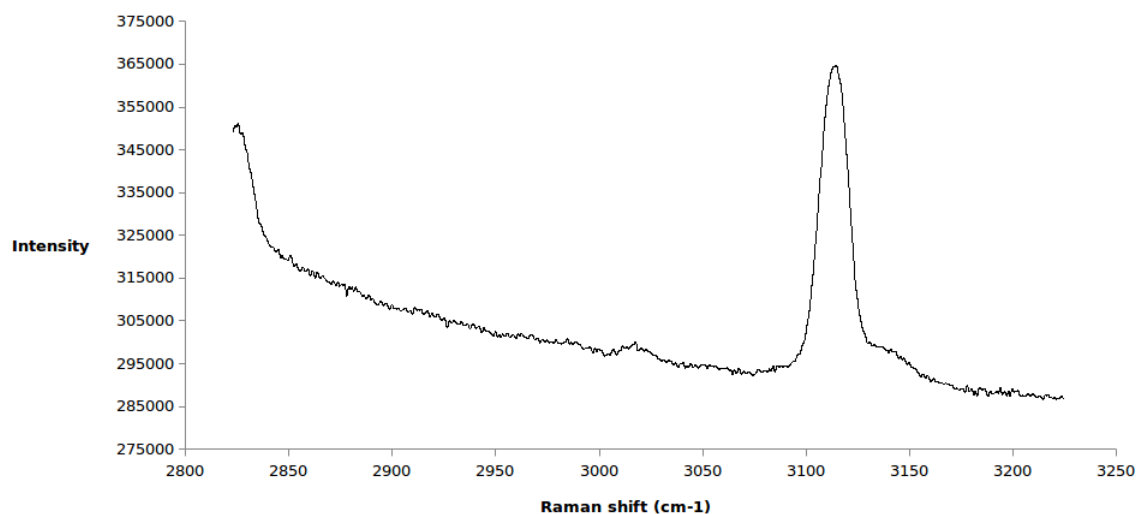


Figure 4: CH<sub>2</sub>Cl<sub>2</sub> Raman spectrum, without baseline correction.

Shift (cm <sup>-1</sup> )		Error (cm <sup>-1</sup> )		Intensity (A. U.)		Properties	
Observed	Literature <sup>[4]</sup>	FWHM	CCD	Observed	Corrected	Symbol	Assignment
266.1	281.5	13.3	2.04	$4.82 \times 10^5$	$5.02 \times 10^5$	A <sub>1</sub>	CCl <sub>2</sub> Scis.
701	713	16.4	2.04	$3.46 \times 10^5$	$3.33 \times 10^5$	A <sub>1</sub>	CCl <sub>2</sub> Sym. Str.
1371	1430.1	13.3	2.04	$4.82 \times 10^5$	$5.02 \times 10^5$	A <sub>1</sub>	CH <sub>2</sub> Scis.
2921	2996	20.0	2.04	$7.50 \times 10^5$	$7.37 \times 10^5$	A <sub>1</sub>	CH <sub>2</sub> Sym. Str.
3045	3040	11.1	1.92	$1.25 \times 10^5$	$1.29 \times 10^5$	B <sub>1</sub>	CH <sub>2</sub> Asym. Str.

Table 4: Assignment and error analysis of CH<sub>2</sub>Cl<sub>2</sub> Raman spectrum. Data was collected with both a 600gr/mm and an 1800 gr/mm grating and a 655, 690, and 780nm window, with 5 accumulations of 1 sec. each.

## 2 CCl<sub>4</sub> force constant calculation

$$4\pi^2\nu_1^2 = \frac{k}{m_{\text{Cl}}} \quad (1)$$

$$4\pi^2\nu_2^2 = \frac{3}{m_{\text{Cl}}}\frac{k_\delta}{\ell^2} \quad (2)$$

Force Constant	Value (N/m)	Literature Value (N/m) <sup>[5]</sup>
$k$	$443.7 \pm 30.5$	345.8
$\frac{k_\delta}{\ell^2}$	$33.62 \pm 5.08$	31.21

Table 5: Force constants for CCl<sub>4</sub>. Values were calculated using  $\bar{\nu}_1 = 460.6 \text{ cm}^{-1}$  and  $\bar{\nu}_2 = 219.59 \text{ cm}^{-1}$ , which were identified by Mulliken symbol ( $\nu_1$  is the symmetric stretch and is A<sub>1</sub>, while  $\nu_2$  is a degenerate deformation and is E.) Alternatively, these values can be found using  $\nu_3$  and  $\nu_4$  and by solving a more complex system of equations.

## 3 CCl<sub>4</sub> depolarization calculation

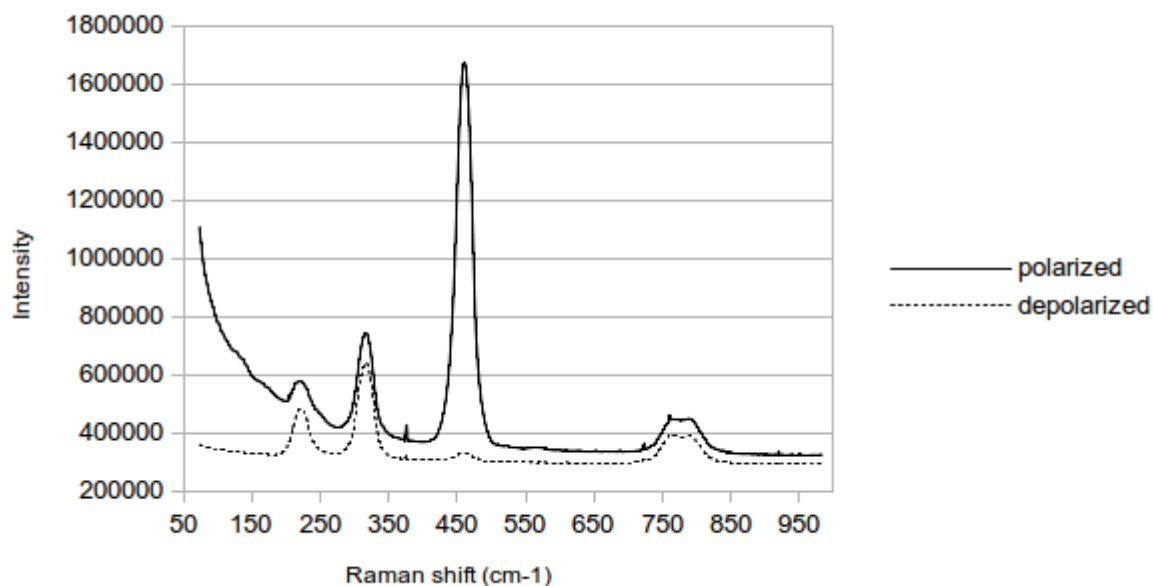


Figure 5: CCl<sub>4</sub> Raman spectrum, depolarized and polarized light

Shift (cm <sup>-1</sup> )	Polarization Intensity	Depolarization Intensity	Depolarization Ratio
219.6	$1.08 \times 10^5$	$1.60 \times 10^5$	1.47
315.9	$3.47 \times 10^5$	$3.23 \times 10^5$	0.931
460.6	$1.31 \times 10^6$	$2.96 \times 10^4$	0.0225
760.5	$1.24 \times 10^5$	$9.61 \times 10^4$	0.776
788.3	$1.13 \times 10^5$	$9.44 \times 10^4$	0.836

Table 6: Calculation of the depolarization ratio for CCl<sub>4</sub> transitions. All intensities are baseline-corrected using Origin.

## 4 CCl<sub>4</sub> temperature calculation

$$\frac{I_A}{I_S} = \left( \frac{v_0 + v_i}{v_0 - v_i} \right)^4 \exp \left( \frac{-hv_i}{k_B T} \right) \quad (3)$$

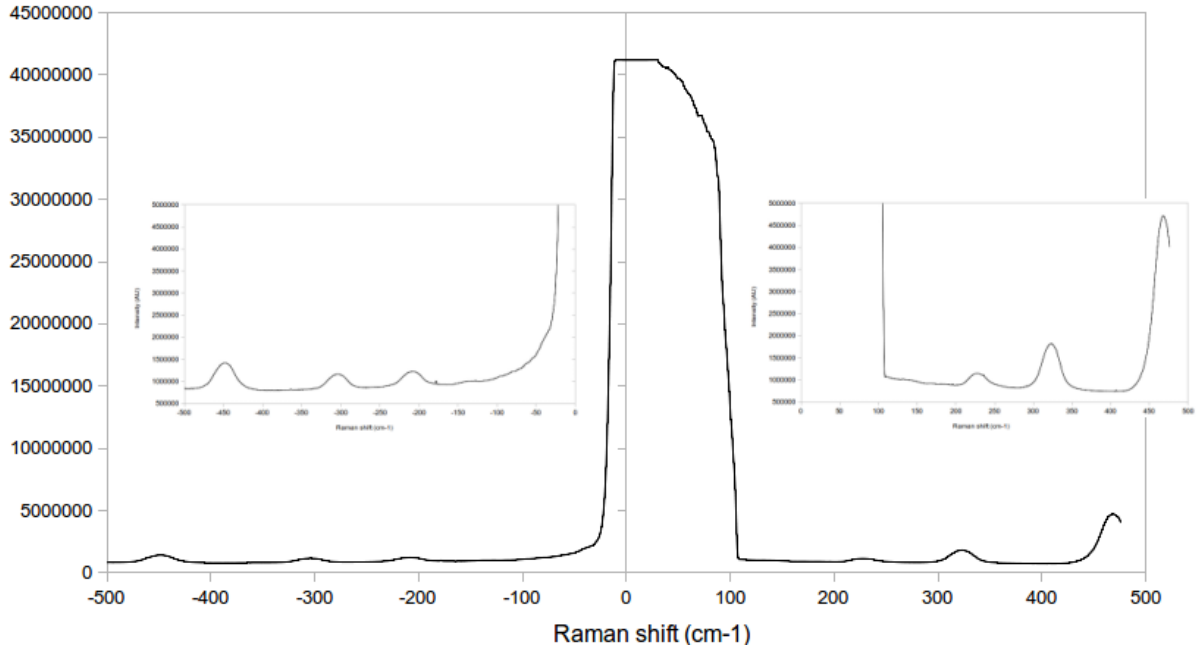


Figure 6: CCl<sub>4</sub> Rayleigh, Stokes-Raman, and anti-Stokes-Raman peaks.

Stokes			Anti-Stokes			Temp. (K)
Shift (cm <sup>-1</sup> )	Error (cm <sup>-1</sup> )	Intensity	Shift (cm <sup>-1</sup> )	Error (cm <sup>-1</sup> )	Intensity	
467.53	23.5	4713085	-447.69	23.5	1415572	382 ± 62

Table 7: Calculation of the CCl<sub>4</sub> sample temperature using Stokes and anti-Stokes transitions. All intensities are baseline-corrected using Origin.

## References

- [1] Shimanouchi, T., *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, National Bureau of Standards, 1972, 1-160.
- [2] Shimanouchi, T., *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, National Bureau of Standards, 1972, 1-160.
- [3] Bermejo, D., Escribano, R. and Orza, J. M. (1977), *Absolute Raman intensities of CHCl<sub>3</sub> and CDCl<sub>3</sub> and force field for chloroform*. *J. Raman Spectrosc.*, 6: 151154. doi: 10.1002/jrs.1250060310
- [4] Shimanouchi, T., *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, National Bureau of Standards, 1972, 1-160.
- [5] *Substituted Methanes. III. Raman Spectra, Assignments, and Force Constants for Some Trichloromethanes*. Zietlow, J.P.; Cleveland, F.F.; Meister, A.G. *J. Chem. Phys.***18**, 1076 (1950); doi: 10.1063/1.1747862
- [6] *Substituted Methanes: V. Infrared Spectra and Calculated Thermodynamic Properties for Some Trichloromethanes*. Madigan, J.R.; Cleveland, F.F. *J. Chem. Phys.***19**, 119 (1951); <http://dx.doi.org/10.1063/1.1747957>
- [7] Shoemaker, Garland, Nibler. *Experiments in Physical Chemistry, 8th ed.*; 2008.



## A Supplementary Graphs

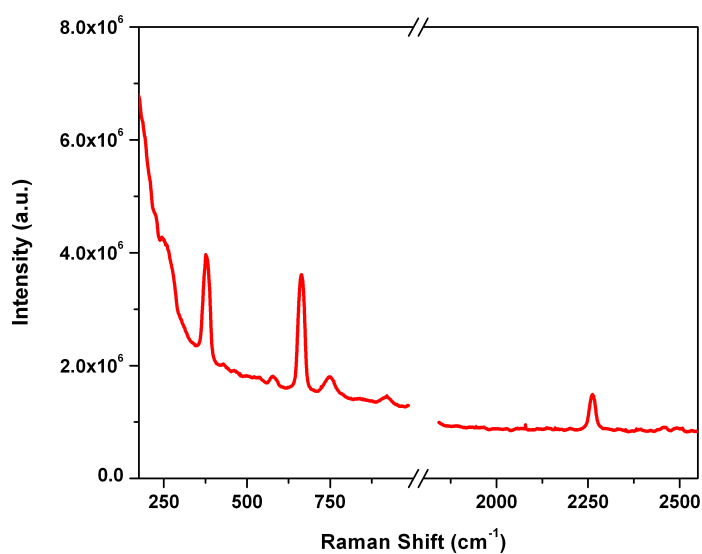


Figure 7: Supplementary CDCl<sub>3</sub> Raman spectrum, without baseline correction. Data and plot by Chung Jui Yu.

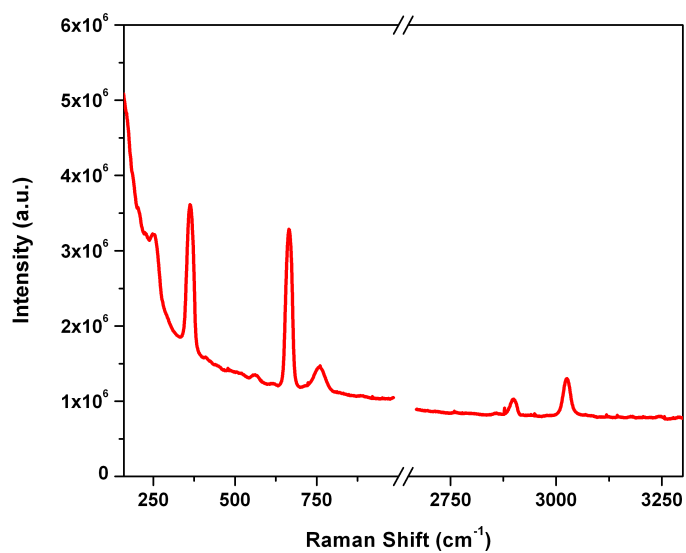


Figure 8: Supplementary CHCl<sub>3</sub> Raman spectrum, without baseline correction. Data and plot by Chung Jui Yu.