

C343 Experiment II

Spectroscopy

1 Rovibrational Spectroscopy

1.1 $^1\text{H}^{35}\text{Cl}$ Rovibrational Spectra

We generated the Rovibrational Spectrum of $^1\text{H}^{35}\text{Cl}$ molecule for the $v=0$ to $v=1$ transition. The Rotational Energy levels are given by the formula:

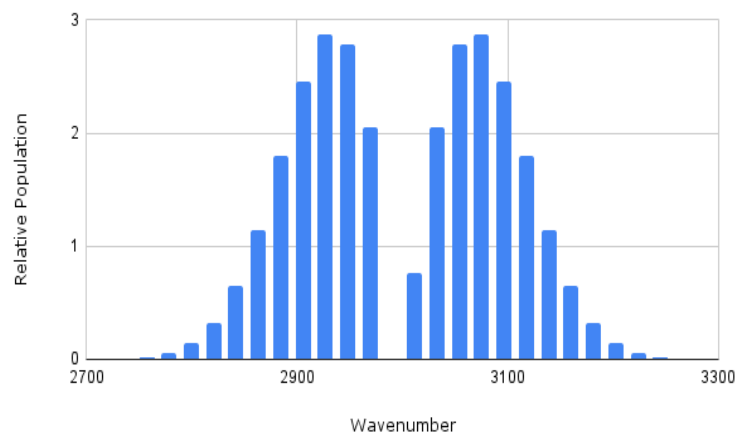
$$E_J = BJ(J+1) \text{ where, } J = 0, 1, 2, \dots$$

The Selection rule for Rovibrational transition under Harmonic and Rigid rotor approximation is :

$$\Delta v = \pm 1, \Delta J = \pm 1$$

The Rotational Constant of $^1\text{H}^{35}\text{Cl}$ is, $B = 10.59341 \text{ cm}^{-1}$. Using this the simulated rovibrational ($v = 0$ to $v = 1$) spectrum of $^1\text{H}^{35}\text{Cl}$ molecule was generated.

$^1\text{H}^{35}\text{Cl}$ Rovibrational Spectra

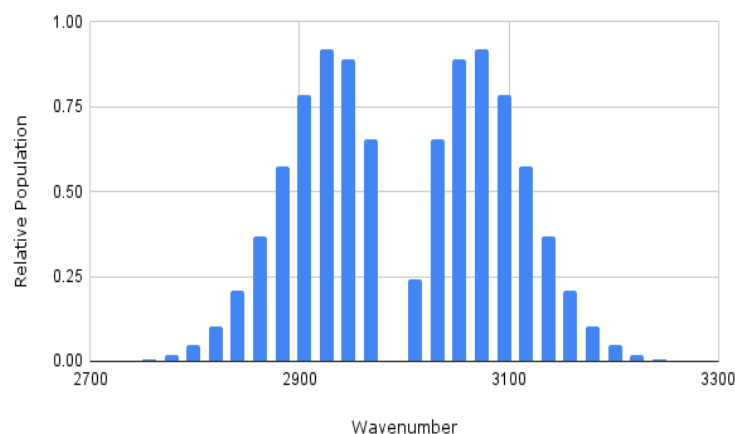


1.2 $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ Rovibrational Spectra

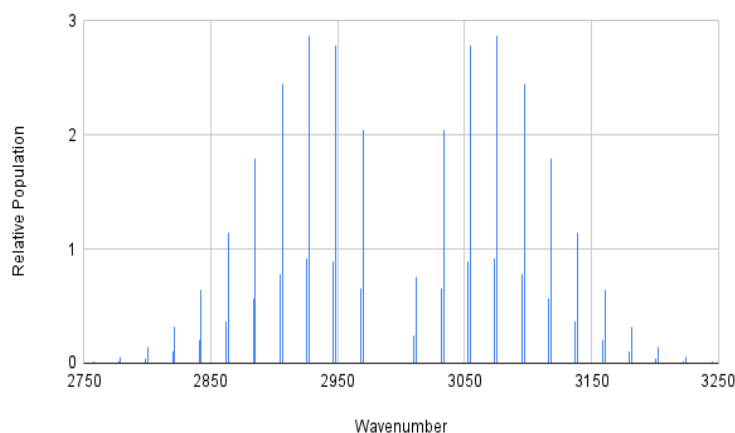
There are two stable isotopes of Chlorine: ^{35}Cl (75.77 %) and ^{37}Cl (24.23 %). Considering both the isotopes, the simulated rovibrational ($v = 0$ to $v = 1$) spectrum of $^1\text{H}^{37}\text{Cl}$ molecule was generated.

Here the population ratio would vary according to the relative abundance of each isotope. The Rotational Constant of $^1\text{H}^{37}\text{Cl}$ is, $B = 10.57750 \text{ cm}^{-1}$. Using this the simulated rovibrational ($v = 0$ to $v = 1$) spectrum of $^1\text{H}^{37}\text{Cl}$ molecule was generated.

$^1\text{H}^{37}\text{Cl}$ Rovibrational Spectra



Both Isotopes Together



2 Rotational Raman Spectra of N₂

Homonuclear diatomic molecules don't have pure rotational spectra as they do not possess a dipole moment. But, they can produce a rotational Raman spectrum. The energy levels still remain the same as before, only the selection rule changes to :

$$\Delta J = \pm 2$$

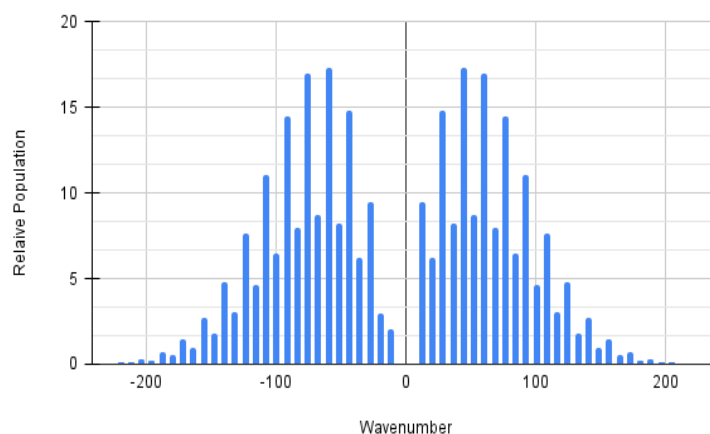
We will be able to observe Stokes and Anti-Stokes lines in Raman spectra. Since in rotational levels, the higher levels are populated more than ground, we expect the first line of anti-Stokes to be of higher intensity than the first line of Stokes. The intensity of Stokes and anti-Stokes would be comparable due to high population of upper levels too.

For N₂, total spin of nucleus $S = 1$ for ¹⁴N. Since S is integer, the nuclei are Bosons and the entire nuclear wave function must be symmetric with respect to their exchange. For any symmetric state there are $(2S+1)(S+1)$ and antisymmetric state $(2S+1)S$ possibilities respectively.

Thus, for $S = 1$ there are 6 symmetric spin states for the two nuclei and 3 antisymmetric spin states. The rotational ground state (and all other even J states) will have a 6 fold spin degeneracy, the next highest energy state (and all others with odd J) will have a 3 fold spin degeneracy. In this case $f(S) = S/(S+1) = 1/2$, So the ratio of Intensity of transitions from even state to odd state will be 2:1.

The Rotational Constant of N₂ is, $B = 1.998241 \text{ cm}^{-1}$. Using this the simulated pure rotational Raman ($v = 0, J$ to $v = 0, J+2$) spectrum of N₂ molecule was generated. The right side of zero corresponds to Anti-Stokes and left side to Stokes respectively.

Rotational Raman Spectrum of N₂



3 Protonated Water Dimer: (H₃O⁺)H₂O

3.1 Binding Energy of (H₃O⁺)H₂O

Geometry Optimisation followed by Frequency Calculation was done for (H₃O⁺)H₂O, H₃O⁺ and H₂O using HF/6-31G** level of Theory.

Molecule	Frequency	Electronic Energy (EE)	Zero Point Energy (ZPE)	Point Group
H ₂ O	1770.50 4145.86 4262.47	-76.023615	0.023189	C _{2v}
H ₃ O ⁺	781.94 1788.56 1788.58 3857.96 3993.86 3994.19	-76.310325	0.036918	C _{3v}
(H ₃ O ⁺)H ₂ O	137.02 214.64 367.74 468.24 492.28 509.61 1416.57 1462.72 1753.95 1793.20 2000.48 4023.65 4089.58 4128.69 4195.63	-152.387944	0.061634	C ₂

Energy Calculation for a Reaction:

Bond dissociation Energy is the difference between sum of Energy of Products and sum of Energy of reactants

$$\Delta_r E^\circ = \Sigma \Delta_f E_{prod}^\circ - \Sigma \Delta_f E_{reac}^\circ$$

$$\Delta_r E^\circ = \Sigma (EE + ZPE)_{prod} - \Sigma (EE + ZPE)_{reac}$$

(i) Energy Calculation for the Reaction: (H₃O⁺)H₂O \longrightarrow H₃O⁺ + H₂O

For (H₃O⁺)H₂O Dissociation:

$$\Delta_r E^\circ = (EE + ZPE)_{H_3O^+} + (EE + ZPE)_{H_2O} - (EE + ZPE)_{(H_3O^+)H_2O}$$

$$\begin{aligned}
&= (-76.310325+0.036918) + (-76.023615+0.023189) - (-152.387944+0.061634) \\
&= 0.052477 \text{ Hartree} \\
&= 137.778373995 = \mathbf{137.778 \text{ kJ/mol}}
\end{aligned}$$

Therefore, Binding Energy of Protonated Water dimer is around 137.7 kJ/mol.

3.2 Level of Theory: HF to DFT

The Same Calculation were done for $(\text{H}_3\text{O}^+)\text{H}_2\text{O}$, H_3O^+ and H_2O using B3LYP/6-31G** level of Theory. We will compare how the geometric and vibrational properties change when going from Hartree-Fock(HF) to DFT.

Molecule	Frequency	Electronic Energy (EE)	Zero Point Energy(ZPE)
H_2O	1664.96 3800.96 3914.24	-76.419737	0.021370
H_3O^+	780.49 1668.42 1668.53 3583.81 3702.93 3703.24	-76.705636	0.034417
$(\text{H}_3\text{O}^+)\text{H}_2\text{O}$	163.57 1450.32 378.41 1540.84 421.05 1690.83 482.20 1769.62 510.86 3751.18 618.41 3760.16 1086.14 3853.93 3854.35	-153.191846	0.057710
$(\text{D}_3\text{O}^+)\text{D}_2\text{O}$	116.85 1051.23 280.55 1118.14 310.87 1240.73 359.09 1304.01 378.10 2699.72 581.27 2710.73 773.98 2830.76 2831.26	-153.191846	0.042345

The Binding Energy Calculated in DFT Method = 0.064544 Hartree
= **169.460 kJ/mol**
Percentage Change in Binding Energy when going from HF to DFT = $(0.064544 - 0.052477)/0.052477 \times 100 = \mathbf{22.99\%}$

There is change by 23% in Energy when the level of theory is increased.

3.2.1 Protonated Water Dimer Geometry

Comparison of Geometrical Properties in Protonated Water dimer when changing level of theory from HF to DFT. In HF the proton is found closer to one of the Oxygen atoms than other, whereas in DFT the proton is equidistant from both Oxygen atoms. There are changes in both bond lengths and bond angles when going from HF to DFT. These are listed below:

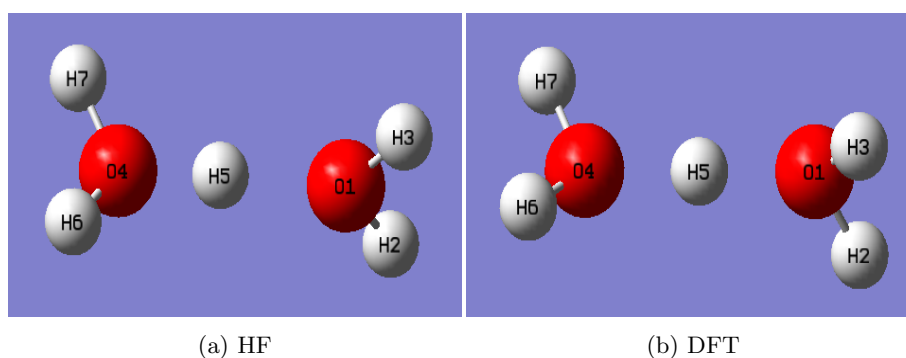


Figure 1: Optimised Geometry of Protonated water dimer

Bond Length/Angle (L/A)	Hartree-Fock (HF)	Density Functional Theory(DFT)
O1-H5(L)	1.32Å	1.19Å
O4-H5(L)	1.07Å	1.19Å
O1-H5-O4(A)	177.19°	174°
H2-O1-H3(A)	110.2°	109.94°
H6-O4-H7 (A)	112.7°	109.94°

As we can see the geometry becomes more symmetrical as we go from HF to DFT, the bond lengths and angles on both sides become equal.

3.2.2 Water monomer Geometry

Comparison of Geometrical Properties in Water monomer when changing level of theory from HF to DFT.

Bond Length/Angle (L/A)	Hartree-Fock (HF)	Density Functional Theory(DFT)	Actual Value
O-H (L)	0.94319 Å	0.96523 Å	0.9572 Å
H-O-H (A)	105.920°	103.745°	104.52°

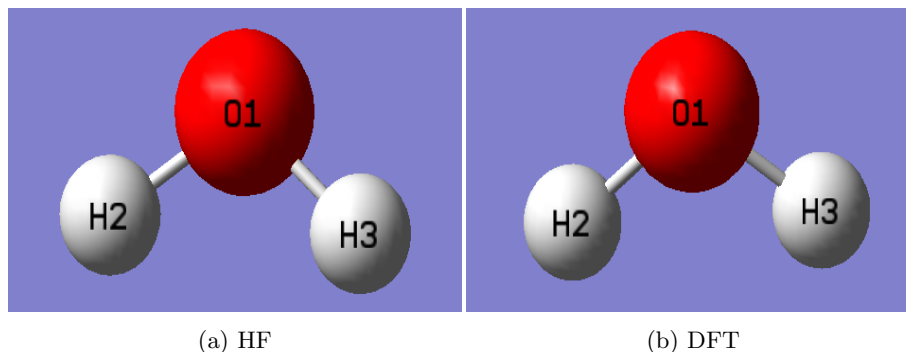


Figure 2: Optimised Geometry of Water Monomer

As we can observe, **the values calculated by DFT level of theory are closer to the actual values than from HF level of theory.** Both Bond angle and bond length of water monomer is closer to the actual value in DFT than HF Theory.

Hence we may say that, **the results of DFT are better than HF level of theory.**

3.2.3 Experimental IRMPD Spectra of Protonated Water Dimer

Comparison between Experimentally observed IRMPD Spectra and calculated vibrational frequency. The following table lists the closest theoretical frequency and its corresponding Vibrational Mode for the experimentally observed peaks.

Molecule	Experimental Frequency	Theoretical Frequency	Normal Mode
$(\text{H}_3\text{O}^+)\text{H}_2\text{O}$	788	618.41	O-H ⁺ -O Symmetric Stretch
	921	1086.14	H ₂ O Bending
	1043	1086.14	H ₂ O Bending
	1317	1450.32	H ₂ O Bending
	1741	1690.83, 1769.62	H ₂ O Scissoring
$(\text{D}_3\text{O}^+)\text{D}_2\text{O}$	697	581.27	O-D ⁺ -O Symmetric Stretch
	795	773.98	D ₂ O Bending
	960	1051.23	D ₂ O Bending
	1296	1240.73	D ₂ O Scissoring

Except the first mode (618.41 cm⁻¹), all the other modes involve O-H⁺-O Asymmetric Stretch. Similarly the D₂O also has asymmetric O-D⁺-O Stretches in all the modes. These modes do not involve any Stretching vibrations of H₂O or D₂O. They involve only the bending vibrations of H₂O or D₂O.