
C343 Lab Report 2

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1 Rovibrational Spectrum of HCl

Energy $E(\mathbf{v}, \mathbf{J})$ of a molecule present at energy state with vibrational quantum number(v) and rotational quantum number(J) under rigid-rotor(with rotational constant B) and harmonic oscillator(of frequency ν) approximations is given by :

$$E(v, J) = (v + \frac{1}{2})h\nu + BJ(J + 1) \quad (1)$$

$$\text{Population}(E(v, J)) = (2J + 1) \exp(-\frac{E(v, J)}{k_B T}) \quad (2)$$

$$\text{Selection Rule used for } (v = 0 \rightarrow v = 1) = \begin{cases} \Delta J = \pm 1 \\ \Delta n = 1 \end{cases}$$

$$\begin{aligned} \Delta E(J \rightarrow J + 1) &= E(1, J + 1) - E(0, J) & \Delta E(J \rightarrow J - 1) &= E(1, J - 1) - E(0, J) \\ &= h\nu + 2B(J + 1) & &= h\nu - 2BJ \quad (J > 0) \end{aligned} \quad \begin{matrix} (3) \\ (4) \end{matrix}$$

(a) Simulated rovibrational ($v = 0 \rightarrow v = 1$) spectrum of $^1\text{H}^{35}\text{Cl}$ for J from 0 to 24

Input Parameters: $B = 10.5933002 \text{ cm}^{-1}$ $\nu = 2990.9248 \text{ cm}^{-1}$

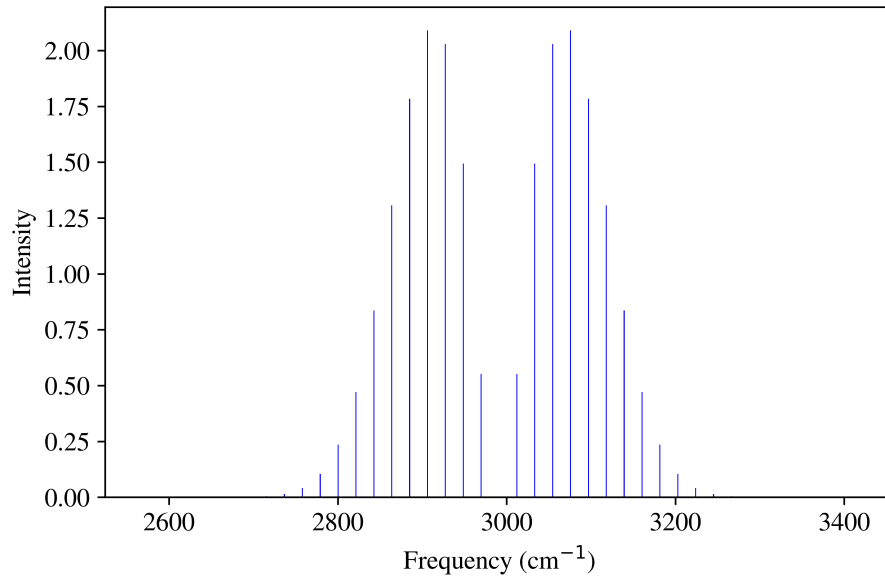


Figure 1: Rovibrational spectrum of $^1\text{H}^{35}\text{Cl}$

(b) Simulated rovibrational ($v = 0 \rightarrow v = 1$) spectrum of HCl molecule with ^{35}Cl and ^{37}Cl

$$\text{Pop}'(E(v, J, A)) = (2J + 1) \exp\left(-\frac{E(v, J, A)}{k_B T}\right) \times \text{Relative Abundance of isomer} \quad (5)$$

Input Parameters: $B(\text{H}^{35}\text{Cl}) = 10.5933002 \text{ cm}^{-1}$ $\nu(\text{H}^{35}\text{Cl}) = 2990.9248 \text{ cm}^{-1}$
[1]

$$\begin{aligned} B(\text{H}^{37}\text{Cl}) &= B(\text{H}^{35}\text{Cl}) * \frac{\text{Reduced mass of } (\text{H}^{35}\text{Cl})}{\text{Reduced mass of } (\text{H}^{37}\text{Cl})} \\ &= 10.5933002 * \frac{35 * 1 * 38}{37 * 1 * 36} \text{ cm}^{-1} \\ &= 10.577394 \text{ cm}^{-1} (\text{using Rigid Rotor approximation}) \end{aligned} \quad (6)$$

$$\begin{aligned} \nu(\text{H}^{37}\text{Cl}) &= \nu(\text{H}^{35}\text{Cl}) * \sqrt{\frac{\text{Reduced mass of } (\text{H}^{35}\text{Cl})}{\text{Reduced mass of } (\text{H}^{37}\text{Cl})}} \\ &= 2990.9248 * \frac{35 * 1 * 38}{37 * 1 * 36} \text{ cm}^{-1} \\ &= 2988.6785 \text{ cm}^{-1} (\text{using Harmonic Oscillator approximation}) \end{aligned} \quad (7)$$

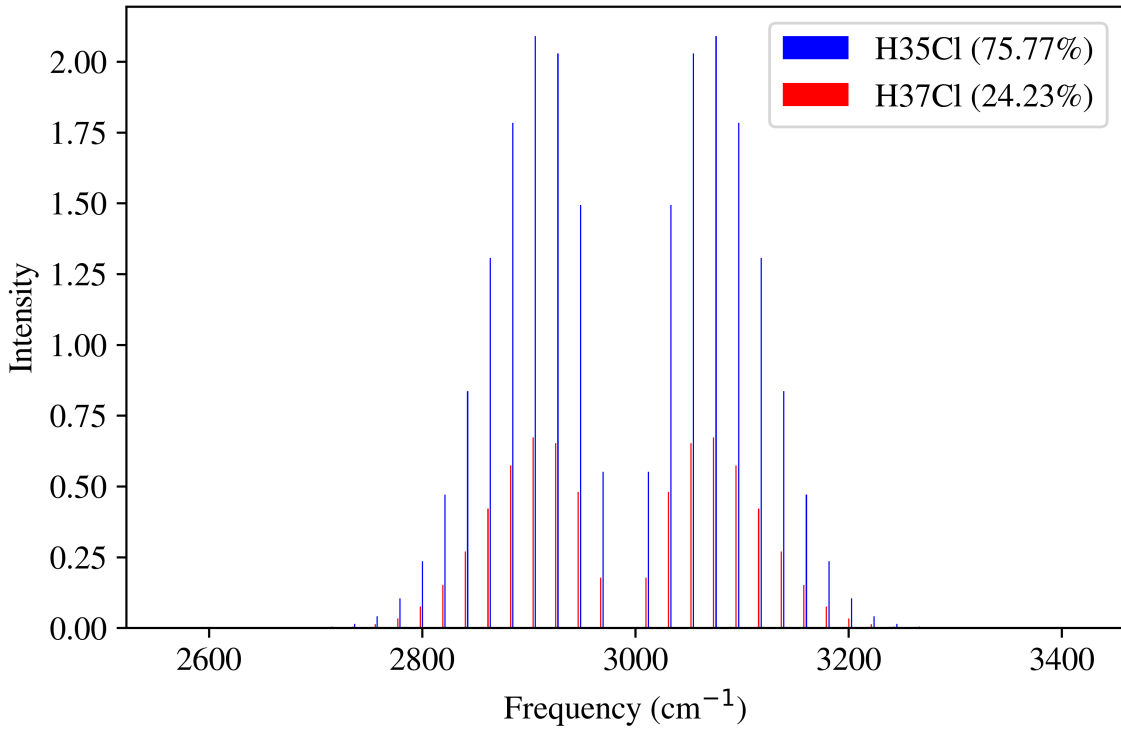


Figure 2: Rovibrational spectrum of HCl considering ^{35}Cl and ^{37}Cl

Reference for Rotational and Vibrational constants

1. Irikura, K. K. (2007). Experimental vibrational zero-point energies: Diatomic molecules. **Journal of Physical and Chemical Reference Data**, 36(2), 389-397.
2. De Lucia, F. C., Helminger, P., Gordy, W. (1971). Submillimeter-wave spectra and equilibrium structures of the hydrogen halides. **Physical Review A**, 3(6), 1849.

2 Pure rotational Raman spectrum of N₂

$$E(J) = BJ(J + 1) \quad (8)$$

$$\text{Nuclear Spin of N (I)} = 1 \quad (9)$$

$$\frac{\text{Population at odd } J}{\text{Population at even } J} = \frac{I + 1}{I} \quad (\text{Integral Spin Value}) \quad (10)$$

$$= 2 : 1$$

$$\text{Population}(E(J)) = \begin{cases} 2 \times (2J + 1) \exp(-\frac{E(J)}{k_B T}) & \text{odd } J \\ 1 \times (2J + 1) \exp(-\frac{E(J)}{k_B T}) & \text{even } J \end{cases}$$

$$\text{Selection Rule for pure rotational Raman} = \begin{cases} \Delta J = \pm 2 \\ \Delta n = 0 \end{cases}$$

$$\begin{aligned} \Delta E(J \rightarrow J + 2) &= E(J + 2) - E(J) & \Delta E(J \rightarrow J - 2) &= E(J - 2) - E(J) \\ &= 2B(2J + 3) & &= -2B(2J - 1) \quad (J \geq 2) \end{aligned} \quad (11)$$

$$(12)$$

$$B(\text{N}_2) = 1.99824 \text{ cm}^{-1} \quad [1]$$

Reference for Rotational constant

1. Irikura, K. K. (2007). Experimental vibrational zero-point energies: Diatomic molecules. **Journal of Physical and Chemical Reference Data**, 36(2), 389-397.

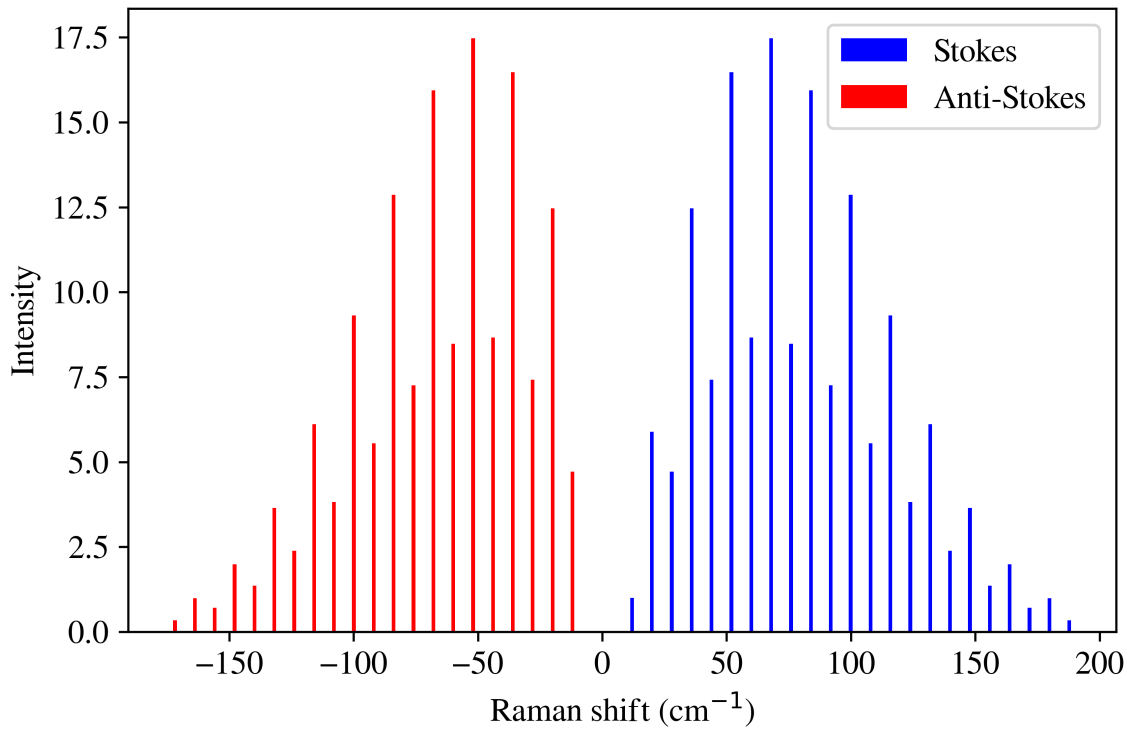
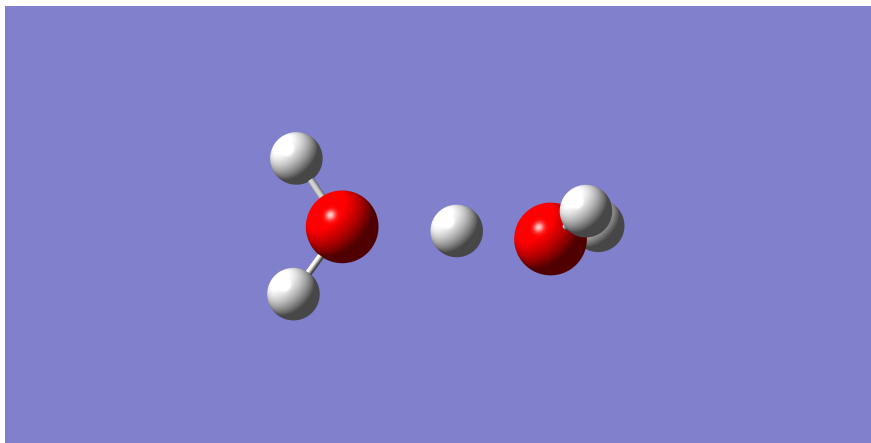


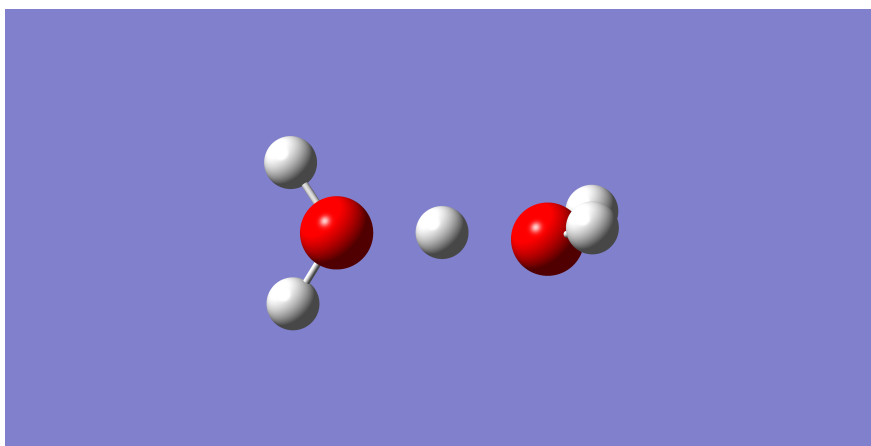
Figure 3: Pure rotational Raman spectrum of N₂ for J from 0 to 24

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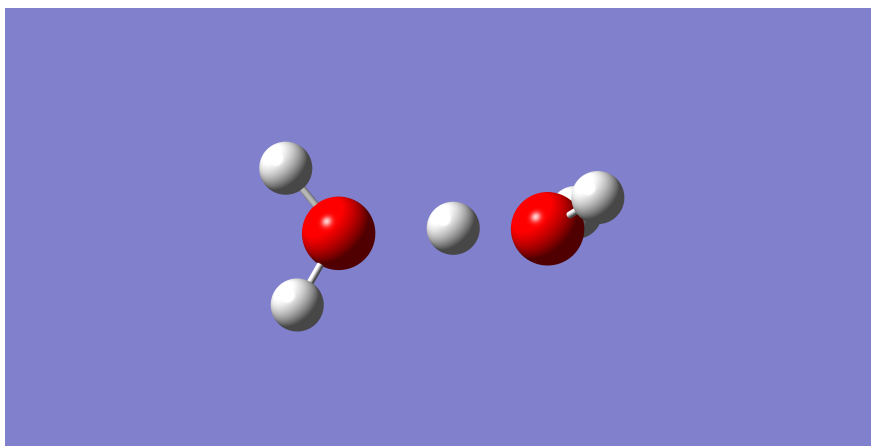
(a) Different Conformers of H_5O_2^+ :



Figuur 4: Point Group: CS Energy: -152.3264306 Ha(HF/6-31G**)



Figuur 5: Point Group: C2 Energy: -153.1443966 Ha(B3LYP/6-31G**)



Figuur 6: Point Group: C1 Energy: -152.3264519 Ha(HF/6-31G**)

Binding Energy Calculation :

$$\begin{aligned}\text{Energy}[\mathbf{H_2O}] &= -76.0004258 \text{ Hartree(HF/6-31G**)} \\ &= -76.398367 \text{ Hartree(B3LYP/6-31G**)}\end{aligned}\quad (13)$$

$$\begin{aligned}\text{Energy}[\mathbf{H_3O^+}] &= -76.2734057 \text{ Hartree(HF/6-31G**)} \\ &= -76.6712234 \text{ Hartree(B3LYP/6-31G**)}\end{aligned}\quad (14)$$

$$\begin{aligned}\text{Binding Energy of } \mathbf{H_5O_2^+(CS)} &= \text{Energy}[\mathbf{H_5O_2^+(CS)}] - (\text{Energy}[\mathbf{H_2O}] + \text{Energy}[\mathbf{H_3O^+}]) \\ &= -0.0525991 \text{ Hartree} \\ &= -33.00593525 \text{ kcal/mol (HF/6-31G**)}\end{aligned}\quad (15)$$

$$\begin{aligned}\text{Binding Energy of } \mathbf{H_5O_2^+(C2)} &= \text{Energy}[\mathbf{H_5O_2^+(C2)}] - (\text{Energy}[\mathbf{H_2O}] + \text{Energy}[\mathbf{H_3O^+}]) \\ &= -0.0748062 \text{ Hartree} \\ &= -46.9408905 \text{ kcal/mol (B3LYP/6-31G**)}\end{aligned}\quad (16)$$

$$\begin{aligned}\text{Binding Energy of } \mathbf{H_5O_2^+(C1)} &= \text{Energy}[\mathbf{H_5O_2^+(C1)}] - (\text{Energy}[\mathbf{H_2O}] + \text{Energy}[\mathbf{H_3O^+}]) \\ &= -0.0526204 \text{ Hartree} \\ &= -33.019301 \text{ kcal/mol (HF/6-31G**)}\end{aligned}\quad (17)$$

(b) Comparison of protonated dimer and water monomer

Change in Geometrical Vibrational properties: O-H bond length is shorter in dimer w.r.t monomer and H-O-H bond angle is a bit smaller in dimer compared to the monomer. There is a decrease in O-H stretching frequency also.

Effect of B3LYP and HF:

The protonated dimer structure has the C2 structure as its minima and CS as transition state(1 negative vibrational frequency) when computed at B3LYP level of theory. But at HF level of theory, it's the opposite the CS structure is a minima and C2 is a transition state(1 negative vibrational frequency)

IRMPD Vibrational Spectra Assignment

(H* is the proton in between the O atoms)

Band	Frequency obtained from			Vibrational Mode(based on HF data)
	Experiment	HF/6-31G**	B3LYP/6-31G**	
a	788	511.8498	618.2005	(O-H*-O) symmetric stretching
b	888,921, 947, 975			
c	1043, 1071, 1100, 1145, 1195		1085.29	
d	1252,1317, 1390, 1460	1409.1275	1451.18	(O-H*-O) out-of plane bending
e	1687,1741, 1850	1749.1060	1769.49	(O-H*-O) in-plane bending

Reference for IRMPD Vibrational Spectra

1. Asmis, K. R., Pivonka, N. L., Santambrogio, G., Brümmer, M., Kaposta, C., Neumark, D. M., Wöste, L. (2003). Gas-phase infrared spectrum of the protonated water dimer. *Science*, 299(5611), 1375-1377.