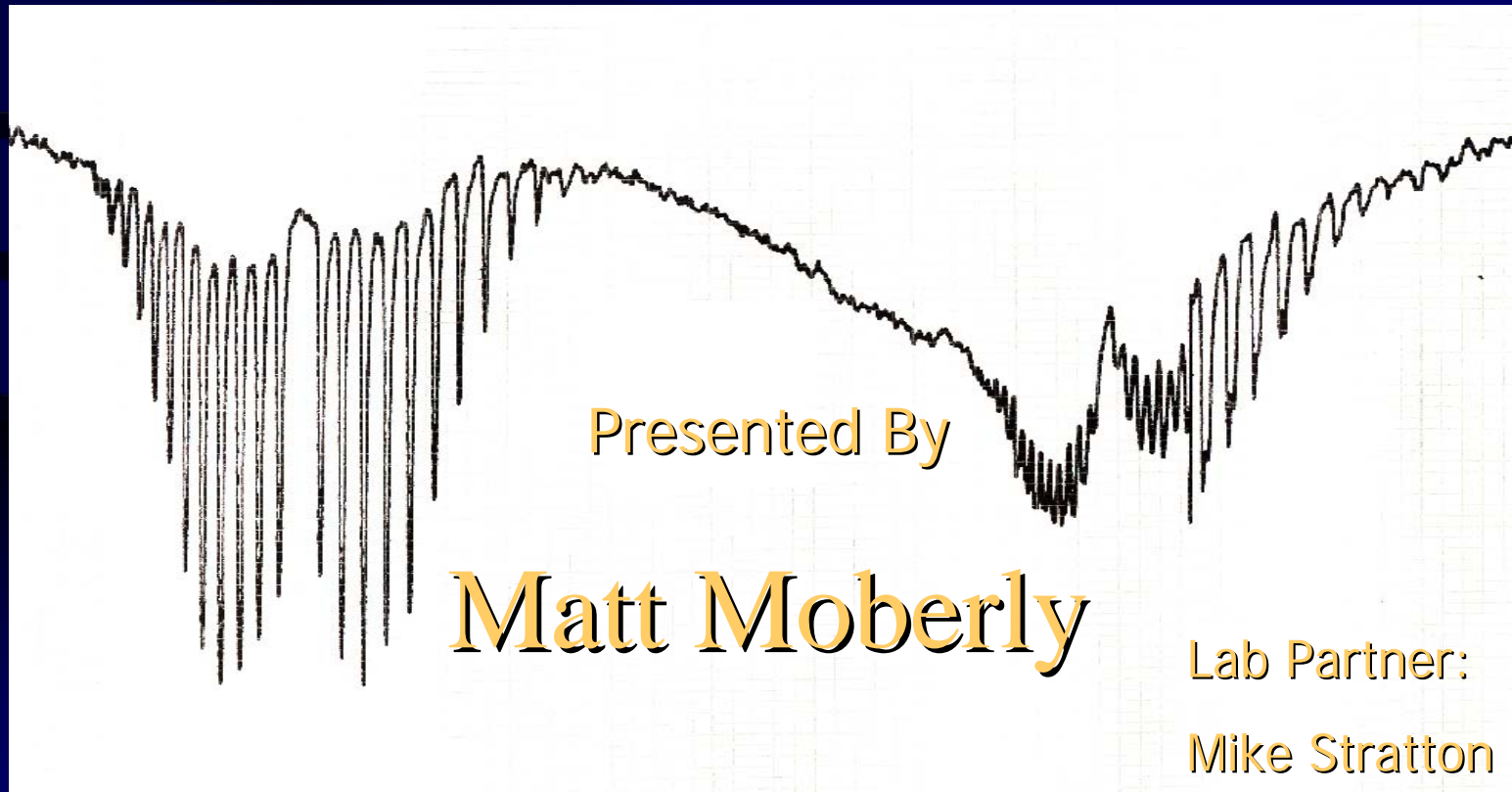


Vibrational-Rotational Spectra of HCl and DCl



Presentation Outline

I. Introduction

- a. Purpose
- b. Theory
- c. Equations

II. Experimental Method

III. Results

- a. Spectra
- b. Calculations and Error Analysis
- c. Theoretical Calculations

IV. Conclusion

V. References

Introduction

Purpose:

Use the infrared vibrational spectrum of HCl and DCl to obtain the following:

- Moment of Inertia, I_e
- Internuclear Separation, r_e
- Force Constant, k
- Evidence of the Isotope Effect

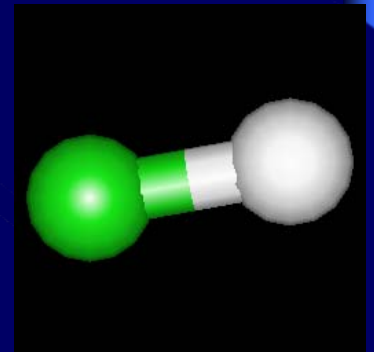
Theory:

Simplest vibrating diatomic model is a harmonic oscillator described by¹:

$$E(\nu) = h\nu(\nu + \frac{1}{2})$$

Simplest rotating diatomic model is the rigid rotor or “dumb-bell” model which can be pictured as two masses joined by a rigid, weightless rod and described by¹:

$$E(J) = \frac{h^2}{8\pi^2 I} J(J + 1)$$



This more complete energy expression contains both rotational and vibrational parts as well as a final coupling portion¹

$$\frac{E(\nu, J)}{hc} = \tilde{\nu}_e \left(\nu + \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(\nu + \frac{1}{2}\right)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e \left(\nu + \frac{1}{2}\right) J(J+1)$$

$\tilde{\nu}_e$ – *Vibrational Frequency*

x_e – *Anharmonicity Constant*

B_e – *Rotational Constant*

D_e – *Rotational Constant*

α_e – *Coupling Constant*



Infrared absorption or emission can only occur at allowed transition levels

- Vibrational: $\nu''=0, \nu'=1$
- Rotational: $\Delta J = \pm 1$
- R and P branches
- Spacing between peaks

Isotope Effect: mass difference between atoms effects the vibrational and rotational energies

- Splitting of peaks (^{35}Cl and ^{37}Cl)
- Compaction of heavier isotope spectrum
- Shift to higher wavelengths, λ

Equations:

Linear Regression Equation²:

$$(1) \quad \tilde{\nu}(x) = \tilde{\nu}_0 + (2B_e - 2\alpha_e)x - \alpha_e x^2 - 4D_e x^3$$

$$\tilde{\nu}_0 = \textit{Forbidden Frequency}$$

Rotational Constant³

$$(2) \quad B_e = \frac{h}{8\pi^2 I_e c}$$



$$(3) \quad I_e = \frac{h}{8\pi^2 B_e c}$$

Rotational Constant is rearranged solving for the Moment of Inertia, I_e

- h , Planks Constant: $6.626076 \times 10^{-34} \text{ J s}$
- c , Velocity of light (in vacuum): $2.99792485 \text{ m s}^{-1}$

Moment of Inertia, I_e ¹

$$(4) \quad I_e = \mu r^2$$



$$(5) \quad r = \sqrt{\frac{I_e N_A}{\mu}}$$

Moment of Inertia is rearranged solving for Internuclear Separation, r

- μ , reduced mass: $m_A m_B / (m_A + m_B)$
- N_A , Avogadro's Constant

Frequency of Forbidden Transmission¹

(6)

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e$$

(7)

$$\tilde{\nu}_0^* = \tilde{\nu}_e \left(\frac{\mu}{\mu^*} \right)^{1/2} - 2\tilde{\nu}_e x_e \frac{\mu}{\mu^*}$$

Frequency equations are used to solve for the two unknowns

$x_e \rightarrow$ *Anharmonicity Constant*

Frequency Equation³

(8)

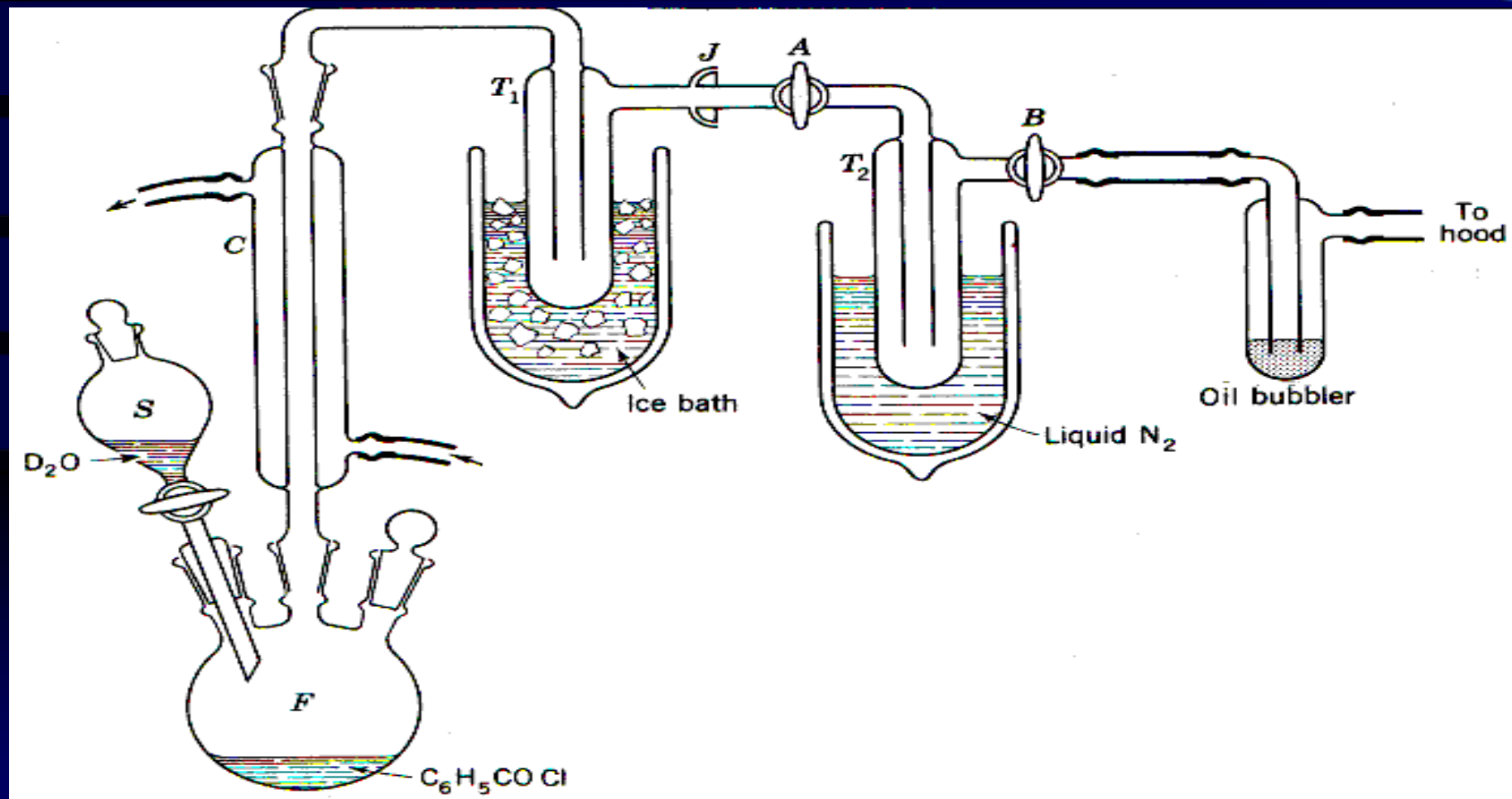
$$\tilde{\nu}_e = \frac{1}{2\pi c} \left(\frac{kN_A}{\mu} \right)^{1/2}$$

(9)

$$k = 4\pi^2 c^2 \tilde{\nu}_e^2 \mu N_A^{-1}$$

Frequency equation is rearranged solving for the Force Constant, k

Experimental Method



Apparatus

- Acetone/Dry Ice bath in first trap condense and trap any D_2O / H_2O or D_3PO_4 / H_3PO_4
- Liquid N_2 bath to protect the pump from formed gasses

Changes to Apparatus⁴

- Water condenser was not included
- Three-way valve was placed at position A
- Manometer was placed between first Acetone/Dry Ice bath and three-way valve

Preparation of HCl and DCl⁴

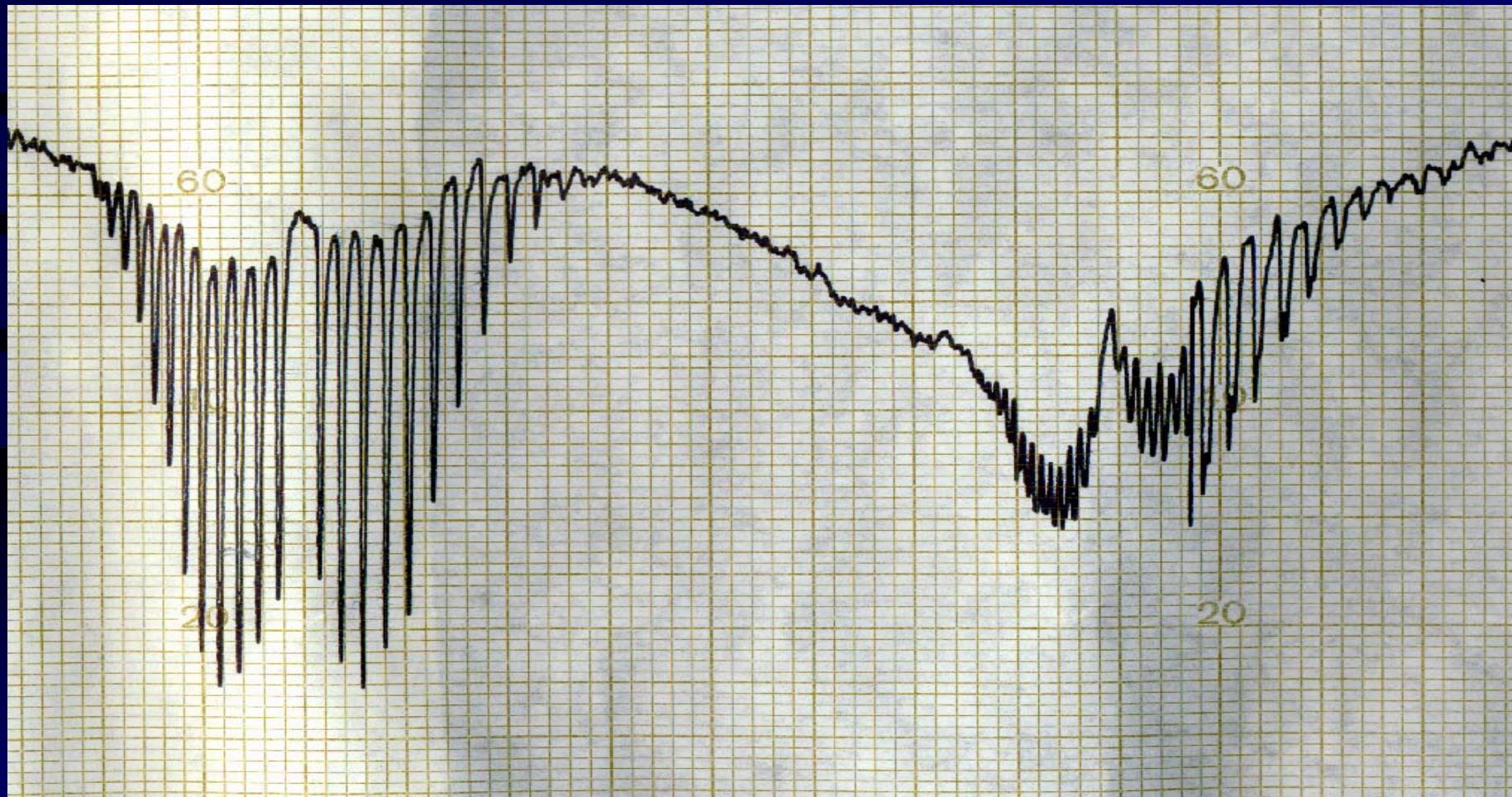


- Since D₂O is not pure both HCl and DCl are formed
- Approx. 2g of PCl₅ (green) was placed in flask F
 - Initial reaction used less than 2 grams PCl₅ which did not produce sufficient amounts of HCl/DCl gas
- The system was evacuated for approx. 15 minutes
- 1.0 ml D₂O was added to flask F with the I.R. cell opened which produced a violent reaction

Gas Collection

- Once reaction was complete, the I.R. cell was closed, detached, and placed in the infrared spectrophotometer for analysis

HCl and DCl Spectrum



Calculations and Error Analysis:

Equation (1): HCl

$$\begin{aligned}\tilde{\nu}_0 &= 2779.23 \text{ cm}^{-1} \\ \alpha_e &= 0.2954 \text{ cm}^{-1} \\ B_e &= 10.558 \text{ cm}^{-1} \\ D_e &= 6.5422 \times 10^{-4} \text{ cm}^{-1}\end{aligned}$$

Herzberg vol. 2

$$\begin{aligned}\tilde{\nu}_0 &= 2885.10 \text{ cm}^{-1} \\ \alpha_e &= 0.3019 \text{ cm}^{-1} \\ B_e &= 10.591 \text{ cm}^{-1} \\ D_e &= \text{NA}\end{aligned}$$

Relative Error

$$\begin{aligned}\tilde{\nu}_0 &\rightarrow 3.682 \% \\ \alpha_e &\rightarrow 2.141 \% \\ B_e &\rightarrow 0.306 \% \\ D_e &\rightarrow \text{NA}\end{aligned}$$

Equation (1): DCI

$$\begin{aligned}\tilde{\nu}_0 &= 2086.65 \text{ cm}^{-1} \\ \alpha_e &= 0.1064 \text{ cm}^{-1} \\ B_e &= 5.474 \text{ cm}^{-1} \\ D_e &= 1.57 \times 10^{-4} \text{ cm}^{-1}\end{aligned}$$

Herzberg vol. 2

$$\begin{aligned}\tilde{\nu}_0 &= 2091.10 \text{ cm}^{-1} \\ \alpha_e &= 0.1118 \text{ cm}^{-1} \\ B_e &= 5.445 \text{ cm}^{-1} \\ D_e &= \text{NA}\end{aligned}$$

Relative Error

$$\begin{aligned}\tilde{\nu}_0 &\rightarrow 0.198 \% \\ \alpha_e &\rightarrow 4.847 \% \\ B_e &\rightarrow 0.537 \% \\ D_e &\rightarrow \text{NA}\end{aligned}$$

Equation (3): HCl

Herzberg vol. 2

Relative Error

$$I = 2.651 \times 10^{-40} \text{ cm}^2 \text{ gm}$$

$$I = 2.643 \times 10^{-40} \text{ cm}^2 \text{ gm}$$

0.307%

Equation (3): DCl

Herzberg vol. 2

Relative Error

$$I = 5.114 \times 10^{-40} \text{ cm}^2 \text{ gm}$$

$$I = 5.141 \times 10^{-40} \text{ cm}^2 \text{ gm}$$

0.534%

Equation (5): HCl

Herzberg vol. 2

Relative Error

$$r_e = 1.277 \times 10^{-8} \text{ cm}$$

$$r_e = 1.2746 \times 10^{-8} \text{ cm}$$

0.162%

Equation (5): DCl

Herzberg vol. 2

Relative Error

$$r_e = 1.272 \times 10^{-8} \text{ cm}$$

$$r_e = 1.2749 \times 10^{-8} \text{ cm}$$

0.258%

Equation (6&7): Equil.
Vibrating Frequency for
HCl and anharmonicity
c o n s t a n t

$$\begin{aligned}\tilde{\nu}_e &= 3239.62 \text{ cm}^{-1} \\ \tilde{\nu}_e x_e &= 230.198 \text{ cm}^{-1} \\ x_e &= 0.071\end{aligned}$$

Equation (9): HCl

$$k = 6.057 \times 10^5 \text{ cm}^{-1} \text{ dyne}$$

$$k_{lit} = 5.159 \times 10^5 \text{ cm}^{-1} \text{ dyne}$$

$$\Delta = 17.414\%$$

Theoretical Calculations⁵:

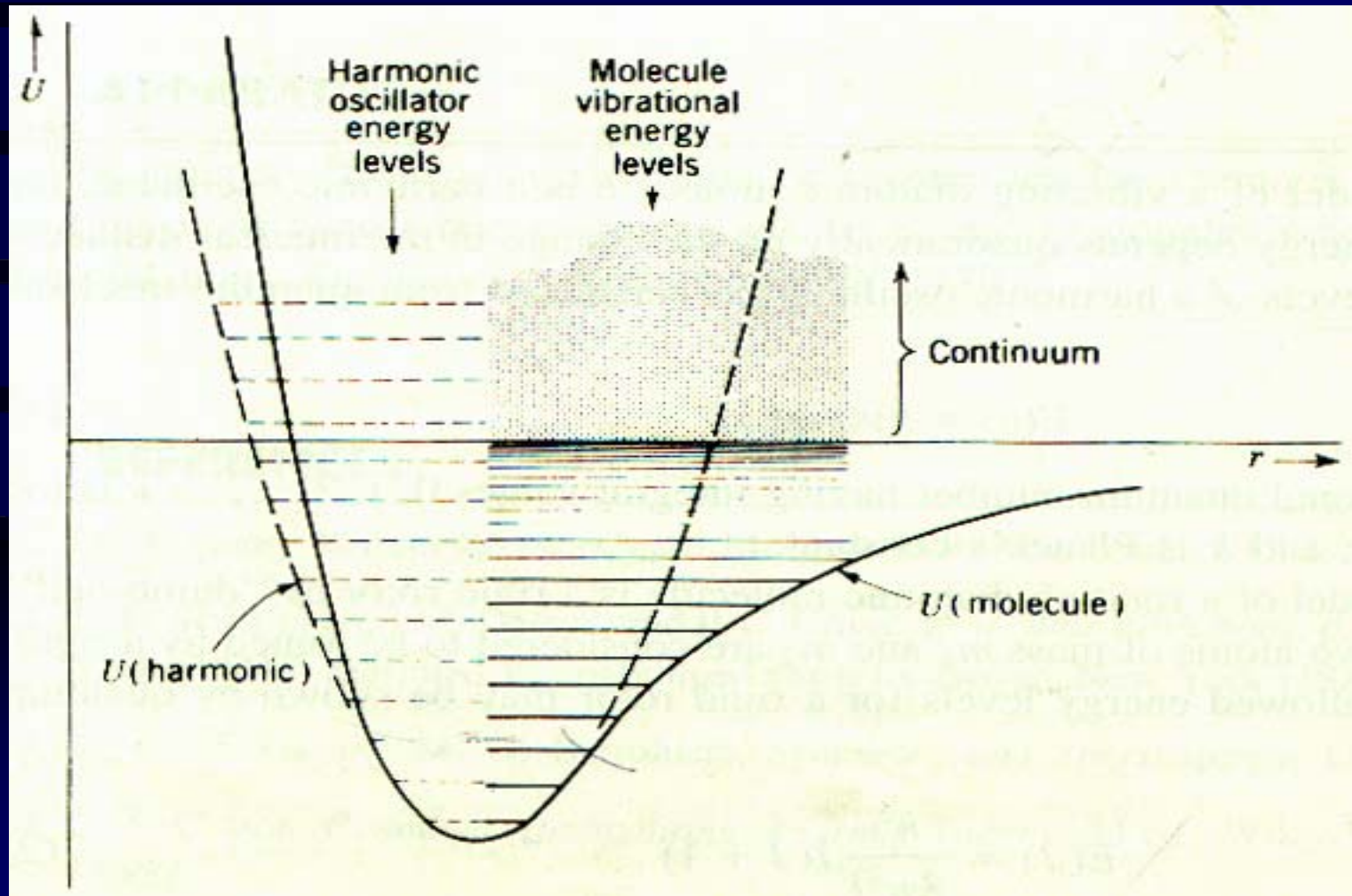
HF Results

$$\begin{aligned}r_e &= 1.313 \times 10^{-8} \text{ cm} \\ \tilde{\nu}_e &= 3372.52 \text{ cm}^{-1} \\ B_e &= 9.977 \text{ cm}^{-1}\end{aligned}$$

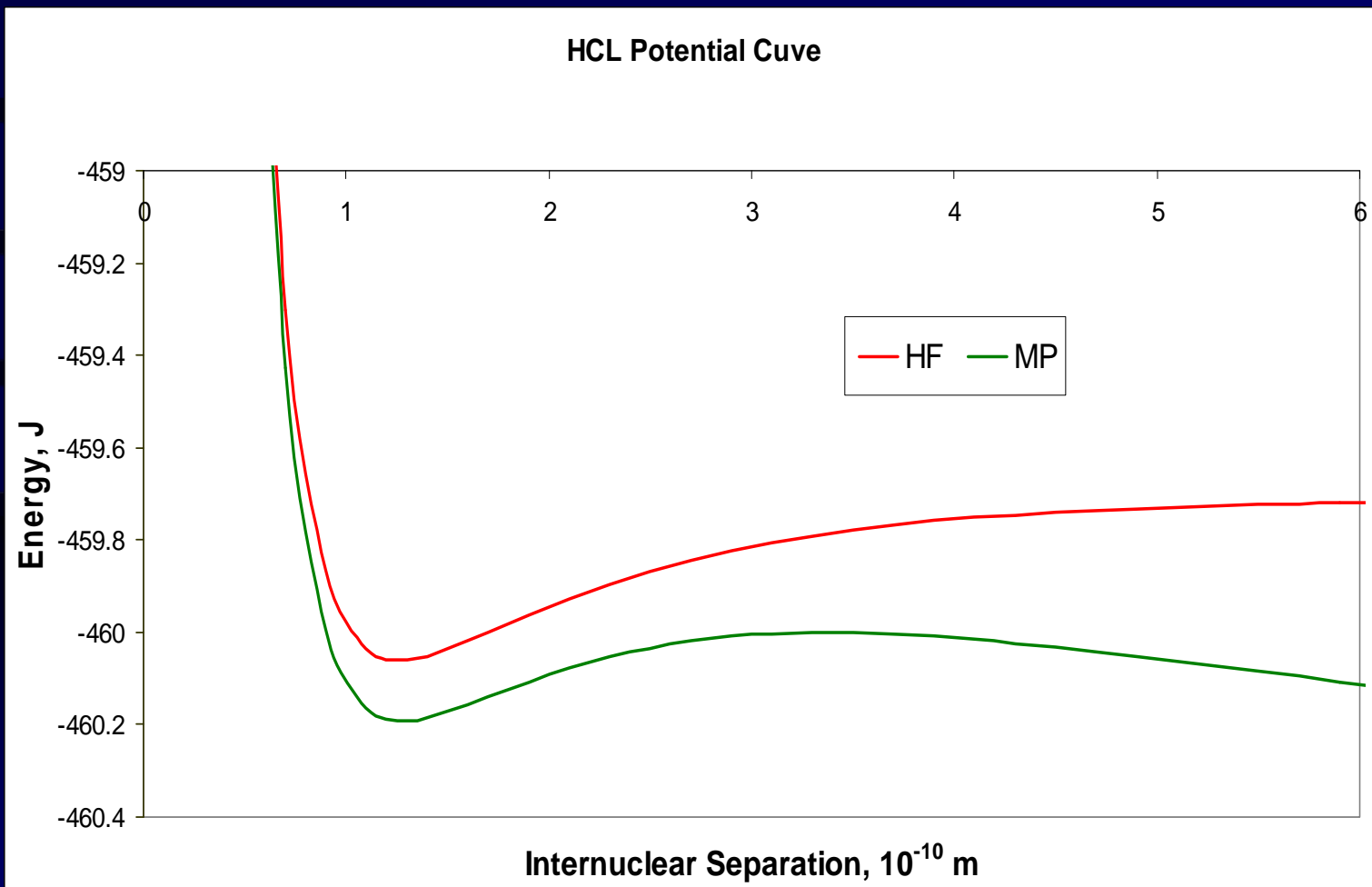
MP Results

$$\begin{aligned}r_e &= 1.280 \times 10^{-8} \text{ cm} \\ \tilde{\nu}_e &= 3049.15 \text{ cm}^{-1} \\ B_e &= 10.502 \text{ cm}^{-1}\end{aligned}$$

Potential Energy as a Function of Internuclear separation, r_e



Potential Curve of HCl using Hartree-Fock (HF) and Moeller-Plessett (MP) Theories



Conclusion

- Largest Source of Error likely from Spectra Readings
 - Force Constant
 - Coupling Constant
 - Reduce systematic error by “zooming” in
 - Use a new I.R. Cell
- Internuclear Separation fluctuates with Moment of Inertia, I_e , obtained is an average
- x_e shows anharmonicity of HCl molecule is small
- Isotope Effect observed for ^{35}Cl and ^{37}Cl

References

- 1 Shoemaker et. al., *Expt. In Physical Chemistry*, 6th ed. pg. 397.
- 2 Poshusta, R.D HCl Spectrum Analysis, Mathcad 20 Dec. 1997.
- 3 Herzberg, G. *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules. 2d ed., chp.III. Van Nostrand, Princeton , N.J. (1950).*
- 4 Henscheid, Leonard. *Supplement to Expt. 38: Rotation-Vibration Spectrum of HCl and DCl.* Chemistry 334 Handout, Washington State University (1998).
- 5 Poshusta, R.D. *Expt.38B: Modeling the Spectrum of HCl with Ab Initio Quantum Chemistry.* Chemistry 334 Handout, Washington State University (1998).