

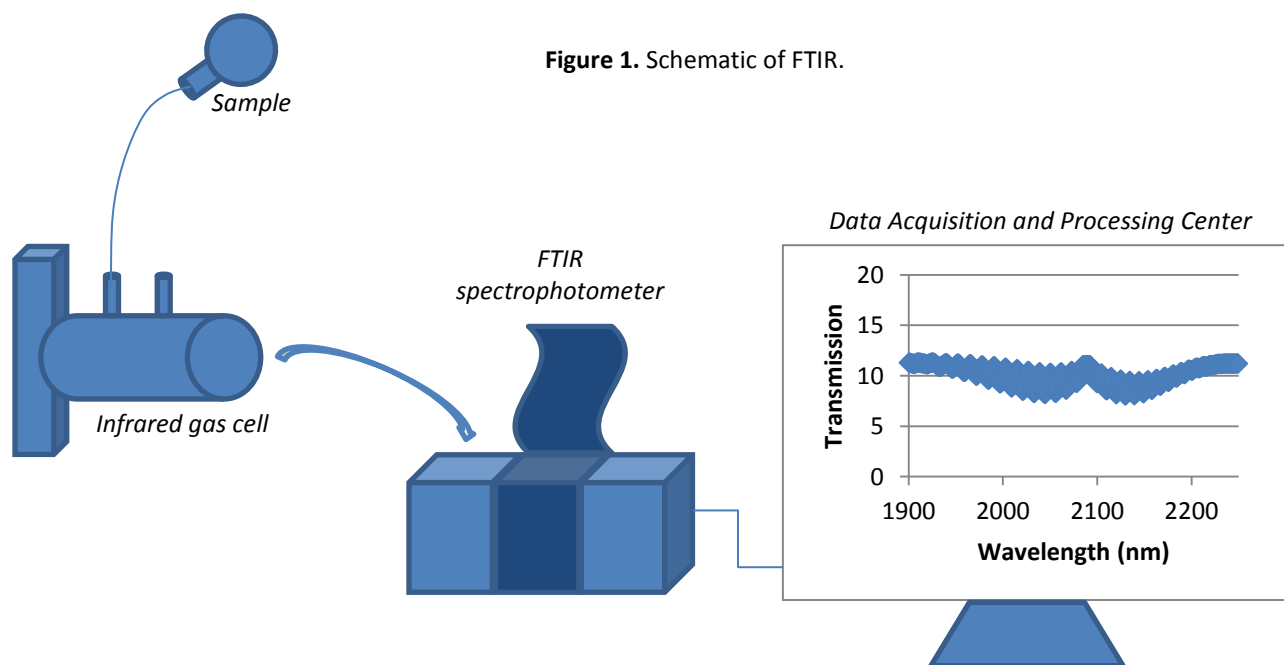
Spectroscopy 1: Rovibrational HCl and DCl

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Abstract. In order to explore the effects of intramolecular rotational and vibrational motions, Fourier transform infrared spectroscopy was performed on linear molecules HCl and DCl in order to find certain intramolecular dimensions such ν_0 , B_e , k , and r_e , among others. Ground vibrational frequency (ν_0) was equal to $2883.881 \pm 0.07 \text{ cm}^{-1}$ for HCl and $2089.122 \pm 0.12 \text{ cm}^{-1}$ for DCl and is the main factor in describing vibrational aspects of each molecule and initial parameters of the spectra. The rotational constant at equilibrium (B_e) was equal to $10.56 \pm 0.02 \text{ cm}^{-1}$ for HCl and $5.46 \pm 0.03 \text{ cm}^{-1}$ for DCl and is the main factor in describing rotational aspects of the molecule. The spring force constant (k) was equal to $479.968 \pm 2.8 \cdot 10^{-7} \text{ kg/s}^2$ for HCl and $490.21 \pm 1.6 \cdot 10^{-6} \text{ kg/s}^2$ for DCl and is vital in determining each molecule's electronic bond. Internuclear separation at equilibrium (r_e) was equal to $1.27 \pm 1.2 \cdot 10^{-3} \text{ \AA}$ for HCl and $1.27 \pm 3.7 \cdot 10^{-3} \text{ \AA}$ for DCl and describes the structure of the molecule. Experimental results were compared to Herzberg "true" values to assess accuracy [2]. Experimental data within a 5% discrepancy are able to be deemed accurate, which applies to all calculated values except D_e .



INTRODUCTION

FTIR schematic. The function of the IR gas cell shown in Fig. 1 is to encase the sample during the moment of phase transition while the liquid vaporizes at room temperature within the cell. The spectrophotometer is able to measure the gas peaks, which are sharper than liquid peaks due to decreased intermolecular interaction. FTIR was used because HCl and DCl are able to reach excited vibrational and rotational energy states when exposed to infrared radiation due to the permanent dipole moment on both molecules. Also, the reduced masses of ^{35}Cl and ^{37}Cl are so similar that a high resolution instrument is required to identify where splitting occurs. Therefore, FTIR is used because it is a high-resolution instrument and works quickly to find the absorption of each molecule while having an appropriate spectral range for mid-range infrared measurements as required for HCl and DCl. Also, DCl is used in order to induce a more pronounced difference in the chlorine isotopic effect.

Rotational, Vibrational aspects. The rotational energy levels for active infrared states of a

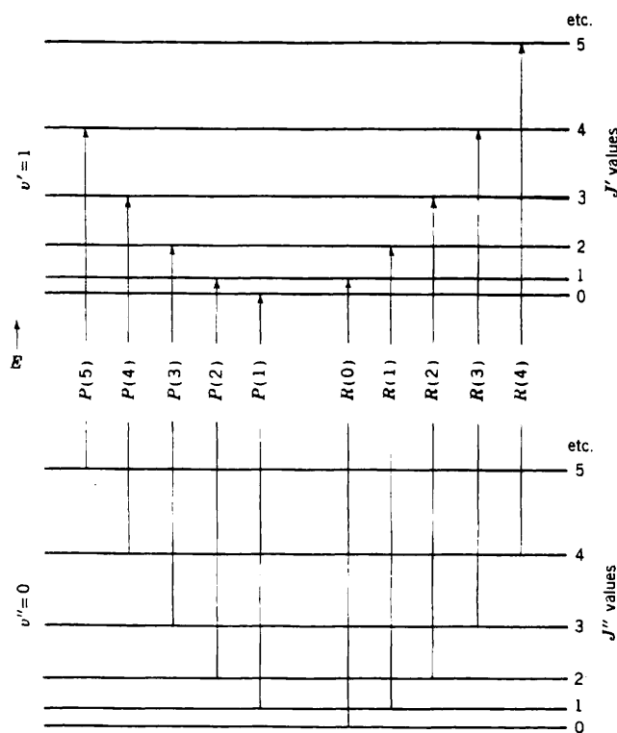


Figure 2. [1] Rotational energy levels for vibrational transition from ground to excited states.

molecule can be expressed in **Fig. 2**. Numbers within the parentheses indicate the lower ground state.

The arrows indicate transitions from the ground ($v''=0$) to first excited ($v'=1$) vibrational states.

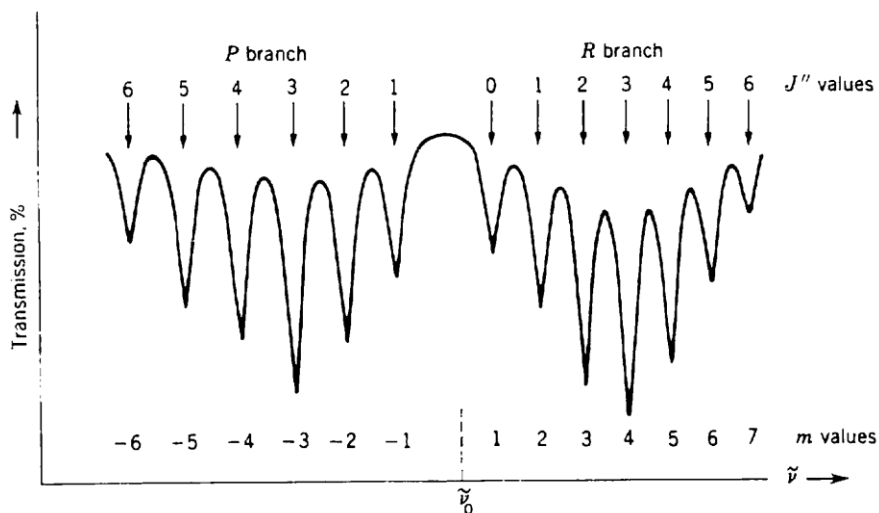


Figure 3. Vibrational-Rotational Spectra trend. [1]

Fig. 3 represents the trend of a diatomic molecule's vibrational-rotational spectra. Peaks are identified by branch, though the forbidden Q branch is not shown as a peak. Rather, it manifests in the absence of a peak between the P and R branches. The absorbance band of a molecule is identified by the zero peak of the R branch.

RESULTS AND DISCUSSION

Preparations. To begin, HCl (l) was pipetted into an infrared gas cell as shown in Figure 1 above. In accordance with the projected range of experimental wavelength values, KBr windows which coincide with the infrared spectral range were used in the cell. This was then placed into the Fourier transform infrared (FTIR) spectrophotometer to measure absorbance, which was converted into transmittance, then processed into graphs of wavelength vs. transmittance, which are gathered in the data processing

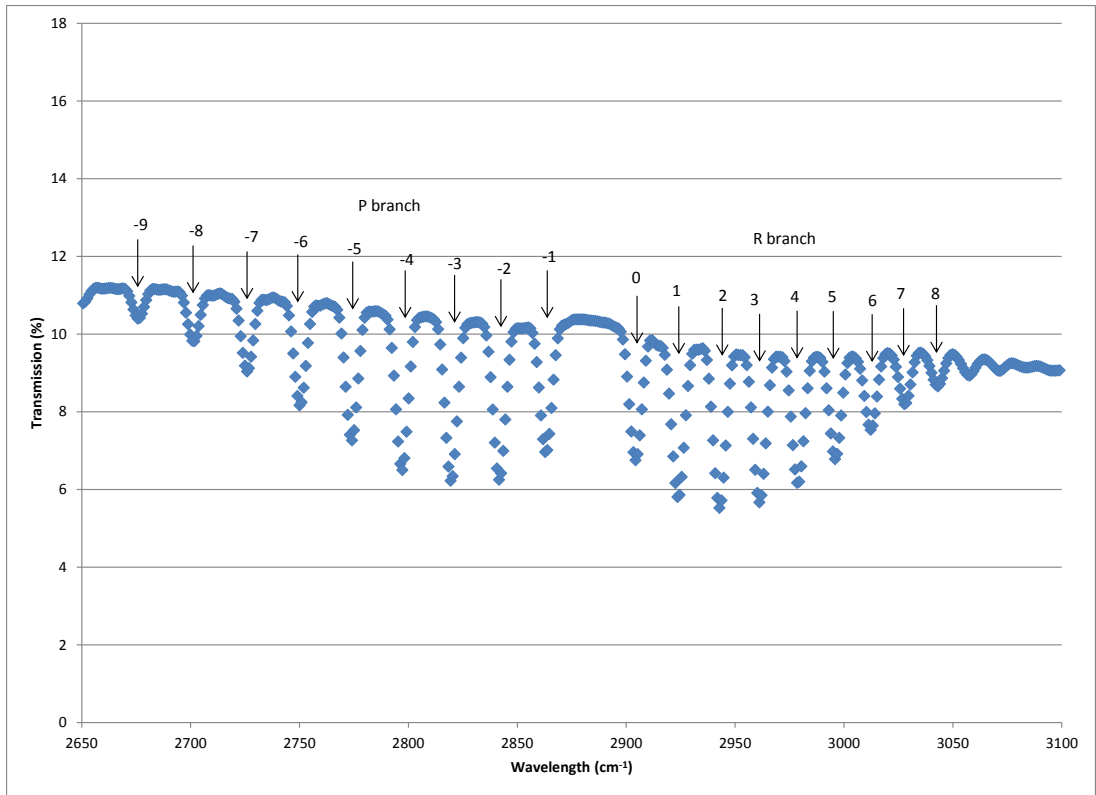


Figure 4. HCl absorption approx. 2900 cm⁻¹ with labeled M peaks

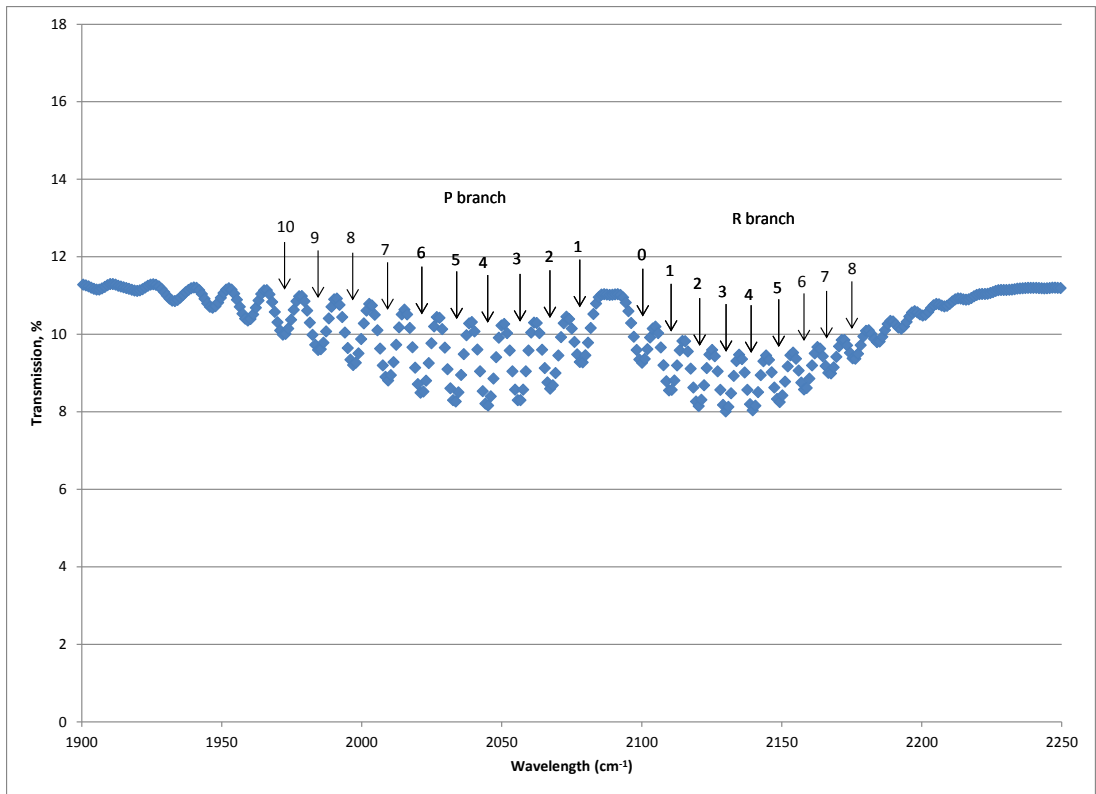


Figure 5. DCl absorption approx. 2100 cm⁻¹ with labeled M peaks

center as seen in **Fig.4** and **Fig. 5**. The Deuterium chloride gas was not prepared commercially, but rather set up by more experienced supervisors, whom synthesized DCl through the reaction between benzoyl chloride and heavy water. [1]

Experimental Data. Unfortunately, the FTIR spectrophotometer was simply not reading an HCl band. Since the spectrophotometer was able to read CO₂ bands from the supervisor simply breathing into the instrument, we can conclude some factor—probably a cracked gas cell—compromised the results, which were unusable. The above graphs are previous experimental data gathered by another group, which is the experimental data used to find the parameters as described in Table 1 below. In **Fig. 4**, HCl shows an absorption band approximately 2900 cm⁻¹ while **Fig. 5** shows an absorption band of about 2100 cm⁻¹ for DCl. The isotopic change in mass affects the rotation and vibration of the molecule.

Table 1. Spectral Peaks of HCl and DCl

Branch	HCl Spectral Peaks		DCl Spectral Peaks	
	M value	Peak value (cm ⁻¹)	M value	Peak value (cm ⁻¹)
P	-9	2675.76	-9	1984.4
	-8	2700.83	-8	1996.94
	-7	2725.9	-7	2009.47
	-6	2750.01	-6	2021.04
	-5	2774.11	-5	2032.61
	-4	2797.25	-4	2045.15
	-3	2819.43	-3	2055.75
	-2	2841.61	-2	2067.32
	-1	2862.82	-1	2077.93
R	1	2904.28	1	2100.11
	2	2923.57	2	2109.75
	3	2942.85	3	2120.36
	4	2961.17	4	2130
	5	2978.53	5	2139.64
	6	2995.89	6	2149.28
	7	3012.28	7	2157.96
	8	3027.71	8	2167.61
	9	3043.14	9	2175.32

Defining the molecules. Calculations were done in accordance with the subsequent equations in order to find B_e , r_e , v_0 , k , $v_e x_e$, D_e , α_e , and I to define each molecule. We applied a non-linear fit to each set of experimental data in Mathematica and **Eq. 1** to find v_0 , B_e , D_e , and α_e .

$$\text{Eq. 1} \quad v(m) = v_0 + (2B_e - 2\alpha_e)m - 2\alpha_e m^2 - 4D_e m^3$$

By using a combination of **Eq. 2** and **Eq. 3** we were able to solve for the isotope equation, **Eq. 4**.

$$\text{Eq. 2} \quad v_e^* / v_e = (\mu / \mu^*)^{1/2}$$

The asterick represents the isotopic molecule DCl.

$$\text{Eq. 3} \quad v_e x_e^* / v_e x_e = (\mu / \mu^*)^{1/2}$$

$$\text{Eq. 4} \quad v_0 = v_e - 2v_e^* x_e^* = v_e (\mu / \mu^*)^{1/2} - 2v_e x_e (\mu / \mu^*)$$

We then solved **Eq. 4** and **Eq. 5** as a system in Mathematica to get the values of v_e and $v_e x_e$.

$$\text{Eq. 5} \quad v_0 = v_e - 2v_e x_e$$

We found the value of k through the restoring force constant equation **Eq. 6**, the value of I through the inertia equation **Eq. 7**, and the value of r_e for **Eq. 8**.

$$\text{Eq. 6} \quad k = [v_e(2\pi c)]^2 \mu$$

$$\text{Eq. 7} \quad I = h / [B_e(8\pi^2 c)]$$

$$\text{Eq. 8} \quad r_e = \sqrt{I/\mu}$$

Eq. 9 below is an expression of a diatomic molecule's energy levels where T is the term value with units of cm^{-1} rather than joules and c is the speed of light in cm/s and v_e is the frequency in cm^{-1} . **Eq. 10** can be used to solve for C_v^{vib} [1].

$$\text{Eq. 9} \quad T(v,J) = E(v,J)/hc = v_e(v+1/2) - v_e x_e(v+1/2)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e (v+1/2) J(J+1)$$

$$\text{Eq. 10} \quad C_v^{\text{vib}} = R [(u^2 - e^{-u}) / (1 - e^{-u})^2]$$

Table 2. HCl internuclear values

Property	HCl value	error	Herzberg	Discrepancy (%)
B_e (cm^{-1})	10.56	0.02	10.593	0.27
r_e (angstrom)	1.27	1.2E-03	1.27	0.00
ν_0 (cm^{-1})	2883.881	0.07	2885.31	0.050
K (kg/s^2)	479.968	2.8E-07	480.45	0.10
$\nu_e \lambda_e$ (cm^{-1})	54.03	0.03	52.819	2.30
D_e (cm^{-1})	0.00035	0.00008	5.32E-04	34.2
α_e (cm^{-1})	0.303	0.002	0.307	1.30
I (J*s^2)	2.65E-47	4.91E-50	2.64E-47	0.36

Table 3. DCI internuclear values

Property	DCI value	error	Herzberg	Discrepancy (%)
B_e (cm^{-1})	5.46	0.03	5.44	0.40
r_e (angstrom)	1.27	3.7E-03	1.27	0.00
ν_0 (cm^{-1})	2089.12	0.12	2090.8	0.080
K (kg/s^2)	490.21	1.6E-06	488	0.45
$\nu_e \lambda_e$ (cm^{-1})	27.76	0.06	27.18	2.14
D_e (cm^{-1})	0.00025	0.00012	4.43E-04	43.6
α_e (cm^{-1})	0.112	0.003	0.113	1.24
I (J*s^2)	5.12E-47	2.96E-49	5.14E-47	0.29

We were able to check the quality of our results using Mathematica to carry out a multiple linear least squares fit of the peaks' m value and corresponding frequencies. Below are the plots for both HCl and DCI. Since an individual point does not seem out of place, we can conjecture that our data is solid at this point and proceed with further calculations. The only hiccup is with the discrepancies of our D_e values. Discrepancy should be less than 5%, much less 43.6% and 34.2%. There is obviously some problem, and this value must be deemed inaccurate. We also found C_v^{vib} to be 20.7876 J/(mol*K) at 298K with a 0.06% discrepancy. At 1000 K, C_v^{vib} was 23.1173 J/(mol*K) with a 0.36% discrepancy.

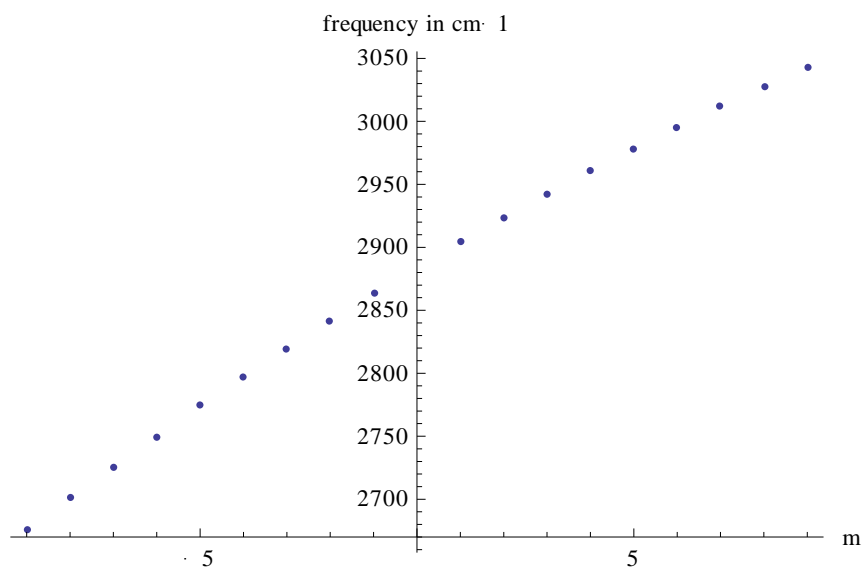


Figure 6. $\Delta v(m)$ vs. m plot for HCl

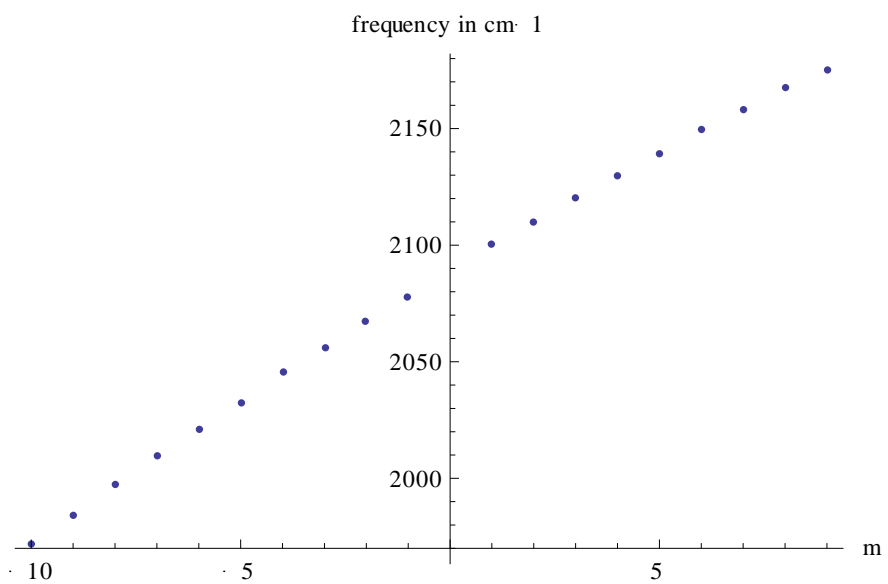


Figure 7. $\Delta v(m)$ vs. m plot for DCl

The value we found for r_e is equal for HCl and DCl, as it should theoretically be. However, we should keep in mind that this is an average value, since the internuclear separation will oscillate as each molecule undergoes vibrational motion. [3] Also, the k values we calculated were approximately equal in relation to each other.

Table 4. HCl vs. DCl

Factor	HCl	DCl	Trend
B_e (cm^{-1})	10.565	5.46	HCl > DCl
r_e (angstrom)	1.27	1.27	HCl = DCl
ν_0 (cm^{-1})	2883.881	2089.122	HCl > DCl
K (kg/s^2)	479.968	490.21	HCl ~ DCl
$\nu_e \times e$ (cm^{-1})	54.03	27.76	HCl > DCl
D_e (cm^{-1})	0.00035	0.00025	HCl > DCl
α_e (cm^{-1})	0.303	0.1116	HCl > DCl
I (J*s^2)	2.65E-47	5.12E-47	HCl < DCl

CONCLUSION

Herzberg values, named after the scientist who ascertained the data, are deemed “true” by the science community and compared against our own measurements in order to judge accuracy. In accordance with these values, our own calculated values can be considered accurate and our experiment a success. As previously stated, internuclear bond distance at equilibrium (r_e) remained the same for both cells along with spring force constant (k). However, the measurements show that a change in reduced mass due to an isotopic effect will result in a change in rotational and vibrational aspects of a molecule, thereby changing other characteristics commonly used in defining a molecule, such as inertia (I). In the future, we should be able to apply similar methods of this experiment to catalogue internuclear distance and the distribution of nuclear size, which are important criteria for grading astrocytomas, a type of neoplasm in the brain. [4]

References

1. Garland, Carl W. *Experiments in Physical Chemistry*. 8th ed. Pages 416-424. New York, NY. The McGraw-Hill Companies, Inc. 2009.
2. G. Herzberg. *Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules*. 2nd ed. Chap. III reprint ed. Krieger, Melbourne, FL (1989); K. P. Huber and G. Herzberg. *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*. Van Nostrand Reinhold, New York (1979).
Although the latter book is now out of print, the content is available at the NIST Chemistry WebBook at <http://webbook.nist.gov>.
3. Encyclopaedia Britannica. "internuclear separation." Online edition.
<<http://www.britannica.com/EBchecked/topic/291530/internuclear-separation>>
4. Nafe R, Van de Nes J, Yan B, Schlote W. Department of Neuroradiology, Clinics of Johann Wolfgang Goethe University, Frankfurt am Main, Germany. r.nafe@em.uni-frankfurt.de. Online article.
<<http://www.ncbi.nlm.nih.gov/pubmed/16465775>>

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