

Experiment 4B: The rotational-vibrational spectrum of HCl

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Abstract

Experiment abstract.

1 Results and Analysis

1.1 Collected Data

Table 1: Rotational absorbances for the fundamental transition.

	J	$R(J) / \text{cm}^{-1}$	$P(J) / \text{cm}^{-1}$	$R(J) - P(J) / \text{cm}^{-1}$	$R(J - 1) - P(J + 1) / \text{cm}^{-1}$
H^{35}Cl	0	2906.4			
	1	2926.03	2865.24	60.79	62.64
	2	2945.05	2843.76	101.29	104.33
	3	2963.42	2821.70	141.72	145.98
	4	2981.14	2799.07	182.07	187.53
	5	2998.19	2775.89	222.30	228.97
	6	3014.57	2752.17	262.40	270.26
	7	3030.27	2727.93	302.34	311.4
	8	3045.28	2703.17	342.11	352.37
	9	3059.52	2677.90	381.62	393.13
	10	3073.10	2652.15	420.95	433.62
	11	3085.88	2625.90	459.98	473.88
	12		2599.22		
H^{37}Cl	0	2904.29			
	1	2923.91	2863.20	60.71	62.53
	2	2942.90	2841.76	101.14	104.19
	3	2961.24	2819.72	141.52	145.76
	4	2978.93	2797.14	181.79	187.25
	5	2995.96	2773.99	221.97	228.62
	6	3012.32	2750.31	262.01	269.86
	7	3027.98	2726.10	301.88	310.95
	8	3042.97	2701.37	341.60	351.84
	9	3057.22	2676.14	381.08	392.57
	10	3070.73	2650.40	420.33	432.99
	11	3083.51	2624.23	459.28	473.20
	12		2597.53		

Table 2: Rotational absorbances for the overtone transition.

	J	$R(J) / \text{cm}^{-1}$	$P(J) / \text{cm}^{-1}$	$R(J) - P(J) / \text{cm}^{-1}$	$R(J - 1) - P(J + 1) / \text{cm}^{-1}$
H^{35}Cl	0	5688.16			
	1	5706.59	5647.71	58.88	62.66
	2	5723.78	5625.50	98.28	104.35
	3	5739.75	5602.24	137.51	145.98
	4	5754.53	5577.80	176.73	187.53
	5	5767.89	5552.22	215.67	229.05
	6	5780.07	5525.48	254.59	270.26
	7	5790.92	5497.63	293.29	311.52
	8		5468.55		
H^{37}Cl	0	5684.12			
	1	5703.13	5643.60	59.53	62.58
	2	5719.67	5621.54	98.13	104.80
	3	5735.61	5598.33	137.28	145.76
	4	5750.30	5573.91	176.39	197.19
	5	5763.27	5548.42	214.85	228.64
	6	5775.12	5521.66	253.46	269.43
	7	5786.65	5493.84	292.81	310.49
	8		5464.63		

1.2 Determination of Rotational Constants

The values of \tilde{B}_0 , \tilde{B}_1 and \tilde{B}_2 were calculated accounting for the centrifugal distortion of the molecules by using equations 1.2.1 and 1.2.2.

$$\begin{aligned}
 R(J) - P(J) &= (4\tilde{B}_1 - 6\tilde{D}_1)(J + \frac{1}{2}) - 8\tilde{D}_1(J + \frac{1}{2})^3 \\
 \frac{R(J) - P(J)}{J + \frac{1}{2}} &= -8\tilde{D}_1(J + \frac{1}{2})^2 + 4\tilde{B}_1 - 6\tilde{D}_1
 \end{aligned} \tag{1.2.1}$$

A similar rearrangement for the transitions with a common excited vibrational state yields equation 1.2.2.

$$\frac{R(J - 1) - P(J + 1)}{J + \frac{1}{2}} = -8\tilde{D}_0(J + \frac{1}{2})^2 + 4\tilde{B}_0 - 6\tilde{D}_0 \tag{1.2.2}$$

Graphs of $\frac{R(J)-P(J)}{J+\frac{1}{2}}$ and respectively $\frac{R(J-1)-P(J+1)}{J+\frac{1}{2}}$ were plotted against $(J+\frac{1}{2})^2$ and linear regressions were performed in order to determine the values for the centrifugal distortion coefficients, \tilde{D}_ν (see table 6 in the supplementary information) and hence the rotational constants, \tilde{B}_ν shown in table 3. The error propagation shown in equation 1.2.3 was then completed to estimate the uncertainties in \tilde{B}_ν , where α_B , α_m and α_c are the uncertainties in \tilde{B}_ν , the gradient and the intercept found in the linear regression respectively.

$$\alpha_B = \sqrt{\left(\frac{3}{16}\alpha_m\right)^2 + \left(\frac{1}{4}\alpha_c\right)^2} \tag{1.2.3}$$

The bond lengths shown in table 3 were determined from the \tilde{B}_ν values using equation 1.2.4. Furthermore the calculus-based approximation¹ was utilised to give the estimation in the uncertainty for r_ν (α_r) given in equation 1.2.5 since the α_B values are small. The uncertainties in the values of the constants and reduced mass used is insignificant compared to that of α_B , hence they were discarded.

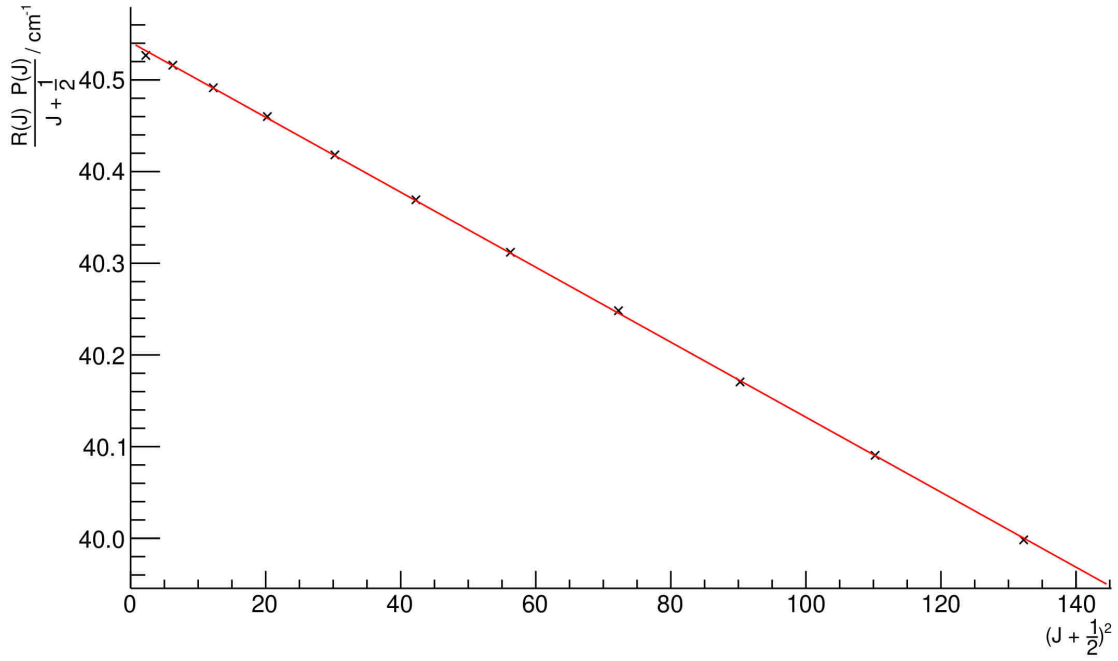


Figure 1: Graph showing the upper transition branch for the fundamental.

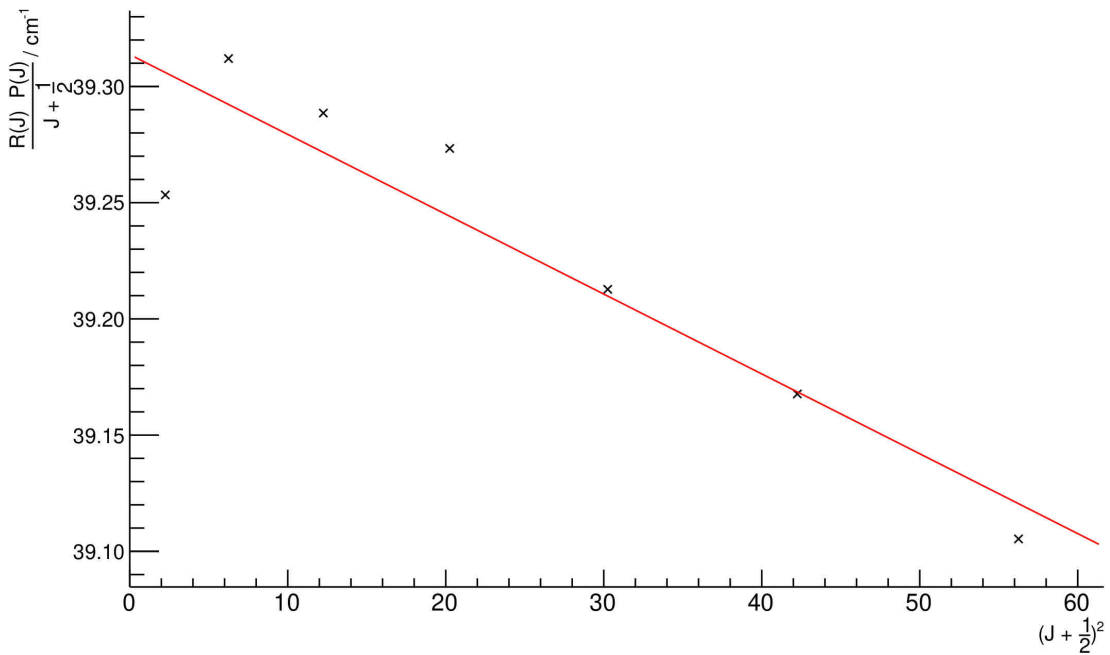


Figure 2: Graph showing the upper transition branch for the overtone.

$$r_\nu = \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}_\nu}} \quad (1.2.4)$$

$$\alpha_r = \frac{1}{2} \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}_\nu^3}} \alpha_B \quad (1.2.5)$$

The reduced mass, μ , was calculated to be $0.972\,937\,750\text{ u} = 1.615\,601\,12 \times 10^{-27}\text{ kg}$ for H^{35}Cl and $0.981\,077\,295\text{ u} = 1.629\,117\,15 \times 10^{-27}\text{ kg}$ for H^{37}Cl .²

Table 3: Rotational constants and bond lengths.

	ν	$\tilde{B}_\nu / \text{cm}^{-1}$	r_ν / pm
H^{35}Cl	0	10.4408 ± 0.0001	128.823 ± 0.002
	1	10.1360 ± 0.0002	130.745 ± 0.001
	2	9.829 ± 0.004	132.77 ± 0.02
H^{37}Cl	0	10.4248 ± 0.0003	128.385 ± 0.002
	1	10.1214 ± 0.0001	130.2953 ± 0.0009
	2	9.86 ± 0.02	132.0 ± 0.1

1.3 Determination of Vibrational Constants

The values for the harmonic constant $\tilde{\nu}_e$ and the dimensionless anharmonicity constant x_e in equation 3.2.1 was determined using equations 1.3.1 and 1.3.2 and tabulated within table 4. The derivation of these equations is included within section 3.2 of the supplementary information.

$$\tilde{\nu}_e = R(0) - 3\tilde{B}_1 + \tilde{B}_2 \quad (1.3.1)$$

$$x_e = \frac{1}{2} \frac{\tilde{B}_2 - \tilde{B}_1}{R(0) - 3\tilde{B}_1 + \tilde{B}_2} \quad (1.3.2)$$

The uncertainties in these values was hence estimated using equations 1.3.3 and 1.3.4 where the uncertainty in $R(0)$ assumed to be negligible since it is determined by reading the wavenumber directly from the spectrum.

$$\alpha_{\tilde{\nu}_e} = \sqrt{(3\alpha_{\tilde{B}_1})^2 + (\alpha_{\tilde{B}_2})^2} \quad (1.3.3)$$

$$\alpha_{x_e} = x_e \sqrt{\frac{(\alpha_{\tilde{B}_1})^2 + (\alpha_{\tilde{B}_2})^2}{(\tilde{B}_2 - \tilde{B}_1)^2} + \left(\frac{\alpha_{\tilde{\nu}_e}}{\tilde{\nu}_e}\right)^2} \quad (1.3.4)$$

Table 4: Vibrational Coefficients.

	H^{35}Cl	H^{37}Cl
$\tilde{\nu}_e / \text{cm}^{-1}$	2885.821 ± 0.004	2883.78 ± 0.02
$x_e / 10^{-5}$	-5.32 ± 0.06	-4.5 ± 0.3

1.4 Determination of Bond Force Constants

The bond force constants, k , shown in table 5 were determined using equation 1.4.1 where μ is the reduced mass of the molecule and the error in k , α_k , was determined using equation 1.4.2 (which utilises the calculus-based approximation) where the error in μ was assumed negligible compared to that in ν_e and is hence discarded.

$$k = 4\pi^2 c^2 \mu \tilde{\nu}_e^2 \quad (1.4.1)$$

$$\alpha_k = 8\pi^2 c^2 \mu \tilde{\nu}_e \alpha_{\tilde{\nu}_e} \quad (1.4.2)$$

Table 5: Force Constants.

	H^{35}Cl	H^{37}Cl
$k / \text{N m}^{-1}$	477.383 ± 0.001	480.698 ± 0.006

2 Discussion

Two methods able to be used to determine the value of \tilde{B}_0 : using either the absorption data from the fundamental or the overtone transition. Much larger signal:noise ratio for overtone due to lower probability of transition, hence greater uncertainty in this value. For the values of \tilde{B}_0 only the data from the fundamental transition was used due to the lower uncertainties in these values. Check for agreement between values and they agreed (CHECK) however didn't combine since would introduce large random error to these values for no reason.

References

- (1) I. G. Hughes and T. P. A. Hase, *Measurements and their Uncertainties*, Oxford University Press, Oxford, 2010.
- (2) *CRC Handbook of Chemistry and Physics*, ed. W. M. Haynes, CRC Press, Boca Raton, 97th edn., 2016.

3 Supplementary Information

3.1 Centrifugal Distortion Coefficients

The values of the centrifugal distortion coefficients, \tilde{D}_ν , were determined from the gradient found by completing linear regressions.

Table 6: Centrifugal distortion coefficients.

	ν	$\tilde{D}_\nu / 10^{-4} \text{ cm}^{-1}$
^{35}Cl	0	5.25 ± 0.04 and 5.4 ± 0.3
	1	5.11 ± 0.02
	2	4.3 ± 0.8
^{37}Cl	0	5.20 ± 0.03 and 9 ± 2
	1	5.13 ± 0.01
	2	11 ± 4

3.2 Derivation of Vibrational Constant Equations

The energies associated with the discrete vibrational energy levels in a molecule are given by equation 3.2.1.

$$\tilde{E}_\nu = \tilde{\nu}_e \left(\nu + \frac{1}{2} \right) - \tilde{\nu}_e x_e \left(\nu + \frac{1}{2} \right)^2 \quad (3.2.1)$$

From equation 3.2.1 we can obtain the energy related to the pure vibrational transition $\tilde{E}(\nu_f \leftarrow 0)$ (the $\nu = 0$ to $\nu = \nu_f$ transition) as equation 3.2.2.

$$\begin{aligned} \tilde{E}(\nu_f \leftarrow 0) &= \tilde{E}_{\nu_f} - \tilde{E}_0 \\ &= \tilde{\nu}_e \left(\nu_f + \frac{1}{2} - \frac{1}{2} \right) - \tilde{\nu}_e x_e \left(\frac{1}{4} - \left(\nu_f + \frac{1}{2} \right)^2 \right) \\ &= \tilde{\nu}_e (\nu_f - (\nu_f^2 + \nu_f) x_e) \end{aligned} \quad (3.2.2)$$

The energy related to the R branch transitions can be determined to yield equation 3.2.3 where J is the rotational state adopted in the lower vibrational state ($\nu = 0$).

$$R(J) = \Delta \tilde{E}(\nu_f \leftarrow 0) + (\tilde{B}_{\nu_f} + \tilde{B}_0)(J + 1) + (\tilde{B}_{\nu_f} - \tilde{B}_0)(J + 1)^2 \quad (3.2.3)$$

Setting $J = 0$ hence gives equation 3.2.4.

$$R(J) - 2\tilde{B}_{\nu_f} = \Delta\tilde{E}(\nu_f \leftarrow 0) \quad (3.2.4)$$

Substituting equation 3.2.2 into equation 3.2.4 yields equation 3.2.5.

$$R(0) - 2\tilde{B}_{\nu_f} = \tilde{\nu}_e (\nu_f - (\nu_f^2 + \nu_f) x_e) \quad (3.2.5)$$

Now from equation 3.2.5 a system of linear equations can be obtained by setting $\nu_f = 1$ and $\nu_f = 2$ (equations 3.2.6 and 3.2.7).

$$R(0) - 2\tilde{B}_1 = \tilde{\nu}_e (1 - 2x_e) \quad (3.2.6)$$

$$R(0) - 2\tilde{B}_2 = \tilde{\nu}_e (1 - 6x_e) \quad (3.2.7)$$

Solving equations 3.2.6 and 3.2.7 for $\tilde{\nu}_e$ and x_e then gives equations 1.3.1 and 1.3.2.