

# 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.

	$J$	$R(J) / \text{cm}^{-1}$	$P(J) / \text{cm}^{-1}$	$R(J) - P(J) / \text{cm}^{-1}$	$R(J - 1) - P(J + 1) / \text{cm}^{-1}$
$\text{H}^{35}\text{Cl}$	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		
$\text{H}^{37}\text{Cl}$	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.

	$J$	$R(J) / \text{cm}^{-1}$	$P(J) / \text{cm}^{-1}$	$R(J) - P(J) / \text{cm}^{-1}$	$R(J - 1) - P(J + 1) / \text{cm}^{-1}$
$\text{H}^{35}\text{Cl}$	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		
$\text{H}^{37}\text{Cl}$	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 and Bond Lengths

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

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

$$\frac{R(J) - P(J)}{J + \frac{1}{2}} = -8\tilde{D}_1(J + \frac{1}{2})^2 + 4\tilde{B}_1 - 6\tilde{D}_1 \quad (1.2.1)$$

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

Separate graphs were plotted of  $\frac{R(J)-P(J)}{J+\frac{1}{2}}$  and  $\frac{R(J-1)-P(J+1)}{J+\frac{1}{2}}$  against  $(J + \frac{1}{2})^2$  then linear regressions were performed as shown in figures 1 and 2. The values of the centrifugal distortion coefficients,  $\tilde{D}_\nu$ , were then determined (see table 6 in the supplementary information) and hence the rotational constants,  $\tilde{B}_\nu$ , shown in table 3 were calculated. The error propagation shown in equation 1.2.3 was then completed to estimate the uncertainties in  $\tilde{B}_\nu$ , where  $\alpha_B$ ,  $\alpha_m$  and  $\alpha_c$  are the uncertainties in  $\tilde{B}_\nu$ , the fit line gradient and intercept respectively.

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

The bond lengths in table 3 were determined from the  $\tilde{B}_\nu$  values using equation 1.2.4. Furthermore the calculus-based approximation<sup>1</sup> was utilised to propagate the uncertainties in  $\tilde{B}_\nu$  for  $r_\nu$  ( $\alpha_r$ ) since the  $\alpha_B$  values are small and the equation used is given in equation 1.2.5. The uncertainties in the values of the constants and reduced mass used were insignificant compared to that of  $\alpha_B$ , and hence they were discarded.

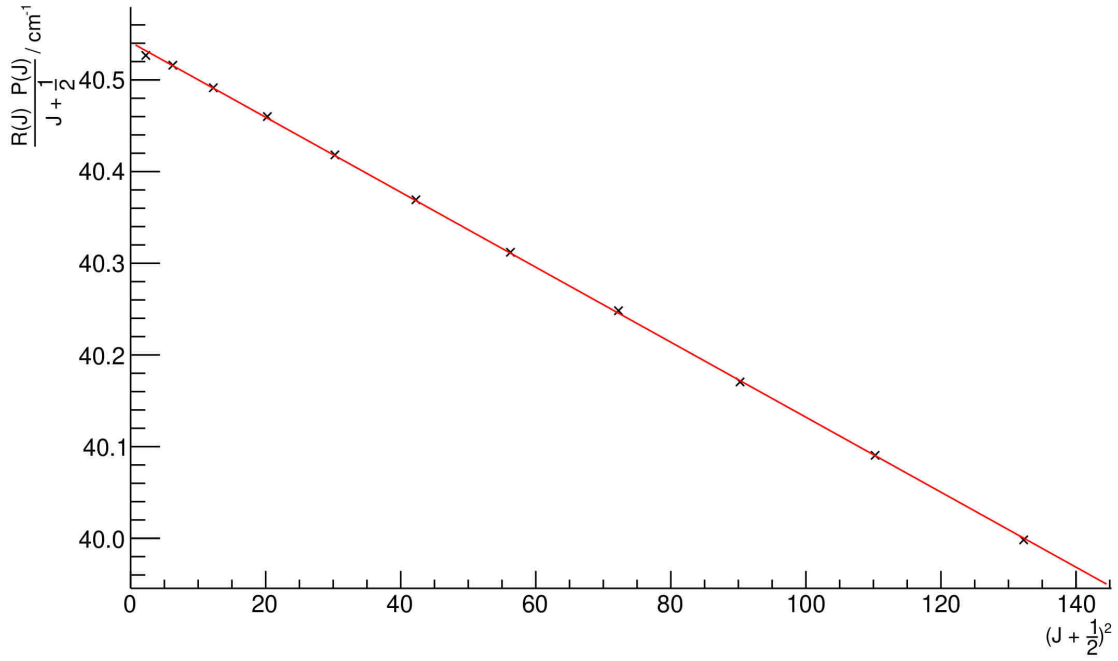


Figure 1: Graph showing the linear regression performed for the upper rotational (R) branch of the fundamental transition in  $\text{H}^{35}\text{Cl}$ .

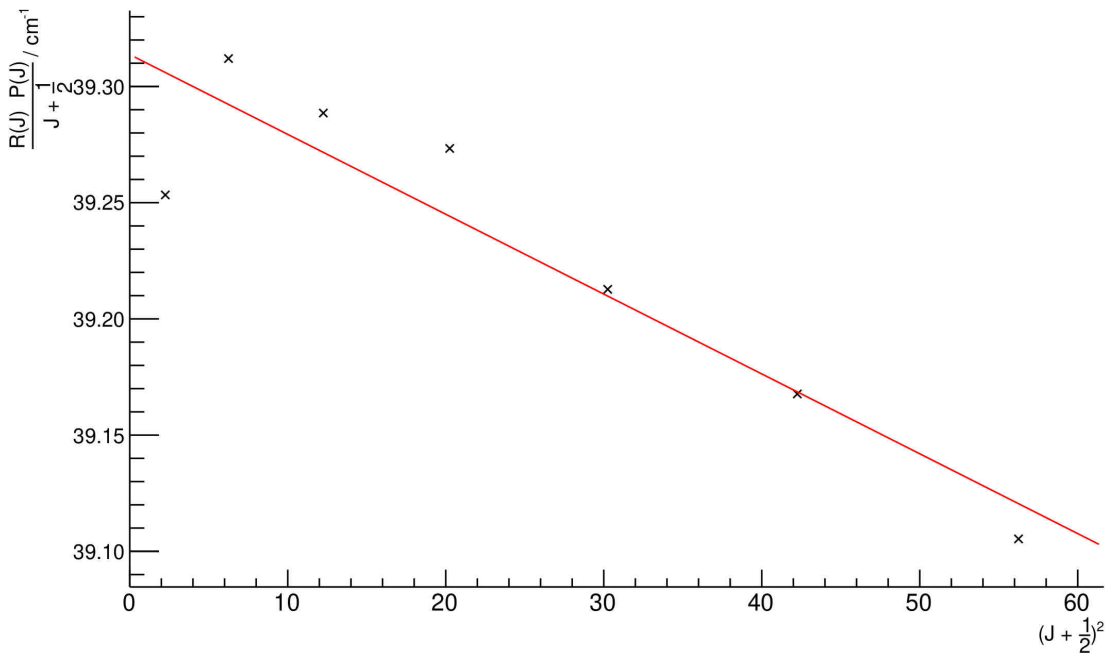


Figure 2: Graph showing the linear regression performed for the upper rotational (R) branch for the overtone transition in  $\text{H}^{35}\text{Cl}$ .

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

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

Table 3: Rotational constants and bond lengths.

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

### 1.3 Determination of Vibrational Constants

The values for the harmonic constant  $\tilde{\nu}_e$  and the dimensionless anharmonicity constant  $x_e$  were determined using equations 1.3.1 and 1.3.2 and tabulated within table 4. The derivation of these equations is included in section 3.2 within 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  $R(0)$  was negligible compared to that in  $\tilde{B}_1$  and  $\tilde{B}_2$  since it is determined by reading the absorption 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.

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

### 1.4 Determination of Bond Force Constants

The bond force constants,  $k$ , shown in table 5 were determined using equation 1.4.1 where the error in  $k$ ,  $\alpha_k$ , was determined using equation 1.4.2 (which utilises the calculus-based approximation). The errors in  $\mu$  and the constants were again negligible compared to that of  $\nu_e$  and hence were 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.

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

## 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.

As can be clearly seen in figure 2 there was a significant deviation of some of the results from the fitted line as shown since this fit had a  $\chi^2$  value of . This pattern of poor linear regression fit and high  $\chi^2$  value can be seen in all of the graphs involving data recorded for the overtone transition. This is likely to partly be due to the greater signal:noise ratio for this transition due to its lower probability of occurrence since it is a forbidden transition if the oscillator is completely harmonic. This also had the effect of reducing the number of data points which could be obtained since some will have been indistinguishable from the noise.

This appears to be particularly bad around the low values for J

This could be improved by recording another spectrum with a greater concentration of HCl gas to increase the intensity of the absorptions due to the overtone transition while ignoring the fundamental transition regions were the absorptions peaks will become too intense and will be cut. This could be done by reducing the range of the spectrometer to just include the overtone region.

Repeated spectra could be obtained to increase the reproducibility of the results and verify the accuracy of them. Currently there are a limited number of data points.

Uncertainties calculated (especially for the values derived from measurements in the overtone region) are likely to be large underestimates due to the limited number of points used in the linear regression. Repeat spectra and the isolated spectra for the overtone region would help with this.

Analysis including effects of centrifugal distortion was completed since from the residual plots a systematic error could clearly be seen since there was a clear pattern in the values of the residuals as opposed to them being randomly distributed.

## 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,  $\tilde{D}_\nu$ , were determined from the gradient found by completing linear regressions.

Table 6: Centrifugal distortion coefficients.

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

### 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.