# Experiment 4B: The rotational-vibrational spectrum of HCl

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**Abstract**

Experiment abstract.

## 1 Results and Analysis

Table 1: Rotational absorbances for the fundamental transition.

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

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 1.0.1 and 1.0.2.

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

$$\frac{R(J) - P(J)}{J + \frac{1}{2}} = -8\tilde{D}_1(J + \frac{1}{2})^2 + 4\tilde{B}_1 - 6\tilde{D}_1 \tag{1.0.1}$$

A similar rearrangement for the transitions with a common excited vibrational state yields equation 1.0.2.

Table 2: Rotational absorbances for the overtone transition.

|  | $J$ | $R(J)$ / cm$^{-1}$ | $P(J)$ / cm$^{-1}$ | $R(J) - P(J)$ / cm$^{-1}$ | $R(J-1) - P(J+1)$ / 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 | | | |

$$\frac{R(J-1) - P(J+1)}{J + \frac{1}{2}} = -8\tilde{D}_0(J + \frac{1}{2})^2 + 4\tilde{B}_0 - 6\tilde{D}_0 \tag{1.0.2}$$

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, $\tilde{D}_\nu$, shown in table 4 and hence the rotational constants, $\tilde{B}_\nu$ shown in table 3.

The bond lengths were calculated from the $\tilde{B}_\nu$ values using equation 1.0.3.

$$r_\nu = \sqrt{4\pi c\hbar\mu\tilde{B}_\nu} \tag{1.0.3}$$

Table 3: Rotational constants and bond lengths.

|  | $\nu$ | $\tilde{B}_\nu$ / cm$^{-1}$ | $r_\nu$ / pm |
|---|---|---|---|
| $^{35}$Cl | 0 | | |
| | 1 | | |
| | 2 | | |
| $^{37}$Cl | 0 | | |
| | 1 | | |
| | 2 | | |

The error propagation shown in equation 1.0.4 was completed to estimate the uncertainty in the values of $\tilde{B}_\nu$ where $\alpha_B$, $\alpha_D$, $\alpha_m$ are the uncertainties in $\tilde{B}_\nu$, $\tilde{D}_\nu$ and the gradient found in the linear regression respectively.

$$\alpha_B = \tilde{B}_\nu\sqrt{\left(\frac{\alpha_m}{m}\right)^2 + \left(\frac{\alpha_D}{\tilde{D}_\nu}\right)^2} \tag{1.0.4}$$

Furthermore the calculus-based approximation[1] was utilised to give the estimation in the uncertainty for $r_\nu$ ($\alpha_r$) given in equation 1.0.5 since the $\alpha_B$ values are small.

$$\alpha_r = \sqrt{\frac{\pi c \hbar \mu}{\tilde{B}_\nu}} \alpha_B \tag{1.0.5}$$

## 1.1 Determination of Vibrational Constants

The values for the harmonic constant $\tilde{\nu}_e$ and the dimensionless anharmonicity constant $x_e$ in equation 1.1.1 (which gives the expected vibrational energy levels if the rotational spectrum is ignored).

$$\tilde{E}_\nu = \tilde{\nu}_e \left(\nu + \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(\nu + \frac{1}{2}\right)^2 \tag{1.1.1}$$

From equation 1.1.1 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 1.1.2.

$$\begin{aligned} \tilde{E}(\nu_f \leftarrow 0) &= \tilde{E}_{\nu_f} - \tilde{E}_0 \\ &= \tilde{\nu}_e \left(\nu_f + \frac{1}{2} - \frac{1}{2}\right) - \tilde{\nu}_e x_e \left(\frac{1}{4} - \left(\nu_f + \frac{1}{2}\right)^2\right) \\ &= \tilde{\nu}_e \left(\nu_f - \left(\nu_f^2 + \nu_f\right) x_e\right) \end{aligned} \tag{1.1.2}$$

The energy related to the R branch transitions can be determined to yield equation 1.1.3 where $J$ is the rotational state adopted in the lower vibrational state ($\nu = 0$).

$$R(J) = \Delta\tilde{E}(\nu_f \leftarrow 0) + (\tilde{B}_{\nu_f} + \tilde{B}_0)(J+1) + (\tilde{B}_{\nu_f} - \tilde{B}_0)(J+1)^2 \tag{1.1.3}$$

Setting $J = 0$ hence gives equation 1.1.4.

$$R(J) - 2\tilde{B}_{\nu_f} = \Delta\tilde{E}(\nu_f \leftarrow 0) \tag{1.1.4}$$

Subsituting equation 1.1.2 into equation 1.1.4 yields equation 1.1.5.

$$R(0) - 2\tilde{B}_{\nu_f} = \tilde{\nu}_e \left(\nu_f - \left(\nu_f^2 + \nu_f\right) x_e\right) \tag{1.1.5}$$

Now from equation 1.1.5 a system of linear equations can be obtained by setting $\nu_f = 1$ and $\nu_f = 2$ (equations xx and xx) for which we can solve to give equations xx and xx.

for which setting $J = 0$ and $\nu_f = 1$ and subsequently $\nu_f = 2$ gives the system of linear equations (equations xx and xx) for which we can solve to give equations xx and xx.

## 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.

### References

(1) I. G. Hughes and T. P. A. Hase, *Measurements and their Uncertainties*, Oxford University Press, Oxford, 2010.

## 3 Supplementary Information

Table 4: Centrifugal distortion coefficients.

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