

Experiment 4B: The rotational-vibrational spectrum of HCl

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30/11/2018

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 , shown in table 5 and hence the rotational constants, \tilde{B}_ν shown in table 3.

The bond lengths were then determined from the \tilde{B}_ν values using equation 1.2.3.

$$r_\nu = \sqrt{4\pi c \hbar \mu \tilde{B}_\nu}
 \tag{1.2.3}$$

The error propagation shown in equation 1.2.4 was completed to estimate the uncertainty in the values of \tilde{B}_ν where α_B , α_D , α_m are the uncertainties in \tilde{B}_ν , \tilde{D}_ν and the gradient found in the linear regression respectively.

$$\alpha_B = \tilde{B}_\nu \sqrt{\left(\frac{\alpha_m}{m}\right)^2 + \left(\frac{\alpha_D}{\tilde{D}_\nu}\right)^2}
 \tag{1.2.4}$$

Table 3: Rotational constants and bond lengths.

	ν	$\tilde{B}_\nu / \text{cm}^{-1}$	r_ν / pm
H^{35}Cl	0		
	1		
	2		
H^{37}Cl	0		
	1		
	2		

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.

$$\alpha_r = \sqrt{\frac{\pi c \hbar \mu}{\tilde{B}_\nu}} \alpha_B \quad (1.2.5)$$

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. 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.

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

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

1.4 Determination of Bond Force Constants

The bond force constants, k , shown in table 4 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 the calculus approximation (equation 1.4.2) where the error in μ was assumed negligible compared to that in ν_e .

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

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

Table 4: Force Constants.

	H^{35}Cl	H^{37}Cl
$k / \text{N cm}^{-1}$		

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

3.1 Centrifugal Distortion Coefficients

Table 5: 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.

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

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.

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

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).

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

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

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.