

Experiment 4B: The rotational-vibrational spectrum of HCl

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30/11/2018

Abstract

Experiment abstract.

1 Results and Analysis

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		

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.

$$\begin{aligned}
 R(J) - P(J) &= (4\tilde{B}_1 - 6\tilde{D}_1)(J + \frac{1}{2}) - 8\tilde{D}_1(J + \frac{1}{2})^3 \\
 \frac{R(J) - P(J)}{J + \frac{1}{2}} &= -8\tilde{D}_1(J + \frac{1}{2})^2 + 4\tilde{B}_1 - 6\tilde{D}_1
 \end{aligned}
 \tag{1.0.1}$$

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

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

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}_ν , shown in table 4 and hence the rotational constants, \tilde{B}_ν , shown in table 3.

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

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

Table 3: Rotational constants and bond lengths.

	ν	$\tilde{B}_\nu / \text{cm}^{-1}$	r_ν / 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}_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.

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

Furthermore the calculus-based approximation¹ was utilised to give the estimation in the uncertainty for r_ν (α_r) given in equation 1.0.5 since the α_B values are small.

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

The values for the harmonic constant $\tilde{\nu}_e$ and the dimensionless anharmonicity constant x_e in equation 1.0.6 (which gives the expected vibrational energy levels if the rotational spectrum is ignored) can be determined by

$$\tilde{E}_\nu = \tilde{\nu}_e \left(\nu + \frac{1}{2} \right) - \tilde{\nu}_e x_e \left(\nu + \frac{1}{2} \right)^2 \quad (1.0.6)$$

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.

	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