A Rudimentary Analysis of the Vibrational-Rotational HCl Spectrum

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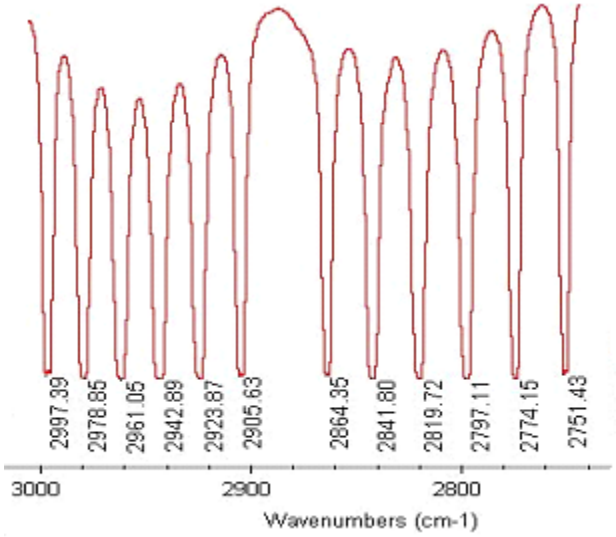
This analysis assumes an harmonic-oscillator, non-rigid rotor model for the vibrational and rotational degrees of freedom of gas-phase HCl. In other words, the magnitude of the rotational constant depends on the vibrational state of the molecule. Using the portion of the $H^{35}Cl$ vibrational-rotational spectrum provided below, this model will be used to calculate the following molecular parameters: ν_0, B_0, B_1, B_e, α_e, r_0, r_1, r_e, and k.



A simple algebraic method (see McQuarrie and Simon, *Physical Chemistry*, pp 502-503), rather than a sophisticated statistical analysis, will be used to extract HCl's molecular parameters from the spectroscopic data. We will see that although the model and the method of analysis are rudimentary, the results compare rather well with literature values for the molecular parameters. This exercise might serve as an introduction to a more rigorous and thorough statistical analysis.

The equations for the R- and P-branch transitions appropriate for this model are given below.

$$\nu_R(J) := \nu_0 + B_1\cdot(J+1)\cdot(J+2) - B_0\cdot J\cdot(J+1) \qquad \nu_P(J) := \nu_0 + B_1\cdot(J-1)\cdot J - B_0\cdot J\cdot(J+1)$$

where $B_v = \dfrac{h}{8\cdot\pi^2\cdot c\cdot\mu\cdot r_v^2}$ $\qquad B_v = B_e - \alpha_e\cdot\left(v+\dfrac{1}{2}\right)$

Fundamental constants, conversion factors and atomic masses:

$h := 6.6260755\cdot10^{-34}\cdot joule\cdot sec$ $\quad c := 2.99792458\cdot10^{8}\cdot\dfrac{m}{sec}$ $\quad u := 1.66054\cdot10^{-27}\cdot kg$ $\quad pm := 10^{-12}\cdot m$

$m_H := 1.0078\cdot u$ $\qquad m_{Cl} := 34.9688\cdot u$

Calculate the reduced mass of HCl: $\mu := \dfrac{m_H\cdot m_{Cl}}{m_H + m_{Cl}}$ $\qquad \mu = 1.627\times10^{-27}\,kg$

Obtain several P- and R-branch transitions from the spectrum:

$$\begin{pmatrix} \text{Transition} & P(2) & P(1) & R(0) & R(1) \\ \text{Frequency} & 2841.80 & 2864.35 & 2905.63 & 2923.87 \\ \hline \text{cm}^{-1} & & & & \end{pmatrix}$$

Set up and solve a system of equations to calculate ν_0, B_0 and B_1 by selecting data from the table above.

$$\left(\nu_0 \quad B_0 \quad B_1\right) := \begin{pmatrix} \nu_P(2) = 2841.80 \cdot \text{cm}^{-1} \\ \nu_P(1) = 2864.35 \cdot \text{cm}^{-1} \\ \nu_R(0) = 2905.63 \cdot \text{cm}^{-1} \end{pmatrix} \left| \begin{array}{l} \text{solve}, \begin{pmatrix} \nu_0 \\ B_0 \\ B_1 \end{pmatrix} \\ \text{float}, 5 \end{array} \right. \rightarrow \begin{pmatrix} \frac{2885.6}{\text{cm}} \\ \frac{10.638}{\text{cm}} \\ \frac{10.002}{\text{cm}} \end{pmatrix}$$

Use the values of B_0 and B_1 to calculate B_e and α_e:

$$\left(B_e \quad \alpha_e\right) := \begin{pmatrix} B_0 = B_e - \alpha_e \cdot \frac{1}{2} \\ B_1 = B_e - \alpha_e \cdot \frac{3}{2} \end{pmatrix} \left| \begin{array}{l} \text{solve}, \begin{pmatrix} B_e \\ \alpha_e \end{pmatrix} \\ \text{float}, 5 \end{array} \right. \rightarrow \begin{pmatrix} \frac{10.956}{\text{cm}} \\ \frac{.63600}{\text{cm}} \end{pmatrix}$$

Now calculate r_0, r_1, and r_e using the values of B_0, B_1 and B_e.

$$r_0 := \sqrt{\frac{h}{8 \cdot \pi^2 \cdot c \cdot \mu \cdot B_0}} \qquad r_0 = 127.189\,\text{pm} \qquad r_1 := \sqrt{\frac{h}{8 \cdot \pi^2 \cdot c \cdot \mu \cdot B_1}} \qquad r_1 = 131.171\,\text{pm}$$

$$r_e := \sqrt{\frac{h}{8 \cdot \pi^2 \cdot c \cdot \mu \cdot B_e}} \qquad r_e = 125.33\,\text{pm}$$

Calculate the force constant using the value of ν_0.

$$k := \nu_0 = \frac{1}{2 \cdot \pi \cdot c} \cdot \sqrt{\frac{k}{\mu}} \left| \begin{array}{l} \text{solve}, k \\ \text{float}, 4 \end{array} \right. \rightarrow .4806\text{e-}1 \cdot \frac{\text{m}^2}{\text{sec}^2 \cdot \text{cm}^2} \cdot \text{kg} \qquad k = 480.6\,\frac{\text{newton}}{\text{m}}$$

Compare the calculated parameter values with the literature values.

Molecular Parameter	Calculated Value	Literature Value	%Error
$\frac{\nu_0}{cm^{-1}}$	2885.6	2886	0.014
$\frac{B_0}{cm^{-1}}$	10.638	10.440	1.90
$\frac{B_1}{cm^{-1}}$	10.002	10.136	1.32
$\frac{B_e}{cm^{-1}}$	10.956	10.593	3.43
$\frac{\alpha_e}{cm^{-1}}$	0.6360	0.307	107
$\frac{r_0}{pm}$	127.2	128.3	0.86
$\frac{r_1}{pm}$	131.2	130.2	0.77
$\frac{r_e}{pm}$	125.3	127.4	1.65
$\frac{k}{newton \cdot m^{-1}}$	480.6	516.3	6.92

Summary: Given the simplicity of the model (harmonic-oscillator, non-rigid rotor) and the rudimentary algebraic (as opposed to rigorous statistical) method of analysis, the results are quite respectable. Naturally, results will vary depending on the P- and R-branch transitions used to calculate the molecular parameters.