4.6: Analyses of the Pure Rotational Spectrum of HCl

This exercise deals with simple algebraic analyses of the microwave spectrum of HCl. This problem is dealt with in a number of current physical chemistry texts. Here the rigid rotor and non-rigid rotor models will be used to analyze the data that follows.

Rotational absorption lines from H^{35}Cl were found at the following wavenumbers (cm^{-1}): 83.32, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60, and 226.86. Given this data our goal is to calculate the rotational constant, the bond length and the centrifugal distortion constant. We also want to assign J quantum numbers to each of the transitions.

Rigid Rotor Model for HCl

For the rigid rotor model the rotational energy levels (in cm-1) are given by the following equation.

$$E_J = BJ(J+1)$$

where

$$B = \frac{h}{8\pi^2 c \mu r^2}$$

For absorption spectroscopy, the rotational selection rule is $\Delta J = \pm 1$. Therefore, the energies of the allowed rotational transitions are,

$$\Delta E(J) = B(J+1)(J+2) - BJ(J+1) \text{ simplify } \rightarrow \Delta E(J) = 2BJ + 2B$$
$$\Delta E(J) = 2B(J+1)$$

We do not know if the first frequency listed above (83.32 cm^{-1}) is the J = 0 to J = 1 transition. However, we do know that the frequencies represent adjacent transitions. So we can use the first two transitions to calculate both J and B.

$$h = 6.62608(10)^{-34} \text{joule sec} \quad c = 2.99792458(10)^8 \frac{m}{sec} \quad u = 1.66054(10)^{-27} kg$$

$$m_H = 1.0078u \qquad m_{Cl} = 34.9688u \qquad pm = 10^{-12}m$$

Calculate the reduced mass:

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} \quad \mu = 1.62661 \times 10^{-27} kg$$

Calculate the bond length:

$$B = \frac{h}{8\pi^2 c \mu r^2} \left| \begin{array}{c} solve, r \\ float, 4 \end{array} \right. \rightarrow \left[\begin{array}{c} \frac{.1286e-8}{\text{m kg}}(\text{m kg joule cm})^{\frac{1}{2}} \text{ sec} \\ \frac{-.1286e-8}{\text{m kg}}(\text{m kg joule cm})^{\frac{1}{2}} \text{ sec} \end{array} \right] = \left(\begin{array}{c} 128.6 \\ -128.6 \end{array} \right) pm$$

Clear memory of J and B to facilitate subsequent calculations:

$$J = J \quad B = B$$

Non-Rigid Rotor Model for HCl

The non-rigid rotor model adds a centrifugal distortion term to accommodate the classical idea that the H-Cl bond will stretch as the rotational energy increases causing the rotational states to become closer together at higher J values.

The rotational energy levels (in cm^{-1}) for the non-rigid rotor are given by,

$$E(J) = BJ(J+1) - DJ^2(J+1)^2$$

The rotational transitions, therefore, appear at the following energies

$$\Delta E(J) = E(J+1) - E(J) \text{ simplify } \rightarrow 2B(J+1) = 2BJ + 2B - 4DJ^3 - 12DJ^2 - 12DJ - 4D$$
$$\Delta E(J) = 2BJ + 2B - 4DJ^3 - 12DJ^2 - 12DJ - 4D$$

Because J values have now been assigned to the rotational transitions, we can use two of them to calculate B and D.

$$(B\ D) = \begin{pmatrix} \Delta E(3) = 83.2 cm^{-1} \\ \Delta E(4) = 104.13 cm^{-1} \end{pmatrix} \left| \begin{matrix} solve, \begin{pmatrix} B \\ D \end{pmatrix} \\ float, 4 \end{matrix} \right. \rightarrow \begin{pmatrix} \dfrac{10.42}{cm} \\ \dfrac{.1111e-3}{cm} \end{pmatrix}$$

Next we calculate the HCl bond length under the non-rigid rotor approximation.

$$B = \dfrac{h}{8\pi^2 c \mu r^2} \left| \begin{matrix} solve, r \\ float, 4 \end{matrix} \right. \rightarrow \begin{bmatrix} \dfrac{.1285e-8}{m\,kg}(m\,kg\,joule\,cm)^{\frac{1}{2}}\,sec \\ \dfrac{-.1285e-8}{m\,kg}(m\,kg\,joule\,cm)^{\frac{1}{2}}\,sec \end{bmatrix} = \begin{pmatrix} 128.5 \\ -128.5 \end{pmatrix} pm$$

Finally we summarize the calculated results and compare them to the literature values. Given the simplicity of the models and the rudimentary method of analysis, the comparisons are satisfactory. The large error in D is not surprising given its small magnitude.

Molecular Parameter	Rigid Rotor	Nonrigid Rotor	Literature
$\dfrac{\text{Rotational Constant}}{cm^{-1}}$	10.41	10.42	10.59
$\dfrac{\text{Bond Length}}{pm}$	128.6	128.5	127.5
$\dfrac{\text{Centrifugal Distortion Constant}}{cm^{-1}}$	.	$1.11(10)^{-4}$	$5.32(10)^{-4}$