Analyses of the Pure Rotational Spectrum of HCl

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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.

$$E_J = B \cdot J \cdot (J+1) \qquad \text{where} \qquad B = \frac{h}{8 \cdot \pi^2 \cdot c \cdot \mu \cdot r^2}$$

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

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

$$\Delta E(J) := 2 \cdot B \cdot (J+1)$$

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.

$$(J \quad B) := \begin{pmatrix} \Delta E(J) = 83.32 \cdot cm^{-1} \\ \Delta E(J+1) = 104.13 \cdot cm^{-1} \end{pmatrix} \left| \begin{array}{l} \text{solve}, \begin{pmatrix} J \\ B \end{pmatrix} \\ \text{float}, 4 \end{array} \right. \rightarrow \begin{pmatrix} 3.004 \\ \dfrac{10.41}{cm} \end{pmatrix}$$

We see that the first transition observed is from J = 3 to J = 4, and we have a value for the rotational constant B. This allows us to calculate the H-Cl bond length using the following fundamental constants and masses of atoms:

$$h := 6.62608 \cdot 10^{-34} \cdot joule \cdot sec \qquad c := 2.99792458 \cdot 10^{8} \cdot \frac{m}{sec} \qquad u := 1.66054 \cdot 10^{-27} \cdot kg$$

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

Calculate the reduced mass: $\mu := \dfrac{m_H \cdot m_{Cl}}{m_H + m_{Cl}} \qquad \mu = 1.62661 \times 10^{-27}\, kg$

Calculate the bond length:

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

Clear memory of J and B to facilitate subsequent calculations: $J := J$ $B := B$

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,

$$E(J) := B\cdot J\cdot(J+1) - D\cdot J^2\cdot(J+1)^2$$

The rotational transitions, therefore, appear at the following energies

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

$$\Delta E(J) := 2\cdot B\cdot J + 2\cdot B - 4\cdot D\cdot J^3 - 12\cdot D\cdot J^2 - 12\cdot D\cdot J - 4\cdot D$$

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

$$(B\quad D) := \begin{pmatrix}\Delta E(3) = 83.32\cdot cm^{-1}\\ \Delta E(4) = 104.13\cdot cm^{-1}\end{pmatrix}\ \left|\begin{array}{l}\text{solve},\begin{pmatrix}B\\ D\end{pmatrix}\\ \text{float},4\end{array}\right.\rightarrow\begin{pmatrix}\frac{10.42}{cm}\\ \frac{.1111e\text{-}3}{cm}\end{pmatrix}$$

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

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

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.

MolecularParameter	RigidRotor	NonRigidRotor	Literature
$\frac{\text{RotationalConstant}}{\text{cm}^{-1}}$	10.41	10.42	10.59
$\frac{\text{BondLength}}{\text{pm}}$	128.6	128.5	127.5
$\frac{\text{CentrifugalDistortionConstant}}{\text{cm}^{-1}}$	.	$1.11 \cdot 10^{-4}$	$5.32 \cdot 10^{-4}$