Chem 3322 homework #9, due April 12, 2024

Problem 1

Calculate the percentage difference in the fundamental vibrational wavenumber of

(a) $^{1}H^{35}Cl$ and $^{2}H^{35}Cl$ using the assumption that their force constants are the same.

(b) $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$ using the assumption that their force constants are the same.

Problem 2

The spacing between vibrational energy levels is substantially larger than the spacing between (low-lying) rotational energy levels, which itself is substantially larger than the spacing between translational energy levels. Consider N_2, for which $\hbar\omega = 2360$ cm^{-1} (note: you need to convert this wavenumber value to an energy) and the bond length is 109.76 picometers.

a) For a given vibrational state, how many rotational states have energy less than the energy gap to the next vibrational state? That is, find ℓ such that the energy of the state (n, ℓ) is greater than or equal to the energy of the state $(n + 1, 0)$. Note that since the vibrational energy level spacing is constant (from the harmonic oscillator approximation), this will be the same for any vibrational level n. Include a sketch to illustrate your answer.

b) After what rotational level does the rotational spacing become larger than the vibrational spacing? Include a sketch to illustrate your answer.

c) Calculate the translational energy level spacing assuming a particle in a three dimensional box model with a box size of $L = 10$ cm. You can assume the transition is from the lowest energy state to the next lowest energy state. What part of the electromagnetic spectrum does this frequency belong to?

Problem 3

The fundamental vibrational frequencies for $^{1}H^{19}F$ and $^{2}H^{19}F$ are 4138.52 cm^{-1} and 2998.25 cm^{-1}, respectively. $D_e = 5.86$ eV for both molecules (Morse model). Work out the difference in bond energy for these two molecules in kJ/mol.

Problem 4

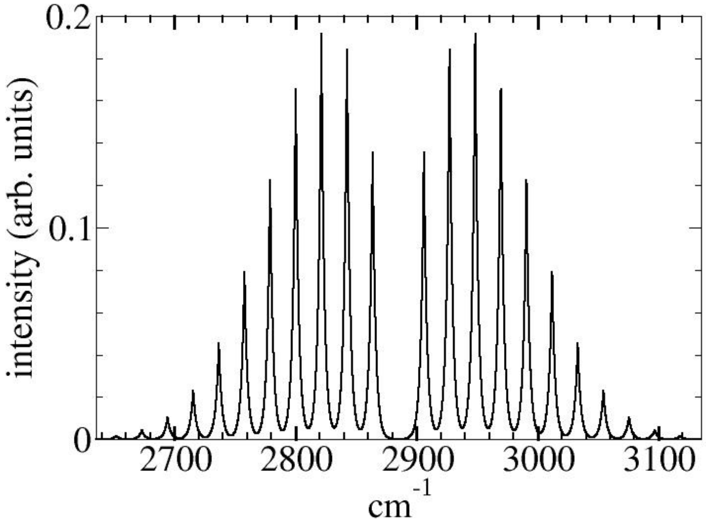

FIG. 1: Rotationally resolved vibrational spectrum of HCl.

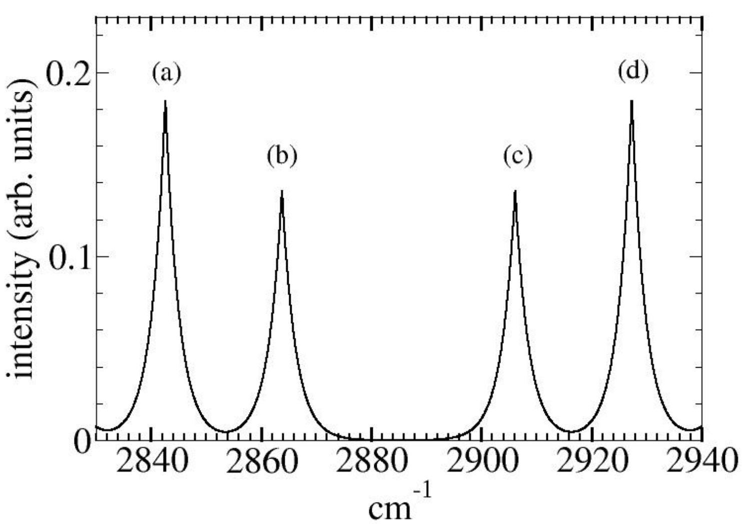

FIG. 2: Detail from Fig. 1. The peak marked (a) is at 2842.63 cm^{-1}, (b) is at 2863.81 cm^{-1}, (c) is at 2906.19 cm^{-1}, and (d) is at 2927.37 cm^{-1}.

For this problem, use $^1H = 1.0078$ amu and $^{35}Cl = 34.969$ amu.

a) From Figures 1 and 2 estimate the equilibrium bond length of $^1H^{35}Cl$.

b) From Figures 1 and 2 estimate the force constant of the $^1H^{35}Cl$ bond.

c) For each of the peaks marked in Figure 2, which are for the $^1H^{35}Cl$ molecule, predict the corresponding peak locations for the $^2H^{37}Cl$ molecule. Use $^2H = 2.0141$ amu and $^{37}Cl = 36.9659$ amu. Assume the force constant is unchanged upon isotopic substitution. Assume the equilibrium bond length is unchanged upon isotopic substitution.