CHEM 260

Assignment 9

34. a) Given that the vibrational energy levels of a diatomic molecule are given by

$$E(n) = \hbar\omega_e \left[\left(n + \tfrac{1}{2} \right) - x_e \left(n + \tfrac{1}{2} \right)^2 \right],$$

write down an expression for $\Delta E(0 \rightarrow n)$ and thence deduce that

$$E(0 \rightarrow n)/n = \hbar\omega_e \left[1 - x_e \left(n + 1 \right) \right]$$

b) The fundamental and first two overtone transitions for the molecular ion H_2^+ have frequencies 2191, 4255 and 6196 cm^{-1}. Plot this data using the above expression to find the vibrational frequency ($\hbar\omega_e$ in cm^{-1}) and the anharmonicity constant x_e.

c) Substitute your answers from part b into the first equation to construct a table of $E(n)$ for the lowest 20 or so vibrational energy levels of H_2^+. Add another column to the table for the energy difference between levels, i.e. $\Delta E(n \rightarrow n+1)$ and thence deduce the number of vibrational levels below the dissociation limit.

d) Calculate the zero-point energy of MuH^+.

35. The following lines are found near the centre of the IR spectrum of $D^{35}Cl$:

2027.7, 2039.9, 2051.6, 2063.2, 2074.6, 2085.5, 2107.1, 2117.3, 2127.5, 2137.5, 2147.2, and 2156.8 cm^{-1}.

a) By looking at the differences between the frequencies decide which lines belong to the P branch and which the R branch. Sketch an energy level diagram showing them. Label them …, P_2, P_1, (Q), R_1, R_2,… Q represents the undetected pure vibrational transition.

b) Plot the frequencies (in cm^{-1}). For the x-axis use the above subscripts, but with negative numbers for the P branch. Fit the data with a parabola.

c) Use your fit (the intercept) to deduce the frequency of the missing Q band, i.e. the frequency corresponding to $(v = 0, J = 0) \rightarrow (v = 1, J = 0)$.

d) Calculate the bond length of the ground vibrational state from the difference between Q and the best fit value for P_1. [This difference is equivalent to $(v = 0, J = 0) \rightarrow (v = 0, J = 1)$.

e) Calculate the bond length of the $v = 1$ vibrational state from the difference between Q and the best fit value for R_1.