CHM201
Problem set 3

1. For the HF molecule, the following equation was found to hold good for the rotational levels.

   $E_J = 20.56hc\ J(J+1)$ (in Joules) ……..(1)

   a) Plot the energy level diagram for this system, for J=0 to J=4, in units of cm^{-1}.
   b) Plot the rotational spectrum for the first 4 transitions and label each transition.
   c) Calculate the bond length for HF.

   Another spectroscopist then performed a more detailed analysis and gave the following equation for the rotational levels, which now includes centrifugal distortion.

   $E_J = 20.56hc\ J(J+1) - 2.13 \times 10^{-3} hc\ [J(J+1)]^2$ (in Joules) .....(2)

   d) Plot the energy level diagram (in units of cm^{-1}) using this equation (alongside the level diagram you drew for problem 1a), and see for yourself where the deviations occur from what you calculated using equation 1. (Actually, you may have to calculate for quite a few J levels before you see substantial deviations.)
   e) Now plot the rotational spectrum for HF which takes into account centrifugal distortion and see how the constancy of rotational line spacing is destroyed.
   f) Calculate the vibrational frequency for this molecule with the data given.

2. Calculate the first three vibrational energy levels for $^1H_2$ given that $\omega_e = 4401.2\ cm^{-1}$, assuming the oscillator to be simple harmonic. Now assume that the oscillator behaves anharmonically, with an anharmonicity constant, $\omega_e x_e = 121.5\ cm^{-1}$. Plot the energy level diagram again for the first three vibrational energy levels for the anharmonic oscillator. Discuss the difference in the two examples. What is the zero-point energy in the two cases?

3. Plot a vibrational spectrum for the above example, for both cases of the harmonic and anharmonic oscillator, stating clearly the selection rules you used in each case. b) Label each transition as fundamental, hot bands and overtones. c) Also indicate 'roughly', the relative intensities of the transitions in both cases. (Just say 'weak' or 'strong' transitions.)