Problem set 4

1. Was given in the last problem set.

2. Hot band transition from v=1 to v=2 depends on the population of v=1 level and hence calculate the population of v=1
   Use the Boltzman equation to calculate the population.

   $$N_v/N_0 = \exp(-\Delta E_v/kT),$$

   where ΔE_v. is the energy of level v, relative to that of level v=0

   The degeneracy of the vibrational levels is 1, for all the levels and hence you do not have to worry about the degeneracy term in the Boltzman equation. [For rotations you had to worry about this term, as the degeneracy of the rotational level is (2J+1)]

   If the frequency is 600 cm^{-1}, it implies ω_e = 600 cm^{-1}.
   Energy of v = 1 is given by the equation

   $$G(v) = \omega_e (v+ ½)$$

   Hence, energy of v=1 level, G(1) is 600 x (1.5), which is 900 cm^{-1}, while energy of v=0 level, G(0) is 300 cm^{-1}. Hence energy of v=1 level is 600 cm^{-1} above the energy of the v=0 level. That is ΔE_v = 600 cm^{-1}. Please recall kT=200 cm^{-1} at room temperature.

   $\exp(-\Delta E_v/kT) = \exp(-600/200) = \exp(-3)$, which is 0.05. That population of level v=1 is 0.05 times that of level v=0, which is about 5%. Hence you will not be able to observe this transition as your machine requires at least a 10% population for the transition to be observed.

3. Data for NO is given. The fundamental is a transition from v=0 to v=1 and the hot band is from v=1 to v=2. (Higher hot bands, from v=2 and higher, can be neglected as these will be progressively weaker.)

   Energy of the vibrational levels, is given by $G(v) = \omega_e (v+ ½) - \omega_e x_e (v+ ½)^2$

   Hence $G(0) = (1/2)\,\omega_e - (1/4)\,\omega_e x_e$
   $G(1) = (3/2)\,\omega_e - (9/4)\,\omega_e x_e$
   $G(2) = (5/2)\,\omega_e - (25/4)\,\omega_e x_e$

   Fundamental is v=0 to v=1 transition, hence the energy involved is
   G(1) – G(0) which is equal to $\omega_e - 2\,\omega_e x_e$
   Overtone transition is from v=0 to v=2. Hence the energy involved here is
   G(2) – G(0), which is equal to $2\omega_e - 6\,\omega_e x_e$
   Therefore $\omega_e - 2\,\omega_e x_e = 1876.1$ and
   $2\omega_e - 6\,\omega_e x_e = 3724.2$
   Solve for ω_e and $\omega_e x_e$

$\omega_e = 1904.1\ cm^{-1}$ and $\omega_e x_e = 14.0\ cm^{-1}$

Use these values to calculate D_e and D_0
For a Morse potential,
$D_e = \omega_e{}^2/4\omega_e x_e$, which is $(1904.1)^2/ (4 \times 14)$ = **$64742.8\ cm^{-1}$**
$D_o = D_e - G(0)$, G(0) being the zero point energy. The expression for G(0) is given earlier. G(0) = 948.6
$D_o = 64742.8 - 948.6$ = **$63794.3\ cm^{-1}$**