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 $\omega_e = 600\ cm^{-1}$.
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 $\Delta E_v = 600\ cm^{-1}$. 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 $\omega_e x_e$

ω_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}**