Chemistry 410A **Exam 5** **Fall 2008**

Solutions

1. **40 points.**

   (a) Write the complete MO configuration that you would expect for B_2, if you follow the line for N_2 in the schematic homonuclear diatomics correlation diagram (Fig. 6.2). **Solution:** B_2 has 10 electrons, and we can put two to an orbital: $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2}$.

   (b) Write the term symbol for the BH_3^+ ion, with MO configuration $1a_1'^2 2a_1'^2 1e'^3$. **Solution:** $S = 1/2$ and the symmetry of e'^3 is the same as e', so $\boxed{^2E'}$.

   (c) Circle the molecule that you would expect to have the **lowest** vibrational constant ω_e: **Solution:** All three molecules are made from atoms with the same valence, so will have similar bonding. In that case, the more massive atoms will give the higher μ and lower k:
   MgO   CaO $\boxed{\text{CaS}}$

   (d) Circle the molecule that you would expect to have the **lowest** vibrational constant for the CC stretch: **Solution:** In this case, the reduced masses are similar but the k values increase from single- to double- to triple-bond:
   $\boxed{H_3CCH_3}$ H_2CCH_2 HCCH

   (e) For the $v = 3$ state of a simple harmonic oscillator:

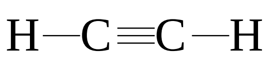
      i. Write the wavefunction in terms of the unitless coordinate y. **Solution:** From Table 7.1:

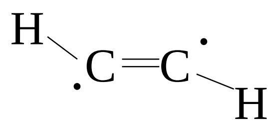
      $$\psi_{v=3} = A_3\, H_3\, e^{-y^2/2} = \left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{48\sqrt{\pi}}\right)^{1/2} (8y^3 - 12y)\, e^{-y^2/2}.$$

      ii. How many nodes does this wavefunction have? **Solution:** $\boxed{3}$.

   (f) How many vibrational modes are there in the simplest amino acid, glycine (NH_2CH_2COOH)? **Solution:** Non-linear with $N = 10$ atoms, so $3N - 6 = \boxed{24}$.

2. Ground state acetylene is linear, but its lowest excited state is a triplet state with C_{2h} symmetry. Give the representations in the C_{2h} limit that correlate to the MO's listed below for the linear molecule.

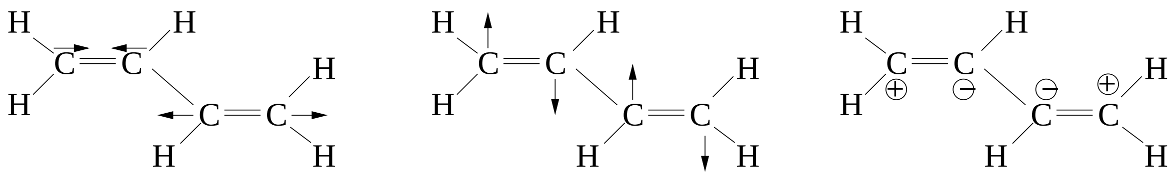




Solution: From the linear to the bent structure, the symmetry elements of C_{2h} are conserved. One of the $\hat{\sigma}_v$ planes in $D_{\infty h}$ becomes the $\hat{\sigma}_h$ plane in C_{2h}, One of the $\hat{C}_2$ axes in $D_{\infty h}$ (perpendicular to the internuclear axis) becomes the principal $\hat{C}_2$ axis in C_{2h}, and $\hat{I}$ is unchanged. Therefore, we can just keep track of the symmetry under $\hat{C}_2$ and $\hat{I}$ to find the correlating representation in C_{2h}:

group	$\Gamma(D_{\infty h})$	$\hat{C}_2$	$\hat{I}$	$\Gamma(C_{2h})$
C—H	σ_g	1	1	a_g
C—H	σ_u	−1	−1	b_u
C≡C	σ_g	1	1	a_g
C≡C	π_u in − plane	−1	−1	b_u
	π_u out − of − plane	1	−1	a_u

3. Give the symmetry representation for each of the vibrational modes below, and indicate whether each mode is IR-active or IR-inactive (in other words, can the mode be excited by an allowed eletctric dipole transition).



a) b_u IR−active   b) a_g IR−inactive   c) a_u IR−active

Solution:

4. The $v = 0 \rightarrow 1$ transition in CH^+ is measured at $2046.3\,\mathrm{cm^{-1}}$. If the force constant is $259.0\,\mathrm{N\,m^{-1}}$, calculate the anharmonicity $\omega_e x_e$. **Solution:** The transition energy depends on ω_e and $\omega_e x_e$. Therefore, to get $\omega_e x_e$ from the transition energy, we need to know the value of ω_e. We can get ω_e from μ and k, so we're all set:

$$\mu = \frac{(1.008)(12.00)}{1.008 + 12.00} = 0.9299\,\mathrm{amu}$$

$$\omega_e\,(\mathrm{cm^{-1}}) = 130.28\sqrt{\frac{k\,(\mathrm{N\,m^{-1}})}{\mu\,(\mathrm{amu})}} = 130.28\sqrt{\frac{259.0\,\mathrm{N\,m^{-1}}}{0.9299\,\mathrm{amu}}} = 2174.3\,\mathrm{cm^{-1}}$$

$$\begin{aligned}\Delta E &= \omega_e\left[(v' + \tfrac{1}{2}) - (v'' + \tfrac{1}{2})\right] - \omega_e x_e\left[(v' + \tfrac{1}{2})^2 - (v'' + \tfrac{1}{2})^2\right] \\ &= \omega_e\left[(3/2) - (1/2)\right] - \omega_e x_e\left[(9/4) - (1/4)\right] = \omega_e - 2\omega_e x_e = 2046.3\,\mathrm{cm^{-1}}\end{aligned}$$

$$\omega_e x_e = \frac{\omega_e - \Delta E}{2} = \frac{(2174.3\,\mathrm{cm^{-1}}) - (2046.3\,\mathrm{cm^{-1}})}{2} = \boxed{64.0\,\mathrm{cm^{-1}}}.$$