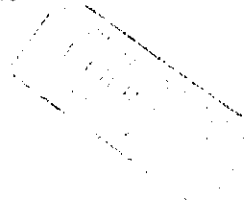


Time: 2  $\frac{1}{2}$  hours

Chemistry 218  
Molecular Structure  
Final Exam

February 5, 1998  
R. Sultan



1. (22 pts) Two *independent* parts:

- a. Give briefly the essence of Wien's law, Stefan's law, and Rayleigh and Jeans' law relating to the phenomenon of blackbody radiation. Do not necessarily give exact formulas. (12 pts)
- b. Show that the vibration of two atoms of masses  $m_1$  and  $m_2$  about an equilibrium position in a diatomic molecule is equivalent to the vibration of the reduced mass of the atoms about the origin placed on one of them. (10 pts)

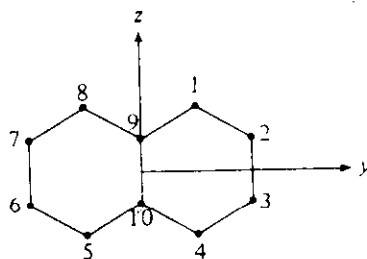
2. (23 pts)

- a. Devise the simplest trial wave function satisfying the boundary conditions of the particle-in-a box problem (call  $L$  the length of the box). (6 pts)

HINT: use a product of simple polynomials.

- b. Using the trial wave function of a), calculate the expectation value of the energy. (12 pts)
- c. Compare your obtained value with that of the exact solution for the ground state (the "true" solution). Comment on the result of the comparison. (5 pts)

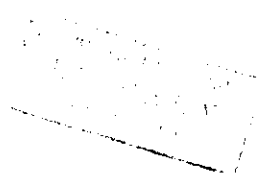
3. (38 pts) Consider from the viewpoint of Hückel molecular orbital  $\pi$ -electron theory, the naphthalene molecule (shown below with an arbitrary numbering).



- a. The solutions for the problem are, in terms of  $x = (\alpha - E)/\beta$ , as follows:

$$x = \pm 0.618, \pm 1, \pm 1.303, \pm 1.618, \pm 2.303.$$

Construct the MOED for the naphthalene molecule showing the energies of the various molecular orbitals. Then show the  $\pi$ -electronic configuration of the ground state in the diagram. (12 pts)



- b. Calculate the delocalization energy (D.E) of naphthalene (6 pts)

GIVEN: Energy of lowest MO in ethylene:  $\alpha + \beta$

- c. The wave functions of the MO's for naphthalene are given as follows:

$$\phi_1 = \frac{1}{2}(\chi_1 + \chi_4 + \chi_5 + \chi_8) \quad \phi_6 = \frac{1}{2}(\chi_1 - \chi_4 - \chi_5 + \chi_8)$$

$$\phi_2 = \frac{1}{2}(\chi_2 + \chi_3 + \chi_6 + \chi_7) \quad \phi_7 = \frac{1}{2}(\chi_2 - \chi_3 - \chi_6 + \chi_7)$$

$$\phi_3 = \frac{1}{\sqrt{2}}(\chi_9 + \chi_{10}) \quad \phi_8 = \frac{1}{\sqrt{2}}(\chi_9 - \chi_{10})$$

$$\phi_4 = \frac{1}{2}(\chi_1 - \chi_4 + \chi_5 - \chi_8) \quad \phi_9 = \frac{1}{2}(\chi_1 + \chi_4 - \chi_5 - \chi_8)$$

$$\phi_5 = \frac{1}{2}(\chi_2 - \chi_3 + \chi_6 - \chi_7) \quad \phi_{10} = \frac{1}{2}(\chi_2 + \chi_3 - \chi_6 - \chi_7)$$

Calculate the  $\pi$ -electron density on all the atoms in the molecule (show your method).  
Comment on the result obtained. (10 pts)

- d. Sketch on the planar skeleton the orbitals shown as electron density regions (lobes), for the first five molecular orbitals. (10 pts)

4. (46 pts)

- a. Draw and label a general molecular orbital energy diagram (MOED) for a 2<sup>nd</sup> period heteronuclear diatomic molecule, showing the parent atomic orbitals on each atom. (8 pts)
- b. Find the molecular term symbol for each of the following diatomic molecules in the ground state:

*BN* (12 electrons):  $KK (2s\sigma)^2 (2s\sigma^*)^2 (2p_x\pi)^2 (2p_y\pi)^1 (2p_z\sigma)^1$   
exceptional configuration

*CN* (13 electrons) }  
*CO* (14 electrons) } *as usual*  
*NO* (15 electrons) }

(16 pts)

- c. The following are some experimental data on the above molecules:

Molecule	Bond Length (Å)	Bond Energy (kcal/mol)
BN	1.281	92
CN	1.172	188
CO	1.128	256
NO	1.150	162

Show how MO theory can account for these observed values. (16 pts)

- d. What electronic configuration gives rise to a  $\Delta$  state? Is it a triplet or a singlet? (6 pts)

5. (20 pts) The orbitals for  $sp^2$  hybridization are:

$$h_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$$

$$h_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

$$h_3 = \frac{1}{\sqrt{3}}s + c_2p_x + c_3p_y$$

- a. Find the constants  $c_2$  and  $c_3$ . (10 pts)
- b. What is the promotion energy for constructing  $sp^2$  hybrid orbitals in the  $\text{BF}_3$  and the ethylene molecules? (10 pts)

6. (51 pts)

- a. The population of a rotational energy level is:

$$P = (2J + 1)e^{-E_J/kT} = (2J + 1)e^{-hcBJ(J+1)/kT},$$

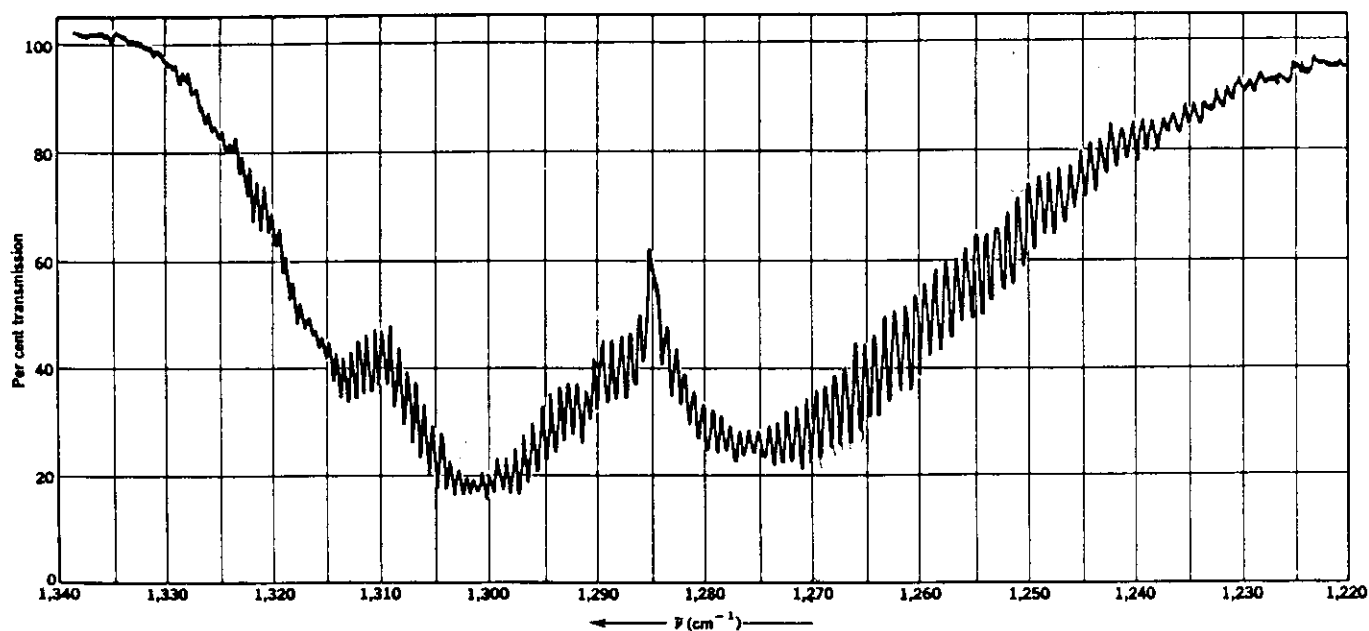
where  $2J + 1$  is the degeneracy of the level. By calculating  $J$  for the maximum population, show that the distance ( $\text{cm}^{-1}$ ) between the maxima of the  $P$  and the  $R$  rotational branches in a vibrational spectral band is:

$$\Delta\bar{\nu} \cong \sqrt{\frac{8BkT}{hc}}.$$

HINT: assume  $B \ll \Delta\bar{\nu}$ .

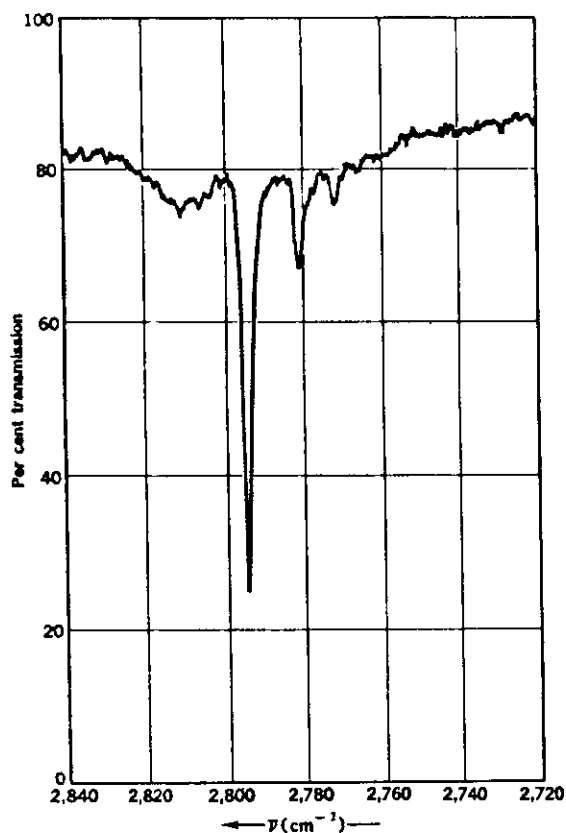
(18 pts)

- b. The following figure shows a band in the IR spectrum of the linear molecule  $\text{N}_2\text{O}$ .



Without a high resolution of the  $P$  and  $R$  branches, estimate the value of the rotational constant  $B$ . (8 pts)

- c. Explain the appearance of the underlying band at  $1312 \text{ cm}^{-1}$ . (7 pts)
- d. Now consider the following low-resolution vibrational band of  $\text{N}_2\text{O}$ .



Show (by detailed calculation) that the two satellite bands of low intensity can be attributed to  $\text{N}_2\text{O}$  molecules that are in a vibrationally excited state. (18 pts)

NOTE: The grade totals up to **200** points.

**Good Luck**

#### USEFUL INFORMATION

Speed of light  $c = 2.998 \times 10^8 \text{ m s}^{-1} = 2.998 \times 10^{10} \text{ cm s}^{-1}$

Planck's constant  $h = 6.626 \times 10^{-34} \text{ J s}$

Boltzmann's constant  $k = 1.380 \times 10^{-23} \text{ J molec}^{-1} \text{ K}^{-1}$

$$\bar{\nu} = (v + \frac{1}{2})\bar{\nu}_0 - (v + \frac{1}{2})^2\bar{\nu}_0 x_e$$