Chem 4A, Fall 2006
Midterm Exam 2, October 20, 2006.
Prof. Head-Gordon, Prof. Moretto

Name: GRADING KEY TA: ____________

Grade:

1. (8 points) ________
2. (5 points) ________
3. (6 points) ________
4. (6 points) ________

Total: /25

Closed book exam. There are 6 pages. Calculators are OK. Set brains to wavelength for stimulated emission of knowledge and go! Use back side of pages for scribble paper

Some possibly useful facts and figures:

$R = 8.3145$ J mol^{-1} K^{-1}
$h = 6.6261\times 10^{-34}$ J s
$c = 2.9979 \times 10^{8}$ m s^{-1}
$m_e = 9.1094 \times 10^{-31}$ kg
$N_0 = 6.0221 \times 10^{23}$ mol^{-1}

molar volume at STP = 22.4 L
$\hbar = h / 2\pi$
$k_B = 1.38066 \times 10^{-23}$ J K^{-1}
1 atm = 101325 Pa

Some possibly relevant equations:

Planck relation: $E = h\nu$

kinetic energy: $T = \frac{1}{2}mv^2$

diatomic rotational energies: $E_J = \frac{h^2}{8\pi^2 I}J(J+1)$ degeneracy $g_J = 2J+1$

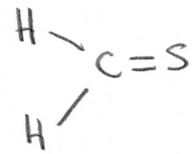
moment of inertia: $I = \mu r^2$

reduced mass of a diatomic: $\mu = \frac{m_1 m_2}{m_1 + m_2}$

harmonic oscillator frequency: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

1. (8 points) Molecular orbitals for the electrons in thioformaldehyde, $H_2C{=}S$.

(a) (2 points) Predict the geometry of the molecule using the VSEPR method. What kind of hybrid orbitals will you use on the C (Z=6) and S (Z=16) atoms to most conveniently predict the molecular orbitals?

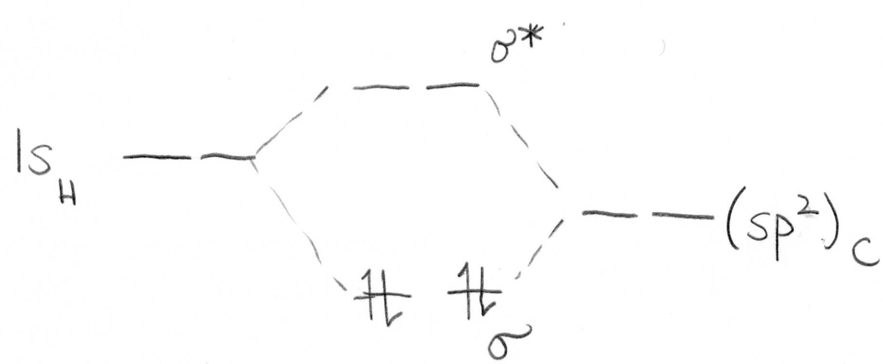


for C, SN = 3

⇒ trigonal planar geometry] 1

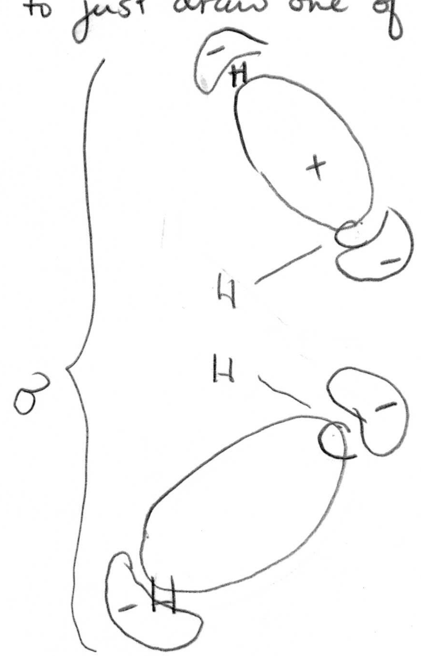
⇒ sp^2 hybrids are most convenient] 1

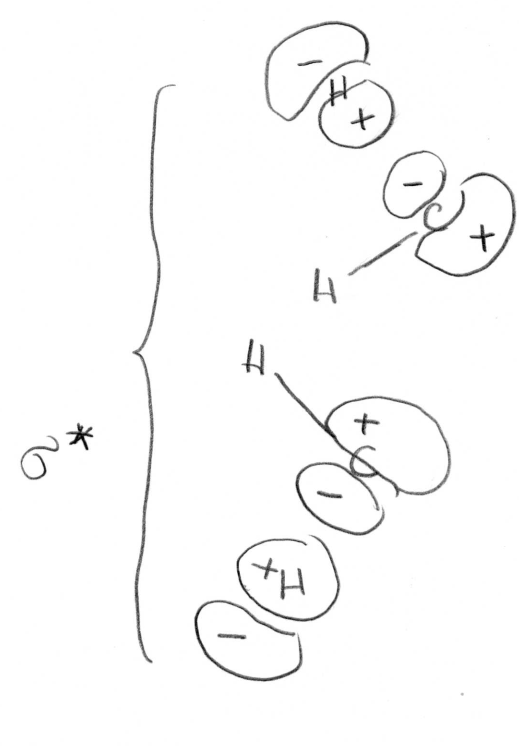
(b) (2 points) Sketch the shape (boundary surface) of the 4 molecular orbitals (σ and σ*) that describe interactions between C and the 2 H atoms. Also draw an energy level diagram showing the AO and MO energies, and which MO's are occupied.



1

(it's OK to just draw one of each...)

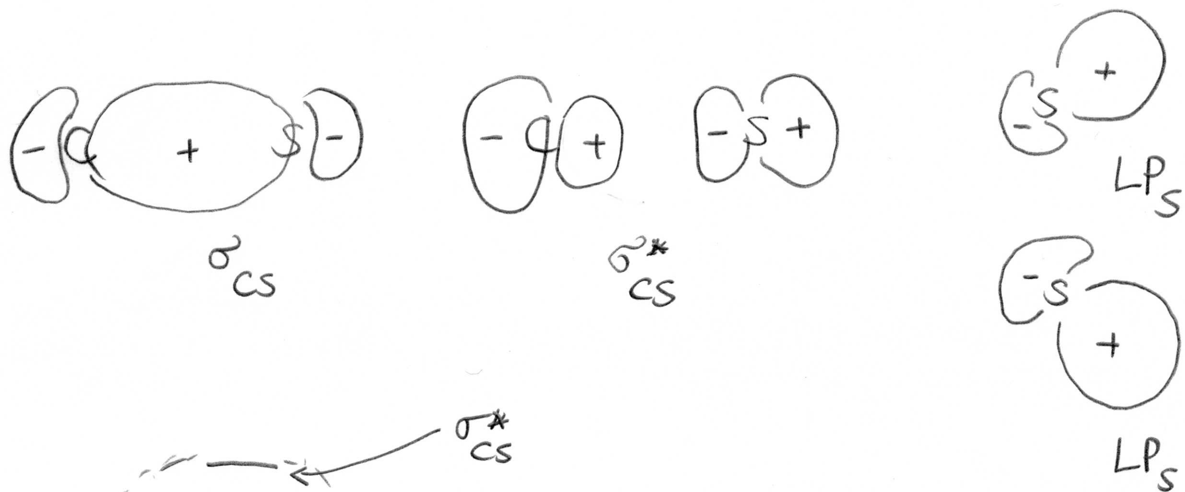




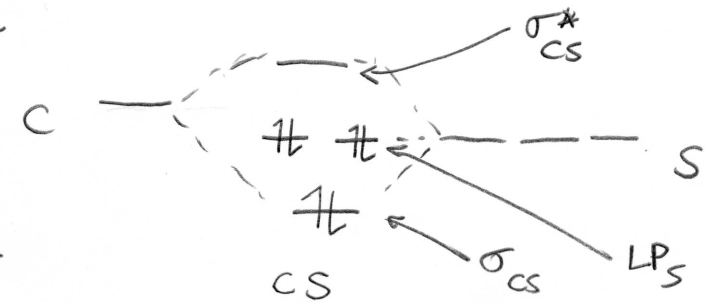
1

(c) (2 points) Sketch the shape (boundary surface) of the 4 (σ and σ^*) molecular orbitals that describe σ interactions between C and S (don't forget lone pairs!). Also draw an energy level diagram showing the AO and MO energies, and which MO's are occupied.

1

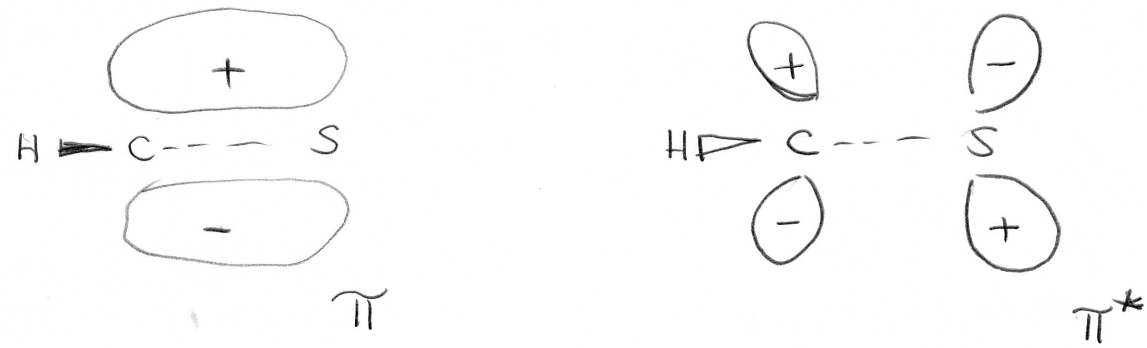


1

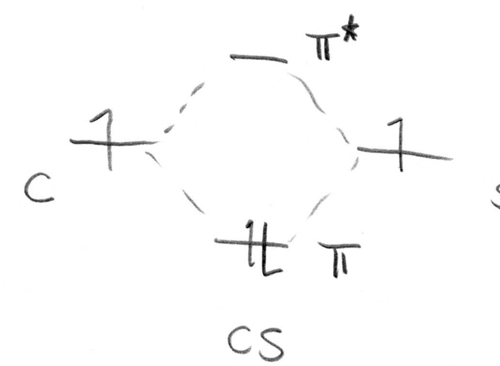


(d) (2 points) Sketch the shape (boundary surface) of the π and π^* molecular orbitals that describe π interactions between C and S. Also draw an energy level diagram showing the AO and MO energies, and which MO's are occupied.

1



1



2. (5 points) It is found that the rotational transition from J=0 to J=1 of the NaH molecule occurs at a frequency of 2.94×10^{11} Hz.

(a) (1 point) Predict the frequency of the J=2 to J=3 transition for the NaH molecule.

$$\nu_{2\to3} = [12-6]\,B = 6B$$
$$\nu_{0\to1} = [2-0]\,B = 2B$$
$$\Rightarrow \nu_{2\to3} = 3\nu_{0\to1} = 8.82\times10^{11}\ \text{Hz}$$

(b) (2 points) From the observed frequency, what is the moment of inertia, *I*, for the NaH molecule? Be sure to include its units.

$$\nu_{0\to1} = \frac{2h}{8\pi^2 I} \quad 1$$

$$\Rightarrow I = \frac{2h}{8\pi^2 \nu_{0\to1}} = 5.71\times10^{-47}\ (\text{J s}^2) \quad 1$$

either OK

$$(\text{J s}^2 = \text{kg m}^2 \text{s}^{-2} \text{s}^2 = \text{kg m}^2)$$

(c) (1 point) Given that the reduced mass of NaH is 1.603×10^{-27} kg, what is the bond length of the NaH molecule?

$$I = \mu R^2$$

$$\Rightarrow R = \sqrt{\frac{I}{\mu}} = 1.887\times10^{-10}\ \text{m}$$

$$(1.887\ \text{Å})$$

(d) (1 point) Explain why you would expect the rotational spectrum of H_2 to be either more intense or less intense than the rotational spectrum of NaH.

H_2 has no dipole moment

NaH has a strong dipole moment

⇒ expect H_2 spectrum to be <u>much</u> weaker

3. (6 points) Suppose absorption of IR radiation of wavelength 3×10^{-6} m excites the vibration of an OH group, such as in alcohols or water, with reduced mass 1.574×10^{-27} kg.

(a) (2 points) What is the force constant for this vibration? Give its units.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow 4\pi^2\nu^2\mu = k$$

$$\nu = c/\lambda \Rightarrow k = \frac{4\pi^2\mu c^2}{\lambda^2}$$

$$\Rightarrow k = 620.5 \text{ N m}^{-1} \quad (\text{or kg s}^{-2})$$

1.5

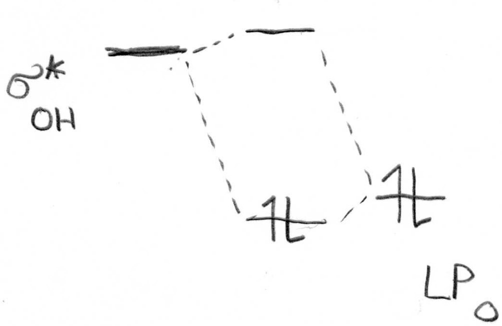
0.5

(b) (2 points) Estimate the ratio of the vibrational frequency of the OD stretch relative to the OH stretch, explaining your logic fully. The atomic masses of O, H and D are 15.9949 amu, 1.0078 amu and 2.0141 amu respectively,

$$\frac{\nu_{OD}}{\nu_{OH}} = \sqrt{\frac{\mu_{OH}}{\mu_{OD}}} \approx \sqrt{\frac{m_H}{m_D}} \approx \frac{1}{\sqrt{2}}$$

i.e. the OD stretch will be about 70% of the frequency of the OH stretch...

(c) (2 points) If the OH bond participates in a hydrogen bond with the lone pair of another oxygen atom (ie. OH····O), draw a donor-acceptor type orbital interaction diagram and suggest how the OH vibrational frequency will be affected.



donor orbital mixes with a small amount of σ^*_{OH}, which will slightly lower the bond order of the OH bond, and thus reduce its frequency

1

1

4. (6 points) Aluminum metal (m=26.9815 amu) reacts with excess aqueous hydrochloric acid (HCl) to produce hydrogen gas and water-soluble aluminum chloride ($AlCl_3$).

(a) (1 point) Write a balanced chemical equation for this reaction.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3\,(aq)} + 3H_{2\,(g)}$$

(b) (2 points) What mass of aluminum is necessary to produce 5 L of hydrogen gas at a pressure of 1 atm and a temperature of 30.0°C?

$$n_{H_2} = \frac{PV}{RT} = 0.201 \text{ mol}$$

$$n_{Al} = \frac{2}{3} n_{H_2} = 0.134 \text{ mol}$$

$$\Rightarrow m_{Al} = n_{Al} M_{Al} = 3.62 \text{ g}$$

(c) (1 point) Suppose the 5L of gas was forced into a 1L container, which was cooled to 0°C. What would be the pressure inside the container be (in atm)?

$$PV = nRT$$

$$\Rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad P_2 = 1\text{ atm},\ V_2 = 5\text{ L},\ T_2 = 303\text{ K}$$

$$V_1 = 1\text{ L},\ T_1 = 273\text{ K}$$

$$\Rightarrow P_1 = \frac{P_2 V_2 T_1}{V_1 T_2} = 1 \times \left(\frac{5}{1}\right) \times \left(\frac{273}{303}\right) = 4.5 \text{ atm}$$

(d) (2 points) Given that the average energy per molecule in the kinetic theory is $3k_BT/2$, obtain an expression for the root mean square speed, and use this to find the root mean square speed of the molecules inside the 0°C container.

$$\bar{E} = \frac{3k_BT}{2} = \frac{1}{2} m\bar{v}^2$$

$$\Rightarrow \bar{v} = \sqrt{\frac{3k_BT}{m}} \qquad m_{H_2} = \frac{2 \times 1.008 \times 10^{-3}}{6.0221 \times 10^{23}} \text{ kg}$$

$$= 3.348 \times 10^{-27} \text{ kg}$$

$$\boxed{\bar{v} = 1840 \text{ m s}^{-1}}$$