Chemistry 4B S'01, Exam II

March 19, 2001
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Problems

1.	(35)	25	
2.	(35)	~~25~~ 20	
3.	(30)	22	

TOTAL EXAM SCORE (100) _____

Rules:

- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Note attached pages with physical constants and useful formulae.

Chemistry 4B S'01, Exam II
Possibly useful formulae:

Name _____

$c = v \cdot \lambda$ for electromagnetic wave

photon energy $E = hv$

DeBroglie wavelength $\lambda = h/p$

Einstein formula, photoelectric effect: $KE_{max} = hv - \Phi$

Two-slit interference experiment:
$$\sin \Theta_{max} = \frac{n\lambda}{d}$$

where d is the distance between the slits and θ_{max} is set of detector angles at which intensity maxima are observed

Coulomb potential, one-electron atom:
$$U(r) = \frac{-Ze^2}{4\pi\varepsilon_o r}$$

Energy levels, one-electron atom:
$$E_n = \frac{-Z^2 e^4 m_e}{8\varepsilon_o^2 n^2 h^2}$$

Energy levels, 1-dimensional particle-in-a-box:
$$E_n = \frac{n^2 h^2}{8mL^2}$$

Heisenberg uncertainty principle:
$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

Boltzmann Population for the state k, relative to the population in the ground state, N_0:

$N_k = N_0 \exp(-E_k/kT)$

$$\beta = \frac{h^2}{8\pi^2 I}$$

Rotational Energies for a rigid-rotor: $E = B J(J+1)$; $B = \frac{h^2}{8\pi^2 I}$, $I = \mu R^2$

Vibrational Energies for a harmonic oscillator: $hv_e(v+1/2)$; $v_e = \frac{1}{2\pi}(k/\mu)^{1/2}$

Reduced Mass: $\mu = m_1 m_2/(m_1 + m_2)$

$$v_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Chemistry 4B S'01, Exam II   Name _____

1. Molecular Orbitals (35 points):

a) (10 points) Draw the molecular orbital correlation diagram for the valence electrons in NF.

$:\ddot{N} = \ddot{F}:$
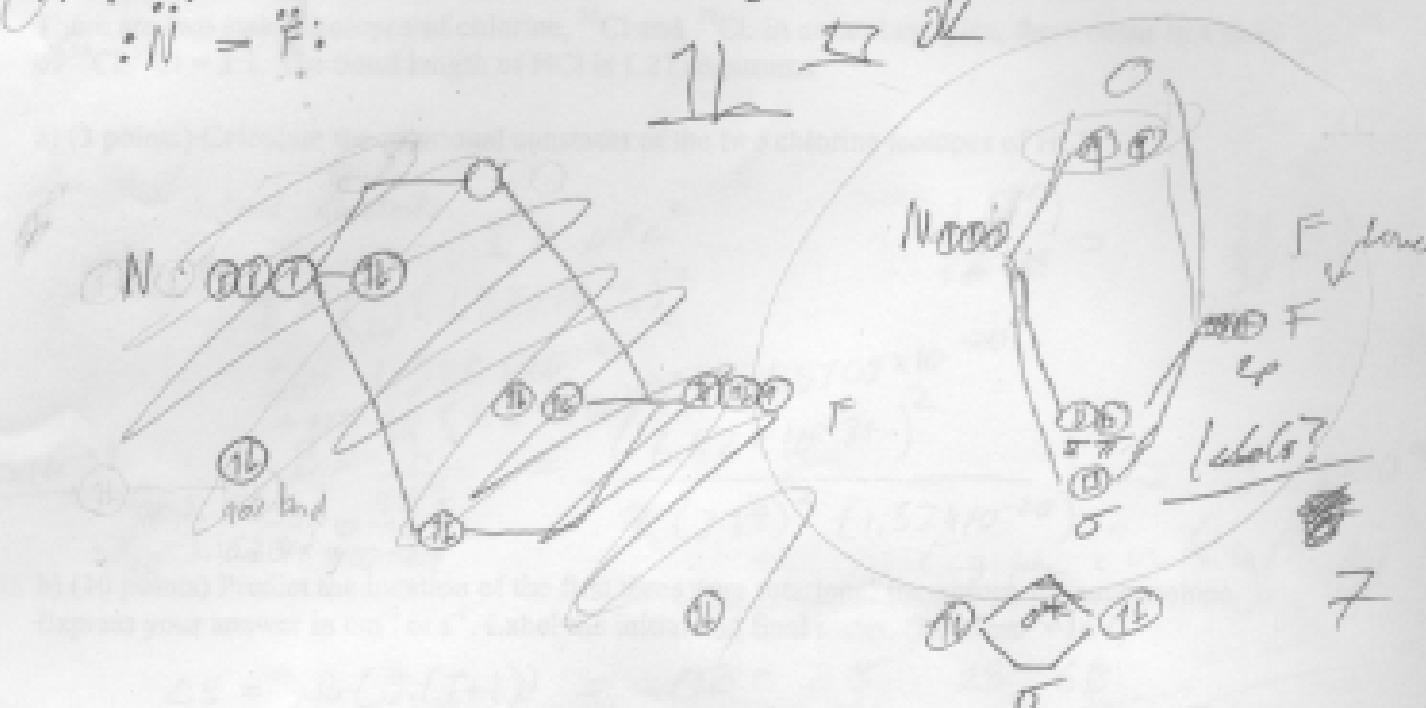
b) (9 points) Write the ground state molecular orbital configuration (σ_s^2 ...) for the molecules CF, NF and OF. CF

$:\ddot{C}-\ddot{F}:$

NF S_{nb}^4 σ_p π_b^4 π_b^{*2} **Sorry!**   3

CF = S_{nb}^4 σ_p^2 π_b^4 π_b^{*1} 3

OF = S_{nb}^4 σ_p π_b^4 2
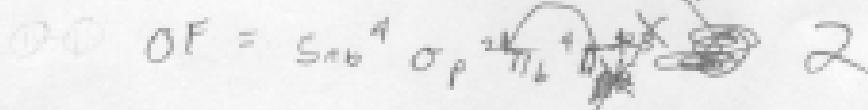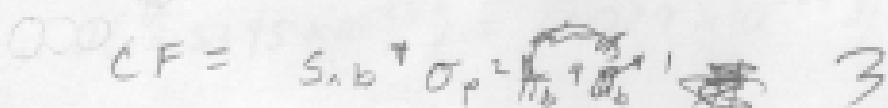
c) (5 points) What is the bond order for each of these 3 compounds?

NF = 2   CF = 2.5   OF = 1.5   5

d) (5 points) Which of these 3 compounds are paramagnetic?

all three   5

e) (6 points) Which of these 3 do you predict will have the largest dipole moment? Why?

NF because it has two or like unpaired spin

2. Spectroscopy (35 points)

There are two stable isotopes of chlorine, ^{35}Cl and ^{37}Cl. In natural samples, these occur in a ratio of $^{35}Cl{:}^{37}Cl = 3{:}1$. The bond length of HCl is 1.27 angstroms.

a) (3 points) Calculate the rotational constants of the two chlorine isotopes of HCl.

rotational constants

$$I = \mu Re^2$$

$$I = \left(\tfrac{35}{36}\right)(1.27\times10^{-10}m)^2$$

$$\frac{1(35)}{1+35} = \frac{35}{36} \approx 1$$

$$I_{35} = 1.568\times10^{-20}$$

$$I_{37} = \tfrac{37}{38}\{1.27\times10^{-10}\}^2 = 1.5705\times10^{-20}$$

$$B = \frac{h}{8\pi^2 I} = \frac{(6.62\times10^{-34})^2}{8(3.14)^2(1.524\times10^{-20})} = 3.64\times10^{-44}$$

$$S.55\times10^{-49}$$
$$\frac{}{I} = B = 3.5353\times10^{-44}$$
$$B_{35} = 3.5395\times10^{-44}$$

μ in kg

b) (10 points) Predict the location of the first three pure rotational transitions for each isotope. Express your answer in cm^{-1} or s^{-1}. Label the initial and final states. ($8066\ cm^{-1} = 1eV$)

$$\Delta E = B(J_i(J+1)) = 0B - 2B \quad 2B - 6B$$
$$2B \qquad 4B \qquad 8B$$

$0\to1$
$$37: 2(3.5353\times10^{-44}) = 7.0706\times10^{-44}J \times 2$$

$0\to1$
$$35: 2(3.5395\times10^{-46}) = 7.079\times10^{-44}J \quad \times2 =$$

$1\to2$
$$4.141\times10^{-43}$$
$$9.282\times10^{-43}$$
$$1.4156\times10^{-43}$$
$$2.83\times10^{-43}$$

c) (10 points) Predict the relative intensities of the first three pure rotational transitions of a sample of HCl. H_{35} or H_{37}

$$N_J = (N_0)(g)e^{-E_J/k_bT}$$

$$\frac{P_i}{P_r} = e^{\left(-(E_{initial} - E_{final})/k_bT\right)}$$

$$\propto \frac{I_i}{I_r}$$

$$diff_i = 2B, 4B, 6B$$

$$e^{\left((-7.07\times10^{44}J)/k_bT\right)}$$

4

d) (2 points) Draw a stick spectrum of your predictions for the pure rotational spectrum of HCL

both for sketch

3 times as much

35

37

good.

2
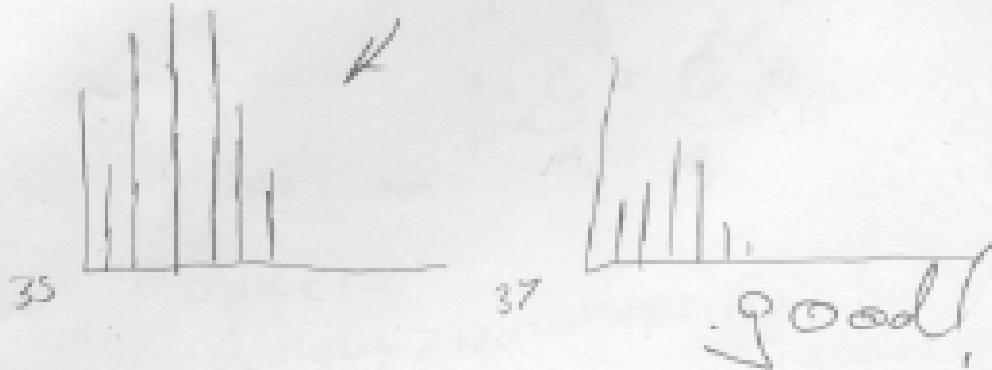
c) (9 points) Observations show the harmonic vibrational energy difference in $H^{35}Cl$ is 2990 cm^{-1}. Calculate the energy difference between the v=0 and v=1 vibrational levels in $D^{35}Cl$.

$H^{35}Cl$.

2990 (8066) = 2417340 ev × 1.602 × 10⁻¹⁹ =

3.8634 × 10⁻¹² J

$V_e = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$ if μ goes

to $\frac{2(35)}{2+35} = 1.892$ from $\frac{35}{36}$, then

V_e now is equal to $\dfrac{V_e \sqrt{1.892}}{\sqrt{\frac{35}{36}}}$ $V_{e \, Dcl} = \dfrac{V_{e \, Hcl}}{\sqrt{\mu_{Dcl}}}$

plug into $\Delta\left(h\nu\left(V+\frac{1}{2}\right)\right) = 2990^{-1}_{cm}$

then ΔE goes up by a factor of

close $\sqrt{\dfrac{1.892}{\frac{35}{36}}} = 1.395 \,(2990) = 4171_{cm}$

5

3. Hydrocarbons

a) (5 points) Use VSEPR theory to estimate the bond angles in the ethylene molecule. Draw your proposed structure.

Sp_2 ~~trick~~

4
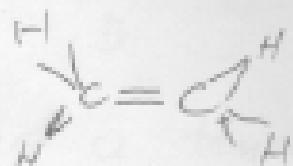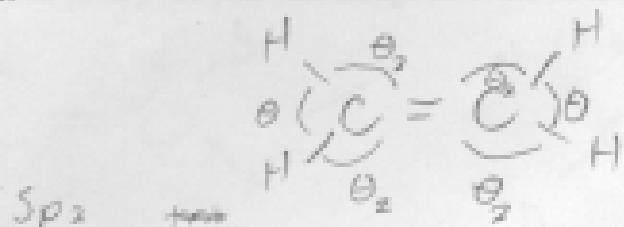
θ slightly $< 120°$

θ_a slightly $> 120°$ VSEPR: $120°$

b) (5 points) What is the hybridization on the Carbon atom?

Sp^2 hybridization

5

c) (5 points) The actual HCH bond angle is $117°$. Suggest a possible explanation for the difference from your proposed structure.

The double bond is a region of increased electron density, and thus acts like a lone pair. Plus, it draws the other C in closer pushing on the two H's

5

d) (8 points) A pure sample of the molecule trans-$D_2H_2C_2$ is left sitting on a shelf in the laboratory. Some months later, a depressed graduate student hoping to use the pure sample finds the sample is a mixture of cis- and trans ethylene. Draw structures of the cis- and trans-compounds. Use MO theory and your knowledge from the laboratory to explain what happened.

Exposure to light caused a temporary dissociation of the π bond allowing for the rotation of the $c=c$ bond. The

e) (7 points) Suppose you were interested in deliberately causing the same cis to trans isomerization in a cis-butadiene compound? What would be the main difference from ethylene?
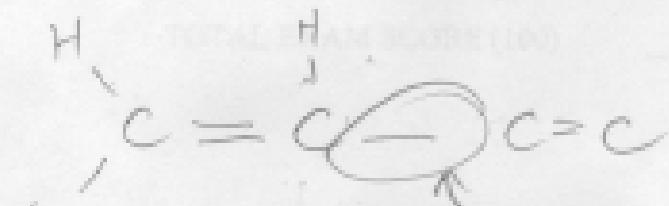
There would already exists a rotational area even without photodissociation of a π bond but π e's are delocalized . . . .