

Final Exam

Chemistry 639
Thursday, May 9, 2002

Your Name:

SSN

This is your final exam. You can use your notes or a textbook but cannot discuss anything with other students. You have 3 hours to complete the exam. Write ALL your derivations either on these sheets of paper or submit additional pages with the exam if you want to get full credit. The exam consists of 6 questions totalling 101 points. If you choose not to use notes and book, you will get additional 10 points. Using character tables is allowed in both cases.

Question 1 (5 points)

- a) (3points) Arrange in order of increasing energy the terms that may arise from the $2p^1 3p^1$ configuration.
- b) (2 points) Identify the lowest energy state in that configuration.

Question 2 (25 points)

The ammonia molecule is pyramidal with the nitrogen atom lying 0.38\AA above the plane.

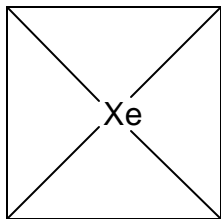
- a) (10 points) Identify molecular symmetry and explain using Walsh correlation diagram why the molecule is not planar

b) (10 points) Identify (label and draw) vibrational modes for this molecule. How many IR-active and Raman-active fundamental frequencies are there?

c) (5 points) Sketch microwave spectrum of NH_3 . $r_{\text{NH}} = 1.1012 \text{ \AA}$

Question 3 (25 points)

Perform vibrational analysis for the planar, XeF_4 . Show by arrows (or write in a form of displacement vectors) and classify by symmetry the normal modes, label them and identify their IR and Raman activities. Hint: treat stretching, bending in plane and bending out of plane modes separately.



Question 4 (10 points)

Identify molecular symmetries and sketch microwave spectra and/or IR spectra for selected ones (neglect centrifugal distortion). Show as many details as you wish but **explain** what you show. $B_e = \frac{h^2}{8\pi^2\mu_e r_e^2} = \frac{16.8576314}{\mu_e^2(\text{amu}\text{\AA}^2)}\text{cm}^{-1}$

Molecule	Symmetric top? What kind?	Microwave Spectrum	IR Spectrum	Bond length
a) H ₂ ^a				$r_{HH} = 0.74\text{\AA}$
b) CH ₃ Cl				
c) C ₆₀ ^a				diameter = 7.1\AA
d) CO ^b				$r_{CO} = 1.128\text{\AA}$
e) CF ₄ ^a				$r_{CF} = 1.323\text{\AA}$
f) HCl ^a				$r_{HCl} = 1.275\text{\AA}$
g) NO ₂ ^a				$r_{NO} = 1.193\text{\AA}$
h) NO ₂ ⁺ ^a				$r_{NO} \sim 1.20\text{\AA}$
i) CO ₂ ^b				$r_{CO} = 1.16\text{\AA}$

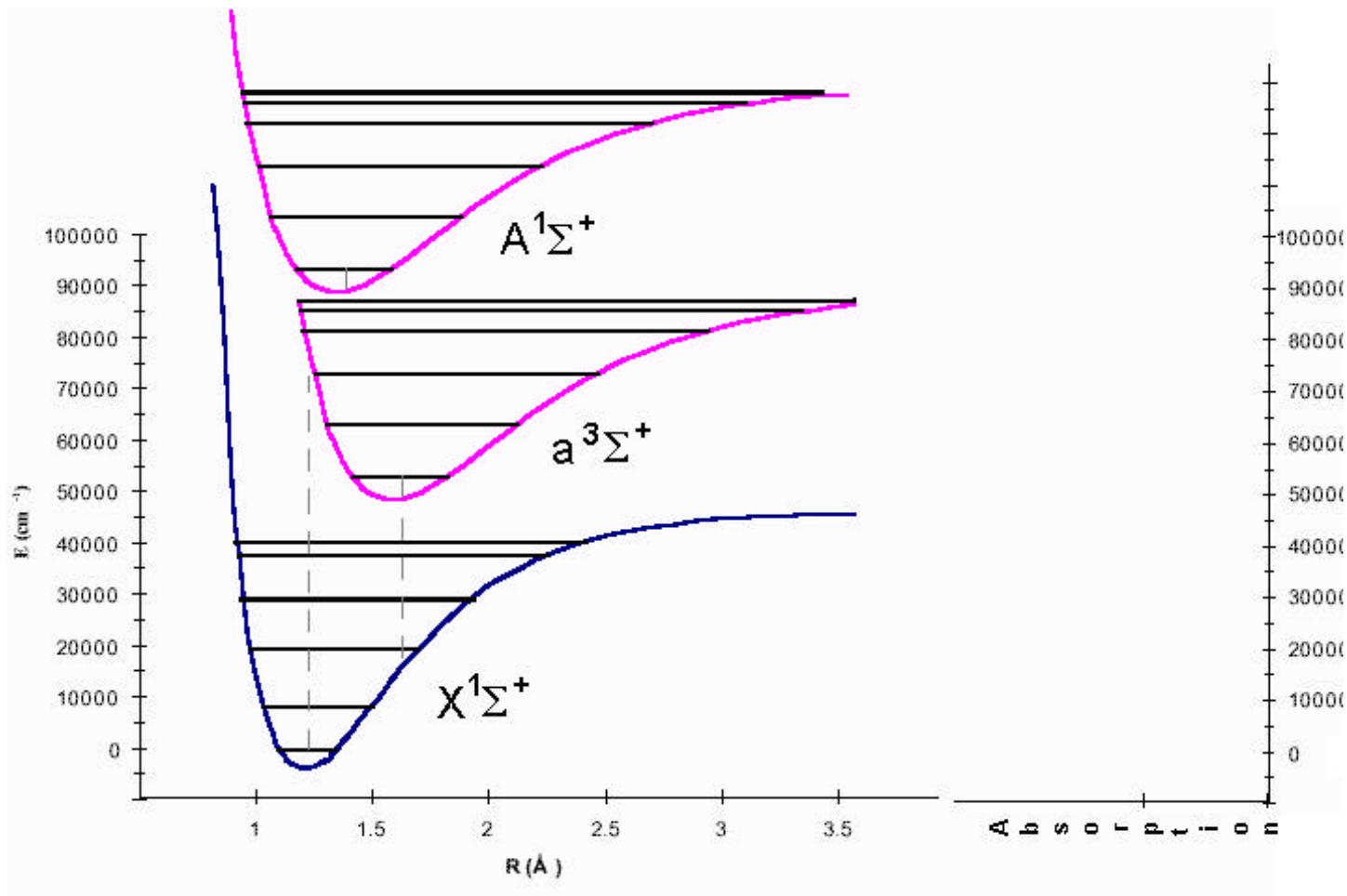
^a - sketch microwave spectrum

^b - sketch IR spectrum

Question 5 (5 points)

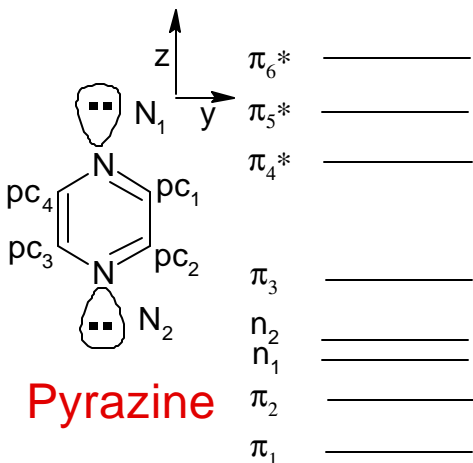
a) (4points) Sketch absorption spectrum of a diatomic molecule, for which the energy diagram is shown below. **Neglect rotational structure.** You can draw the spectrum to the right of the energy diagram as a series of sticks with their heights corresponding to intensities and positions - to the transition energies. Pay attention to the relative intensities (qualitatively) or describe them in words.

b) (1 point) What would be different if it were a homonuclear diatomic?



Question 6 (26 points)

a) (16 points) Using Huckel approximation, **estimate** energies (i.e. not values but the order of MO is asked) of pyrazine molecule shown below. Label appropriate n and π molecular orbitals by their symmetries. Use the table for choosing appropriate α' and β' for the two nitrogens. For lone pair electrons on nitrogens take that their energies are somewhere under π_3^* . as shown on the picture.



Huckel parameters for conjugated heteroatoms			
$\alpha' = \alpha + h\beta$		$\beta' = k\beta$	
Heteroatom	h	Heteroatom bond	k
$\overset{\cdot}{C}$	0	$\overset{\cdot}{\simeq}C\overset{\cdot}{\simeq}C\overset{\cdot}{\simeq}$	1.0
$\overset{\cdot}{N}$	0.5	$\overset{\cdot}{\simeq}C\overset{\cdot}{\simeq}N\overset{\cdot}{\simeq}$	1.0
$\overset{\cdot\cdot}{N}$	1.5	$\overset{\cdot}{C} - \overset{\cdot\cdot}{N} -$	0.8

b) (8 points) From the electronic configurations identify the ground and the first two excited states of pyrazine. Are both (any) transitions dipole allowed? For allowed transition(s) show the orientation of the transition moment in the molecular frame.

c) (2 points) Based on the energy diagram, what can be said about stability of 1,4-dihydropyrazine shown below? Explain

