

# Chem 344 Final Exam

## Wednesday, Dec. 10, 2008, 6-?? PM (230 SES)

**Closed book exam**, only pencils and calculators permitted. You may bring and use one 8 1/2 x 11" paper with anything on it. No Computers. Put all of your work in the answer book. If you need graph paper there are sheets available. If you work out graphical values like slope and intercept on your calculator, you should fully explain your method, write out intermediate values and describe the result. "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam. Questions struck through should be ignored. When offered a choice of questions to answer, do only those, just the first answers found in your book are graded. **Good Luck!!**

- (6) When we do protein crystal structures with conventional x-ray source, we often use Cu  $K\alpha$  x-rays with a wavelength of 1.54 Å (154 pm) because the wavelength has to be of the order of the spacing of molecules and atoms in the crystal. Longer wavelength radiation would result in less resolution.
  - What is the momentum of the photons emitted from the Cu  $K\alpha$  source?
  - We can also get similar structural data with electron diffraction. What electron energy would be needed to get equivalent resolution data as with Cu  $K\alpha$  x-rays (please express answer in eV)?
- (10) Energy levels for the particle in a box problem diverge (get further apart) as  $n$  increases and those for a harmonic oscillator have a constant separation, however for a truncated (finite potential) box, for the anharmonic oscillator and for the H-atom problem, the separation between energy levels collapses as the quantum numbers increase.

**Answer both of the following, c & d:**

- ~~Briefly give a physical explanation for this behavior, i.e. what part of the physical problem, what aspect of the Hamiltonian, leads to these differences in the patterns of energy level spacing and what physical consequence does it have.~~
  - ~~The particle in a box wave functions terminate ( $\psi=0$ ) at the walls ( $V=\infty$ ), but if the walls are shortened to  $V=V_0$  ("stubby box"), the wave functions penetrate the walls. Briefly explain this difference.~~
  - Describe the behavior of a particle originally in one box if the finite,  $V=V_0$ , barrier between it and another box of identical size were made thinner.
  - The anharmonic wave functions shift in position and in energy with respect to the solutions for a harmonic oscillator. Briefly explain.
- (10) **For only 2 (two) of the following questions, sketch requested** H-atom wavefunctions:
    - $R_{nl}(r)$  for  $n = 2, l = 0$ , and  $n = 2, l = 1$
    - $4\pi r^2 R_{nl}(r)$  for the same values of  $n, l$  as in part a
    - $Y_{lm}(\theta, \phi)$  for  $l = 1, m = 0$  and  $l = 1, m = 1$
    - $3d_{x^2-y^2}$  and  $3d_{xz}$  and  $3d_{xy}$  orbitals

4. (10) We developed the Schrödinger Equation and applied it to a number of model problems in an effort to show it applies to Chemistry. The only real “chemical” we can solve (in an exact manner) is the hydrogen atom (and technically the  $H_2^+$  ion). For all other problems relevant to chemistry, we use a succession of approximations.

**Answer only 2 (two) of the following (b, c or d):**

- ~~The H-atom solution gives the same energies as Bohr derived and these can be fit to the Balmer (and Lyman, etc.) series of spectral lines. Why do Bohr and QM agree with Balmer et al. (simple answer)? What assumption was required to relate energy levels to spectra?~~
- For the H-atom orbitals, energy only depends on the principle quantum number. Briefly describe how this is different for atomic orbitals in multielectron atoms?
- Although the H-atom solutions do not work quantitatively for multielectron atoms, outer electron transitions in Li, Na, K, and Rb do reflect the patterns in the Balmer, Paschen, etc. series. Briefly explain why this might happen and how they avoid the complications from energy levels depending on more than  $n$  [Hint: selection rule!].
- What is the fundamental problem in using the Schrodinger equation to solve the multielectron atom problem (i.e. what part of the Hamiltonian makes this a difficult problem and why)?
- ~~Why are multielectron atom solutions still characterized by angular momentum, e.g. term symbols (i.e. what is the important characteristic in the energy operator that makes the solutions have this property)?~~

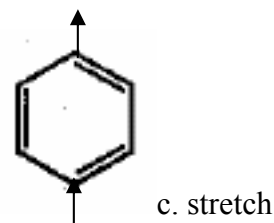
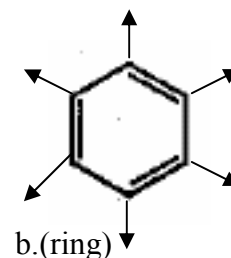
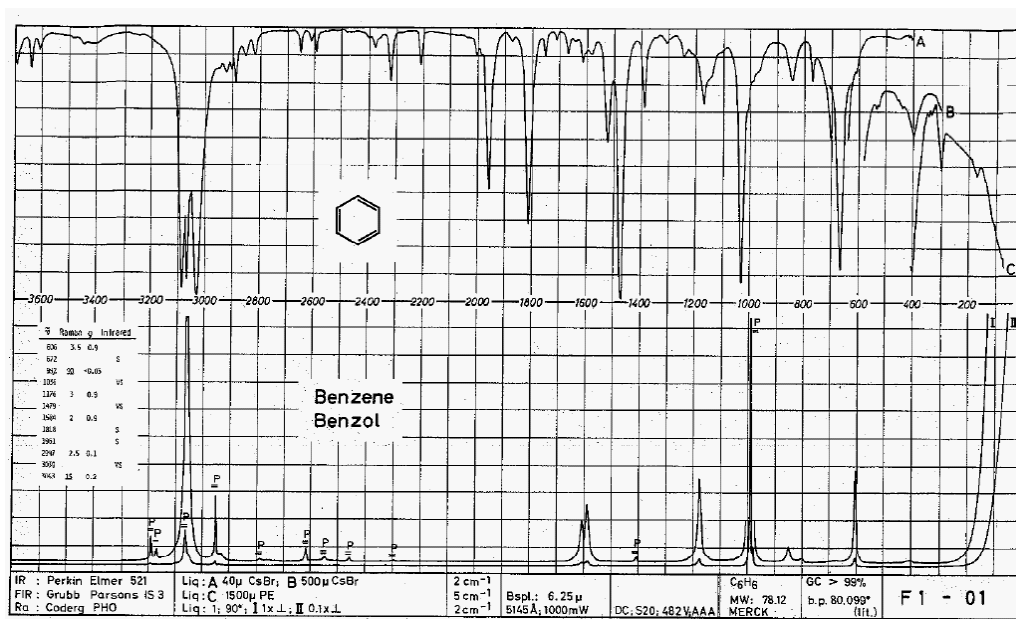
5. (10) **Briefly explain only 2 (two) of the following**

- Franck-Condon principle favoring vertical transitions
- Born-Oppenheimer principle separating vibrational and electronic states
- Variation principle for optimizing a wave function
- Hartree-Fock approximation for determining MOs

6. (24) Consider the LiH diatomic molecule in its ground state. This question is about vibrational and rotational spectra: **Answer only 4 (four) of the following**

- If  $\mathbf{r}$  is the distance from Li to H, the harmonic potential energy for LiH vibrations is:  $V = \frac{1}{2} \mathbf{k}(\mathbf{r}-\mathbf{r}_e)^2$ . What if the potential were anharmonic, what would be its form? how would you determine the equilibrium bond distance,  $\mathbf{r}_e$ ?
- If the fundamental frequency of LiH is  $2400 \text{ cm}^{-1}$ , what is  $\mathbf{k}$ ? (*assume harmonic*) (watch your units!, AtWt: Li = 7, H = 1)
- What is the fundamental vibrational frequency of LiD? (MW: D = 2)
- In the gas phase, the LiH IR spectrum has rotational structure. Describe which transitions are observed and what kinds of spectral bands result. Sketch your prediction of this spectrum, label axes.
- What is the spacing of the transitions in *part d*, if  $\mathbf{r}_e = 1.1 \text{ \AA}$  (110 pm)?
- Briefly explain what would happen to the predicted vibrational spectrum if the potential were more realistic, i.e. if it were anharmonic, what added transitions would appear and what energies would they have in the IR?

7. (14) Consider  $\text{H}_2\text{O}$ , a 10 electron molecule.
- Sketch an MO diagram for  $\text{H}_2\text{O}$ , indicate relative energies of the AOs and MOs, the filling of the AOs and MOs, the types of MOs made from the AOs
  - Use your diagram to determine the ground configuration and first excited configuration for  $\text{H}_2\text{O}$ . Indicate the possible spins (or singlet, triplet notation) for each
  - ~~Two variants of  $\text{H}_2\text{O}$  are  $\text{H}_3\text{O}^+$  and  $\text{HO}^-$ , which both also have just 10 electrons. Use your diagram and configuration ideas from above and briefly justify your proposal for the relative bond energies of the O-H bonds in  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$  and  $\text{HO}^-$ . You may be able to relate this to relative acidity of these three species.~~
8. (12) Consider Benzene vibrational spectra: **Answer only 3 (three) of the following**
- Raman and IR both measure vibrations, but the spectra below do not overlap, offer a brief explanation.
  - Explain why for benzene the ring breathing mode (where all Cs move in and out in phase, as indicated in “ring” diagram below) is not observed in the IR spectrum (upper trace) but it is in the Raman (lower trace, in spectra, *see below*).
  - Explain why the out-of-phase C-H stretch (where two C-H bonds opposite each other move so that one contracts while the other stretches) is seen in the IR. (*see below*)
  - For the benzene spectrum below, briefly explain the nature of the vibrational motion leading to transitions at  $\sim 3000\text{ cm}^{-1}$ .
  - Determine the total number of fundamental vibrational modes for benzene.
  - Briefly explain why the IR spectrum is more complex, has more transitions than the Raman spectrum.



**9. (15) Answer only 3 (three ) of the following:**

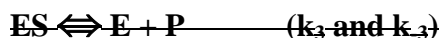
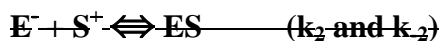
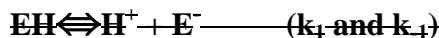
- Explain why fluorescence and absorption spectra of the same molecule are often mirror image band shapes, with absorbance at higher frequency.
- Briefly explain what you can determine about the excited state potential surface if the 0-0 transition is the most intense vibronic (Frank-Condon component) band in an absorption profile (for ground  $\rightarrow$  excited state transition).
- Explain how linear dichroism can be used to determine the orientation of an antibiotic in a cell membrane (for a model system).
- Briefly describe what can be learned from fluorescence anisotropy and how it is measured.
- Circular dichroism is very useful for stereochemical studies. Briefly explain any restrictions on this measurement.
- Briefly explain how FRET (fluorescence resonant energy transfer) can be used to determine distances between specific sites in a protein.

10. (20) The hydrolysis of sucrose by the enzyme invertase can be followed by measuring the initial rate of change of optical rotation (with a polarimeter, since CD does not work well for sugars). The data below list initial rates in terms of change of rotation,  $\alpha$ , at various initial concentrations of sucrose. (Rotation measured will be proportional to concentration of sucrose). The reaction can be inhibited by urea. The second set of rate data below are with addition of 2M urea:

[sucrose] mM	29.2	58.4	87.6	117	175	234
rate: $v_0=(d\alpha/dt)_0$	0.182	0.265	0.311	0.340	0.372	0.410
rate (2M urea): $v'_0$	0.083	0.119	0.154	0.172	0.192	0.204

- Determine the Michaelis constant,  $K_M$ , and maximum rate  $v_M$  for this enzymatic reaction.
- Determine what type of inhibitor is urea, competitive or non-competitive and justify your answer, and evaluate the modified Michaelis constant,  $K'_M$

- ~~11. An enzyme contains a single ionizable group at its active site. For catalysis to occur, this group must dissociate, i.e. it must lose a  $H^+$  to become the  $E^-$  form. The substrate bears a positive charge,  $S^+$ , which helps promote the formation of the enzyme-substrate complex,  $ES$ , with the negative enzyme,  $E^-$ . This is a proposed mechanism for this reaction:~~



- ~~$H^+$  is an inhibitor of the formation of P by this enzyme. What kind of inhibitor is it? Give a reason why.~~
- ~~Determine an expression for the initial rate in terms of  $E_0$ , S and  $H^+$  for this mechanism. Show steps in derivation for full credit. Explain change from M-M result.~~