Analytical cumulative examination Crib **January 2007**

1) Demonstrate your general knowledge about mass spectrometry and related topics by answering the following questions:

a) Why do mass spectrometers usually operate on gas-phase ions (*e.g.*, require the analyte to be charged and under collision-free conditions)?

Because gas-phase ions are easy to manipulate – charge allows manipulation by electric and magnetic fields, and absence of collisions allows the ions to keep their trajectories.

b) Give a definition for mass resolution, and explain its importance in mass spectrometric analyses.

The ability to separate peaks with very close m/z-values. Very low resolution would not allow mass separation.

c) Give a specific example where high resolution is absolutely necessary.

Analysis of very complex mixtures without prior separation.

d) Explain the difference between precision and accuracy.

Precision: ability to remeasure a value with only small scatter in the data.
Accuracy: ability to measure a value close to the known true value.

e) Define dynamic range.

Ability to measure simultaneously very high and low signals.

2) Demonstrate your general knowledge about mass spectrometers by answering the following questions:

a) Give an example of a mass spectrometer with high resolution and another one with low resolution. Explain why this is so.

High resolution: ICR because it measures frequency.
Low resolution: B alone because of distribution of ion velocities.

b) Why are time-of-flight mass spectrometers commonly used to analyze very large biomolecules?

Unlimited mass range.

c) Why is electrospray ionization (ESI) the commonly used ionization method in these experiments?

Because it is gentle enough to evaporate and ionize biopolymers without fragmentation.

3) In order to demonstrate your general knowledge on what the local mass spectrometrists are excited about and why, please answer these three questions:

a) What is the new invention that Professor Graham Cooks made recently on sample introduction into mass spectrometers, and why is everybody excited about this invention?

DESI – desorption electrospray ionization. This involves carrying out ESI directly on a sample on a surface and extraction of the ions into a mass spectrometer. This is exciting because no sample preparation is required.

b) Why is Professor Hilkka Kenttämaa receiving funding from Pharmaceutical industry to develop gas-phase ion/molecule reactions for structural characterization of compounds?

Because ion/molecule reactions provide for detailed structural information for unknown compounds than CAD, and because MS can be used to directly analyze mixtures without separation.

c) Why is Professor Scott McLuckey so famous for his studies on reactions that reduce the charge states of ESI-generated multiply charged peptide ions?

Charge reduced peptide ions provide different structural information than unreduced ones; and analysis of complex mixtures of peptides is much easier if each component does not have a very large number of charges.

4) Demonstrate your general knowledge about the chemistry and energetics related to mass spectrometry experiments by answering the following questions:

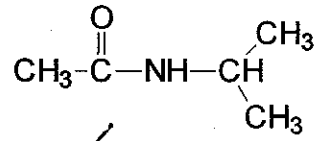
a) Give a rough estimate for the energy typically required to cause dissociation of an ionized organic molecule, and for the average energy that gas-phase ions gain in collision-activated dissociation (CAD).

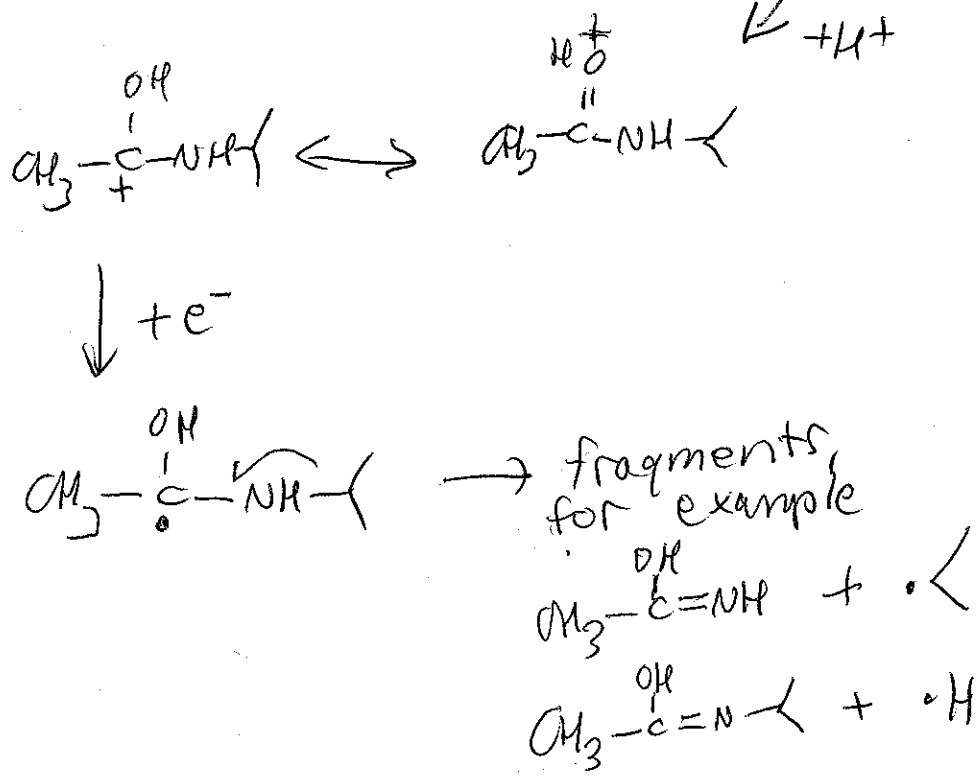
Dissociation: 2-3 eV, CAD: 1-2 eV

b) Explain what factors control the dissociation products obtained in CAD experiments. What theories could you use to predict (calculate) a mass spectrum, and what information do you need to do that?

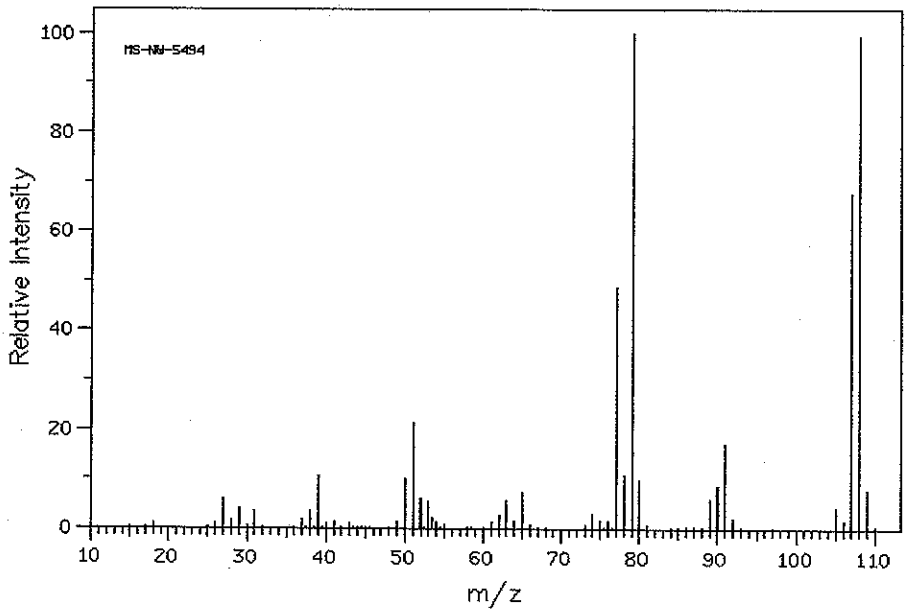
Parent ion structure, fragmentation activation energies, parent ion's internal energy distribution, reaction time, number of identical dissociations, entropy factors. RRKM/QET: the above information.

c) A new method to fragment protonated analytes in mass spectrometry is called electron transfer-induced dissociation. This method involves bombarding protonated analytes with electrons to generate the corresponding radicals by electron capture. These radicals then undergo structurally characteristic fragmentations. Show that you understand the process by writing the chemical equations for every step of the experiment (starting with ionization) for the molecule shown on right.

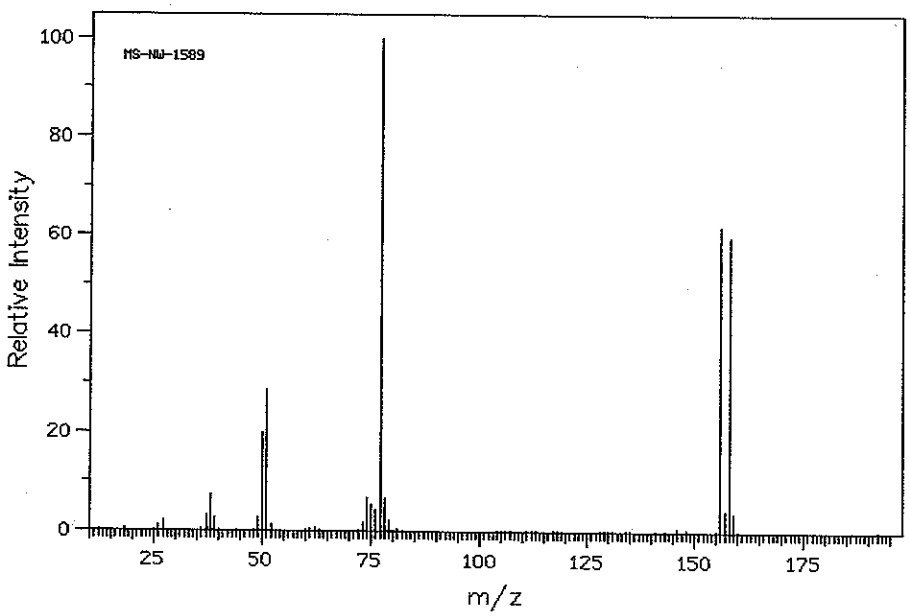




5) Consider the positive ion EI mass spectra given below. What sort of structural information can you extract from them?



Molecular ion 108; aromatic compound; no N, Cl, Br, B; 91: benzyl cation; 91: loss of OH; very favored α-cleavage leads to loss of H; compound is benzyl alcohol. Isomers: methoxybenzene – no major loss of H, methylphenol: no loss of OH.



Molecular ion 156; contains Br; aromatic; compound is bromobenzene.

No Biochemistry crib available

January 13, 2007

Written by Professor VanEtten

Inorganic Chemistry Cumulative Exam Crib

Purdue University

January 13, 2007

There are 100 possible points in this exam.

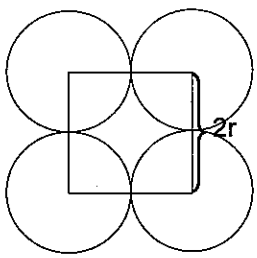
1. (54 points) Consider metal spheres that are packed to form a primitive, a body-centered, and a face-centered cubic structure. Fill in the blanks assuming that the edge of each cube is 4.0 Å long.

	Primitive Cubic	Body-Centered Cubic	Face-Centered Cubic
Distance to a nearest neighbor (nm)	(a) **0.4**	(g) **0.35**	(m) **0.28**
Number of first nearest neighbors	(b) **6**	(h) **8**	(n) **12**
Distance to a second nearest neighbor (nm)	(c) **0.57**	(i) **0.4**	(o) **0.4**
Number of second nearest neighbors	(d) **12**	(j) **6**	(p) **6**
Distance to a third nearest neighbor (nm)	(e) **0.69**	(k) **0.57**	(q) **0.49**
Number of third nearest neighbors	(f) **8**	(l) **12**	(r) **8**

2. Consider a metal atom of radius *r* (so the volume of the atom is $4/3\pi r^3$). Assume that these atoms are packed to form a primitive cubic structure with each atom touching adjacent atoms. The packing efficiency of a lattice is defined as the volume occupied by metal atoms per unit cell divided by the volume of the unit cell.

a) (5 points) Express the edge of the cube in *r*.

Edge of the cube = 2r

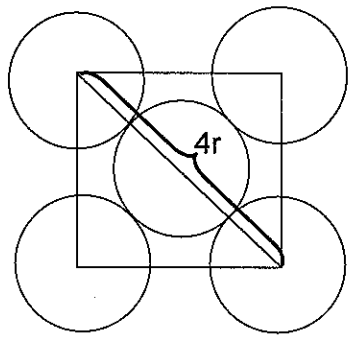


b) (5 points) Calculate the packing efficiency for a primitive cubic structure.

$V_c = 8r^3$ **$V_s = 4/3\pi r^3$ x 1 (one metal atom per cube)**
Packing efficiency = 52.3 %

c) (5 points) Consider the same metal spheres packed to form a face-centered cube. Express the edge of the cube in *r*.

Edge of the cube = 2.83r



d) (5 points) Calculate the packing efficiency for a face-centered cubic structure.

$V_c = 22.7\ r^3$ $V_s = 4/3\pi r^3 \times 4$ (four metal atoms per cube)
Packing efficiency = 73.6%

3. The perovskite structure shown below is adopted by many oxides that have the chemical formula, ABO_3. The general crystal structure is cubic, with the A-cation in the middle of the cube, the B-cation in the corner, and the anion, commonly oxygen, in the centre of the edges. Assuming that the edge of the cube is 4 Å, answer the following questions.

a) (6 points) What is the lattice type of this structure (e.g. primitive cubic, body-centered cubic, face-centered cubic)?

Primitive cubic (all the lattice points must be identical)

b) (4 points) How many oxygen atoms (nearest neighbors) are coordinated to B?

Six oxygen atoms

c) (4 points) How many oxygen atoms (nearest neighbors) are coordinated to A?

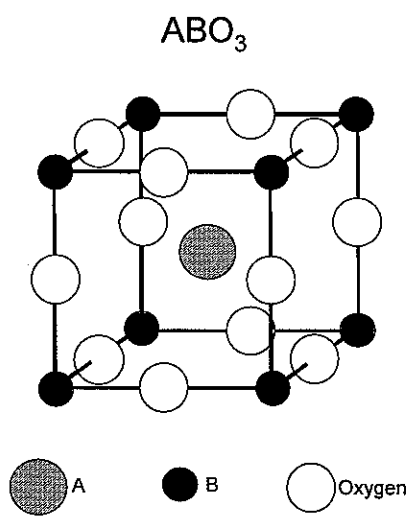
Twelve oxygen atoms

d) (4 points) What is the shortest A-O distance?

2.8 Å

e) (4 points) What is the shortest A-A distance?

4.0 Å



f) (4 points) $BaTiO_3$ has a perovskite structure and is a technologically important material due to its interesting ferroelectric and piezoelectric properties. Is this compound paramagnetic? Explain.

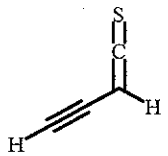
It is not paramagnetic because this compound does not have unpaired electrons (Ba^{2+}; Ti^{4+}; O^{2-}).

Organic Cumulative examination Crib
Jan. 13, 2007

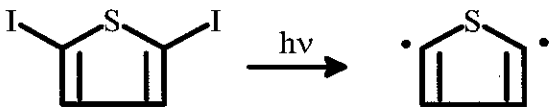
30pts

1) The IR band at 1760 suggests a carbonyl. However, C=S stretches should be lower than normal carbonyl, so it is not an isolated thiocarbonyl. However, the normal ketene stretch is around 2200 cm^{-1}, so this seems like a reasonable drop. The IR data suggests a thioketene C=C=S. The C-H stretch is pretty high, more in the range for an acetylenic C-H stretch

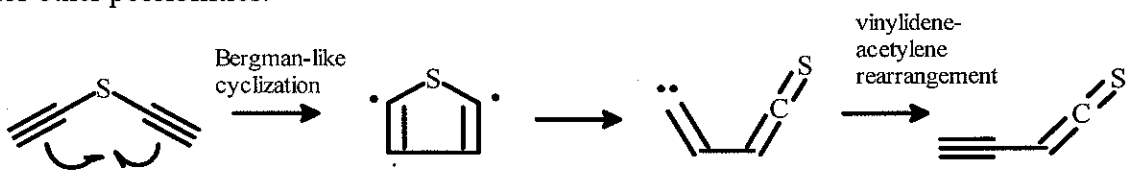
a) Proposed structure:



b)

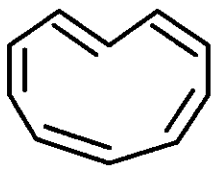


c) The mechanism suggested by the observations above is shown below. See the original paper for other possibilities.



10pts

2) a) i)



ii) Density functional theory

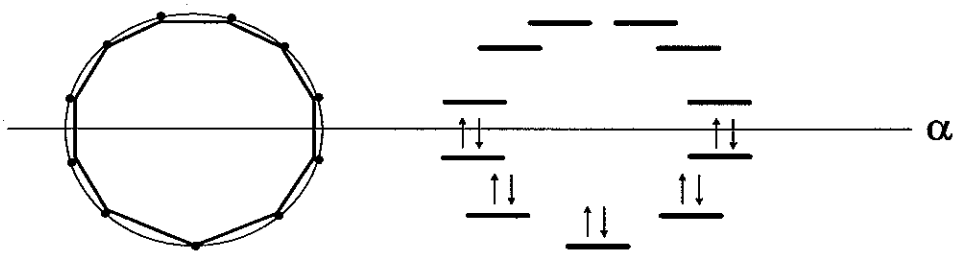
One proton does stick in the middle of the ring, but it is reasonably uncrowded.

15pts

b)
1) Energy stabilization (aromatic stabilization energy)
2) Magnetic properties (NMR, diamagnetic susceptibility)
3) Structural (decrease in bond length alteration)

20pts

c) Frost circle for $C_{11}H_{11}^{+}$: Put the ring point down, orbital energies are at the vertices. The α level is in the middle of the ring. $C_{11}H_{11}^{+}$ has 10 π electrons.



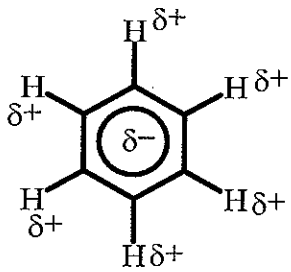
All the π electrons in the cation are in bonding orbitals. In contrast, the radical and the anion will have electrons in anti-bonding orbitals and are open-shell

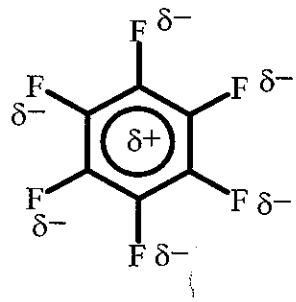
5 pts

d) Shaik argues that the delocalized π system is not a stable electronic structure, and that it is the σ system that prefers equal bond lengths.

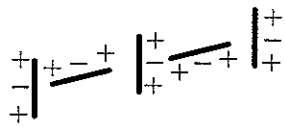
20 pts

e) C_6H_6 and C_6F_6 interact in an edge-to-face fashion. Benzene is polarized with negative charge density inside the ring, and positive charge outside the ring. Hexafluorobenzene is polarized in an opposite fashion.

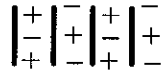




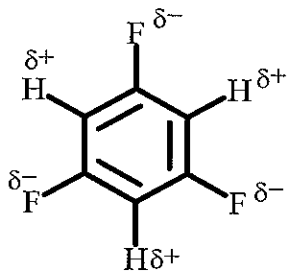
From an edge view, the rings look like quadrupoles:

By stacking edge-to-face, the poles can interact: 

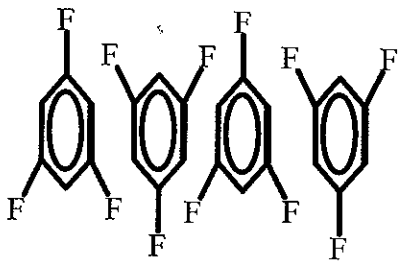
However, the mixture of C_6H_6 and C_6F_6 can stack face-to-face:



ii. Trifluorobenzene is a combination



and can π stack in an alternating fashion



physical Chemistry Crib
Jan. 2007

1. Spectroscopy:

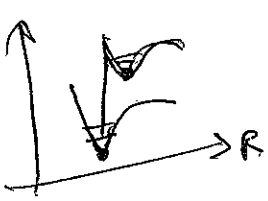
(10) (a)

Microwave	Far Infrared	Infrared	Visible an UV
Rotation of polyatomic molecules	Rotation of small molecules	Vibrations of bonds	Electronic transitions

(5) (b) Fundamental $V=0 \rightarrow V=1$ second-overtone $V=0 \rightarrow V=3$

(5) (c) B.O for potential energy $(m_p \gg m_e)$ and F.C predicts relative intensities of vibrational transitions

(5) (d)



The minimum position of the excited state is <u>shifted</u>

(10) (e) $I_{xx} = I_{yy} < I_{zz}$ BCl_3 is an oblate symmetric top

$I_{xx} = I_{yy} > I_{zz}$ CH_3I is a prolate symmetric top

2.

$\psi(0) = \psi(L) = 0$ $E = \frac{n^2 h^2}{8mL^2}$ $n = 1, 2, \ldots$

(10) (a) Yes because of symmetry and $\psi(0) = \psi(L) = 0$

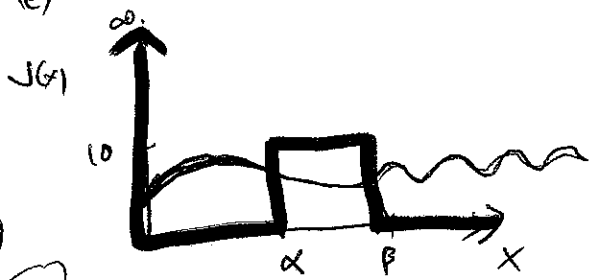
(5) (b) $V(x) = 0$ First $\underline{211}$ $\underline{121}$ $\underline{112}$

(5) (c) ~~the~~ degeneracies (111) — classical = Yes

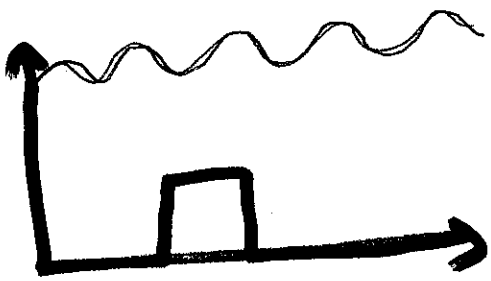
(5) (d) Heisenberg uncertainty principle

(10) (e) Boundary Condition $\psi(0) = \psi(L) = 0$

(3)



(a) (15)



(15) (b)