

SOLUTIONS TO SAMPLE EXAM

(sample exam appears on the Library website under “Course Reserves”)

Question 1 Refer to the molecular orbital picture of NO, an important neurotransmitter and component of smog. A blank MO template is given.

- (i) Determine the number of electrons and put them in the molecular orbitals.

N has 5 valence electrons and O has 6. Therefore we add 11 electrons to our template (from the bottom up).

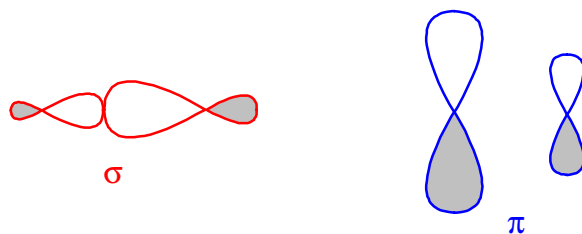
- (ii) N is on the left (higher energy), O is on the right (lower energy). Why?

(a) N has a smaller electro-negativity (smaller Z_{eff})

- (iii) What is the bond order?

(d) 2.5

- (iv) Draw a picture of the orbitals labelled σ and π^* (you only need to draw one of the π^* orbitals).



- (v) Is NO likely to form an anion? Which one?

NO might not want to be neutral because it's a radical! Of the choices NO^+ and NO^- , we see that NO^+ removes an electron from an antibonding level, which strengthens the bond. NO^- would weaken the bond by adding to the π^* level. Therefore NO^+ is more likely.

Question 2 (i) How can the “centrosymmetric rule” be used?

Checking the point groups (last page), you will see that D_{6h} is centrosymmetric (has i) while D_{3h} is not. Therefore, running the IR and Raman experiments on aromatic benzene will not produce any common lines, whereas if there were alternating double and single bonds, there would be overlap (e.g. those vibrations with E' symmetry).

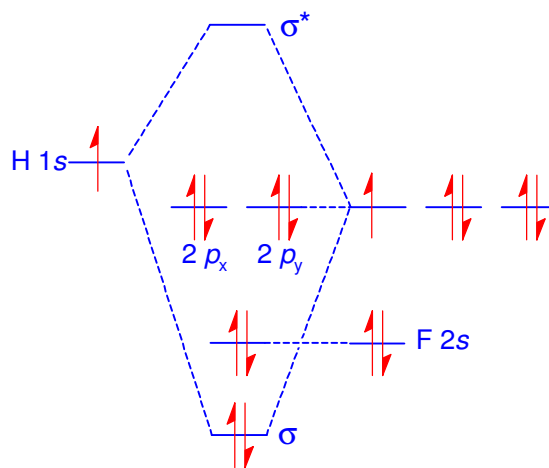
- (ii) (a) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 = A_{1g} = only Raman active
 (b) 1 -1 1 -1 -1 1 1 -1 1 -1 1 1 = B_{2g} = inactive
 (remember, C_6 is the z -axis, other solutions are possible depending on how you define the x and y axes (one will be C_2' , the other is C_2''))
 (c) 1 1 1 -1 -1 -1 = A_1'' = inactive

Question 3 (i) Based on the relative energies, the H 1s is likely to interact with:

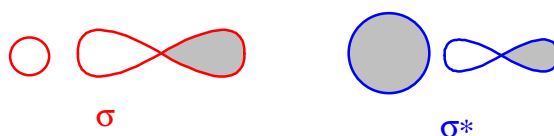
(c) with a fluorine 2p only

(ii) Based on the answer for (i), draw the MO diagram:

The picture is consistent with the Lewis structure for HF, in that they both have one bond and three pairs of non-bonding electrons (lone pairs). The only real difference is that MO theory predicts that the three lone pairs do not have the same energy (nor do they point to the corners of a tetrahedron, as implied by VSEPR theory).



(iii) Draw the σ and σ^* orbitals.

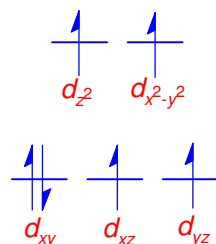


Question 4 Point groups.

O_h C_{3v} D_{2d}

D_{3h} C_{2v} C_s

Question 5 (i) Draw the d -orbital configuration for the complex $\text{Fe}(\text{OH})_6^{4+}$ (OH^- is a weak-field ligand), label the atomic orbitals, and fill in the electrons:



(ii) What is Δ_O if $\lambda_{\text{MAX}} = 980 \text{ nm}$?

(b) 122 kJ/mol

(iii) What is the magnetic moment?

(c) 4.90 μ_B

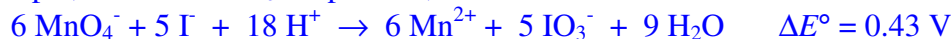
- (iv) What would be the value of Δ_t for $\text{Fe}(\text{OH})_4^{2-}$?
- (a) 54 kJ/mol
- (v) $\text{Ru}(\text{OH})_6^{4-}$ has no magnetic moment, why?

Note the Ru^{2+} is also d^6 , and it must have no unpaired electrons so the complex is low spin. The reason for this is that all 2nd and 3rd-row transition metals are strong field (no matter what the ligand is), and ruthenium is in the 2nd transition series.

PART 2

- (1) Because the e_g set are actually σ^* in character, the stronger the bond, the more the bonding orbital goes down in energy and the more the antibonding orbital goes up in energy. Thus, as the bond strength increases, σ^* (e_g) goes up in energy and Δ_o increases.
- (2) Diamagnetic compounds contain only paired electrons, and repels from a magnetic field. Paramagnetic compounds contain randomly oriented unpaired electrons and attract to a magnetic field. Ferromagnetic compounds are paramagnetic compounds with all the spins aligned throughout the solid, and form a permanent magnet.
- (3) The defects we covered were (any three of these for full marks):
- a missing formula unit (Schottky)
 - a missing anion replaced by an electron (F-centre)
 - ions displaced from their correct sites (e.g. T-hole instead of O-hole, or cation-anion swap) (Frenkel)
 - extended defect (like two crystals growing together)
- (4) not covered this year
- (5) Fe^{3+} is considerably harder than Cd^{2+} , so the softer end of the ambidentate ligand is likely to attach to the cadmium and the harder end to the iron. Thus, $\text{Fe}^{3+}\text{-NCS-Cd}^{2+}$.
- (6) not covered this year
- (7) There are four possible answers – basically any two species that overlap and are not the starting materials. Thus, possible product pairs are:
- $\text{MnO}_2 + \text{H}_5\text{IO}_6$
 $\text{MnO}_2 + \text{IO}_3^-$
 $\text{Mn}^{2+} + \text{IO}_3^-$
 $\text{Mn}^{2+} + \text{I}_2$

For example, for $\text{Mn}^{2+} + \text{IO}_3^-$ as product,



NOTE: $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ is $(1.70 \times 3 + 1.23 \times 2) / 5 = 1.51 \text{ V}$
 $\text{I}^- \rightarrow \text{IO}_3^-$ is $(-0.53 \times 1 - 1.19 \times 5) / 6 = -1.08 \text{ V}$