

No Analytical crib available
November 15, 2008
Written by Professor Kenttämää

No Organic crib available
November 15, 2008
Written by Professor Thompson

No Physical crib available
November 15, 2008
Written by Professor Slipchenko

Inorganic Chem Nov 2008

FORM A
APPROVED FOR USE IN
PURDUE UNIVERSITY

1. CrO_4^{2-} d^0 HOMO on oxide ligands

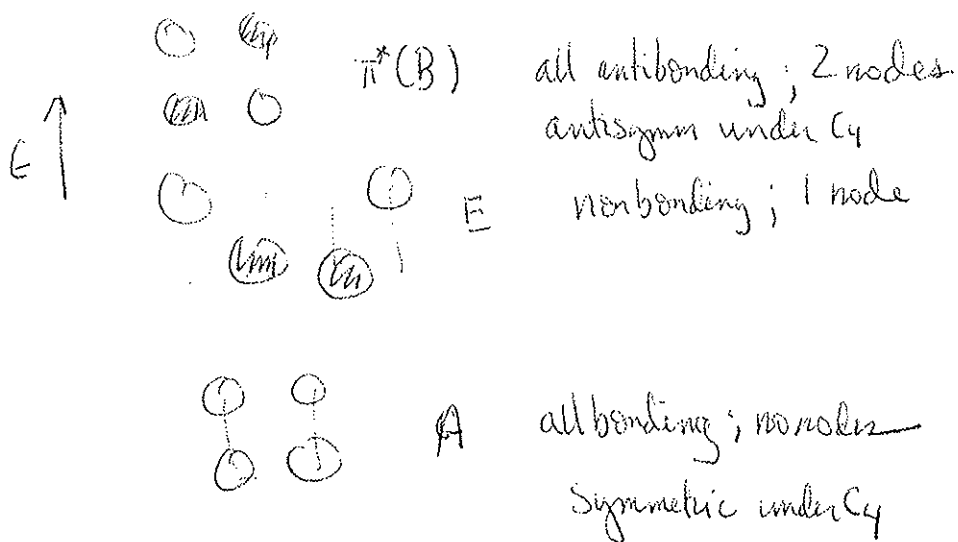
LMCT

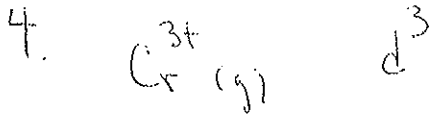
$Cr(phen)_2^+$ d^1 LUMO a π^* of phen

MLCT

2.
$$\phi_{isc} = \frac{k_{isc}}{k_r + k_n + k_{isc}}$$
 efficiency of triplet formation

3.





$(M_L)_{max} = 3$

	↑	↑	↑	-	-
m_l	2	1	0	-1	-2

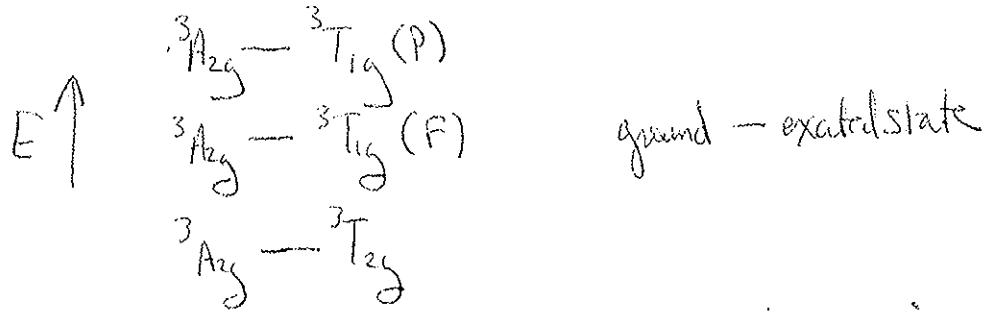
$\Rightarrow F$ term

$S = 3/2 \Rightarrow 2S+1 = 4$

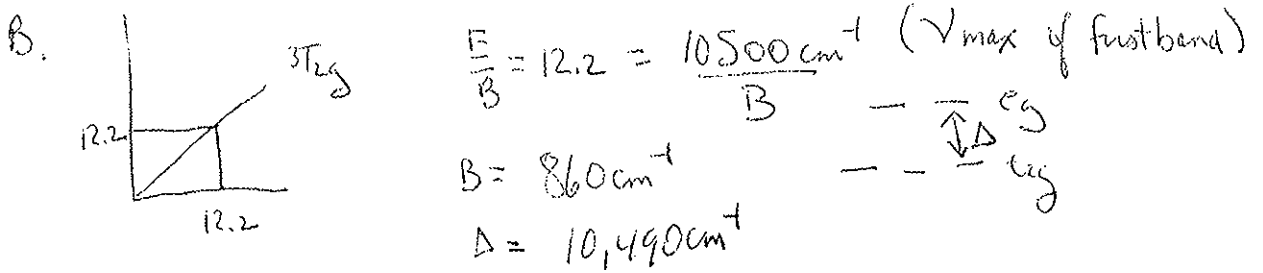


$(2S+1)(2L+1) = 28$ microstates

5. A. Look for spin-allowed ($\Delta S=0$) transitions



d-d transitions are g-g and are symmetry forbidden



C. Delocalization of d electrons onto the ligand orbitals leads to 'cloud' expansion and reduced repulsions. Nephelauxetic effect.

Answers to the Biochemistry Cumulative Exam Questions (November 15, 2008)

1. Most mammalian plasma membranes have a strong predominance of choline containing lipids (phosphatidylcholine and sphingomyelin) in their outer leaflets and aminophospholipids (phosphatidylserine and phosphatidylethanolamine) in their inner leaflets. The aminophospholipids are rapidly moved to the inner leaflets of membranes by an ATP-dependent enzyme called the flippase or aminophospholipid translocase. All lipids are very slowly moved to the outer leaflet by a nonspecific floppase. Then, when triggered by an influx of calcium or apoptosis, all lipids are rapidly scrambled to a symmetric distribution by a scramblase. This scramblase moves phosphatidylserine, which exists normally exclusively on the inner leaflet of a membrane to the outer leaflet of a membrane. The exposed phosphatidylserine serves to trigger blood clotting at the site of a wound and phagocytosis of any apoptotic cell by macrophages.

2. The structure of stearyl sphingomyelin is shown below. Sphingomyelins tend to associate into sphingolipid-rich domains because i) they have an extra hydroxyl on their backbone that enables intersphingolipid H-bonding, and ii) they are generally highly saturated and gel-like lipids that do not mix well with shorter chain, fluid phospholipids.

3. A transmembrane potential is established primarily by the action of ion pumps that use energy (primarily ATP) to pump charges asymmetrically across a membrane. The major pump responsible for most transmembrane potential that exist across mammalian plasma membranes is the Na/K-ATPase, that pumps 3 sodiums out of a cell for every 2 potassiums that it pumps in. This sets up a charge separation across the membrane that is responsible for the electrical potential.

The electrical potential is used to transmit nerve impulses via a wave of depolarizing cation currents. It is also used to pump nutrients into cells against their concentration gradients by coupling their uphill transport with a cation's downhill transport. Further, they can be used to generate ATP from the electrical potential, as in the case of the coupling factor in the mitochondrion that generates ATP from the electrochemical gradient established by electron transport.

4. Membrane-spanning proteins are comprised almost exclusively of alpha helices and beta pleated sheets because these are the only protein structures that are entirely internally H-bonded. That is, unsatisfied H-bonds are strongly thermodynamically disfavored, and to avoid positioning them within the membrane

bilayer where no water exists to satisfy such unoccupied H bonds, membrane-spanning proteins must form secondary structures that satisfy them entirely internally.

A hydropathy plot is constructed by assigning the average hydrophobicity of a stretch of 9 to 15 consecutive amino acids to the central amino acid within that amino acid stretch. This average hydrophobicity is then plotted as a function of the position of that central amino acid in the protein sequence. This plot yields a measure of the average hydrophobicity of the long windows of amino acids within a protein structure and can thereby assist in identifying membrane-spanning helices of proteins.

A hydropathy plot cannot be used to identify membrane-spanning segments of beta sheets or beta barrels, because the side chains of every other amino acid within a beta sheet/barrel point outward and inward. Those that point outward generally interact with lipid and are hydrophobic, whereas those that point inward commonly interact with water or polar solutes that pass through the interior of a protein channel (e.g. porin). Because every other amino acid in such sheets is polar/nonpolar, no extended hydrophobic or hydrophilic structure can be identified by hydropathy.