No Crib for Analytical Cume
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No Crib for Biochemistry
Cume
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1. (20 pt) Identify point symmetry group for each of the following molecules/ions.

(a) cyclooctatetraene $D_{2d}$

(b) $C_{2h}$

(c) cyclopropane $D_{3h}$

(d) Assign the complex ion at the bottom $D_5$

2. (15 pt) (A) Predict the shape of the PF$_5$ molecule based on the VSEPR model. (B) The $^{19}$F NMR spectrum of PF$_5$ recorded at the ambient temperature exhibits one doublet (each chemically distinct F nucleus gives arise to a doublet), but that recorded below -150 °C displays two doublets. Explain (including necessary structural sketches to support your argument).

(a) 5 pairs, trigonal pyramidal

(b) PF$_5$ is highly fluxional, and the exchange rate of apical and equatorial F is much faster than NMR time scale, and hence cannot be distinguished. But, the exchange rate slows down significantly that two types of F can be resolved on NMR time scale;

The exchange proceeds via Berry pseudorotation, apical F2 and F3 rotate 30 deg to become equatorial (as red arrows indicate); Equatorial F4 and F5 rotate 30 deg to become apical (as blue arrows indicate)
3. (20 pt) Aqueous solutions of MnSO₄ are almost colorless. Please provide a detailed explanation on the basis of what you have learned from CHM641.

Aqueous solutions contain Mn(H₂O)₆²⁺

H₂O is a weak field ligand

Mn²⁺ is d⁶, and high spin

Draw actual ligand field diagram and filling scheme

\[ e_g \]

\[ t_{2g} \]

Based on the scheme above, a d-d transition would require the "flip" of the spin of excited electron to conform to the Pauli principle. In doing so,
1. (60 points) Provide mechanisms for the reactions involved in steps 1-5. Use curved arrow formalism and show all likely intermediates. Assume an aqueous workup after each reaction. Your mechanism in step 5 should account for the formation of both products.
2 (Cont'd)

TMSO₂C

OMOM OPMB

H₂O (workup)

OMOM OPMB

H₂C-NN

H₂C-N

MeO

OMOM OPMB

(-N₂)

N₂CH₃

OMOM OPMB

3

R

R

R

R

R

DDQ

SET

H₂O

R

R

R

R

R

R

(p-MeOPhCHO)
2. (40 points) Provide detailed explanations for the stereoselectivities observed in steps 1 and 2.

The first case is an example of Crand's Rule selectivity, which the Felkin-Ahn model explains:

The second case is an example of chirality transfer in a [3,3] sigmatropic reaction. This can be explained by the preference for a chair-like transition state where the substituent R occupies an equatorial position preferentially:
A diatomic molecule $A_2$ in electronic state $S_0$, with $n = 0$ and $J = 0$ strongly absorbs ultraviolet light. The resulting spectrum is structured (no continuous absorption) but it is observed that after a while (that is, not quickly) the molecule is dissociated. Sketch a set of potential energy curves and rotational, vibrational levels to describe this process. Explicitly describe all the processes that change the electronic state. Explicitly indicate any nonadiabatic processes.

**Solution**
For the two diagrams presented below identify and define the process corresponding to the numbered arrows. Be sure to state whether the process involves a photon or is a radiationless, whether it is adiabatic or non adiabatic. If the process involves a photon, state whether the spectrum will be structured (line spectrum) or continuous. Note $S_0 =$ lowest singlet state, $S_1 =$ first excited singlet state, and $T_1 =$ first triplet state. The rotational Quantum numbers are ignored here.

Arrow 1: $S_0$, n=0 to $S_1$, n=4
Arrow 2: $S_1$ n=0, to $S_0$ n= 3
Arrow 3: $S_1$, n = 0 to an isoenergetic (same energy) $T_1$ state.
Arrow 4: $S_1$, n = 4 to $S_1$ n= 0. You need not consider whether or not this process involves a photon.
Arrow 5: $S_0, n = 3$ to $S_1$

Arrow 6: an $S_1$ process

**Solution**


Arrow 2: Fluorescence: an excited molecule emits a photon and returns to ground state. Line spectrum.

Arrow 3: Internal conversion: radiationless process where a molecule passes to another electronic state, and the total energy is conserved. Adiabatic.


Arrow 6: Direct dissociation, continuous absorption.
Solution

1. O₂ and O₃ protect the earth from harmful radiation in a CONTINUOUS range, with wave lengths shorter than ~340 nanometers (the exact value of this limit is unimportant here). Absorption occurs into a dissociative electronic state. Even though the ground electronic states of O₂ and/or O₃ have discrete energy levels, they have dissociative excited electronic states. So, once an electron is excited, then it behaves like a free electron which has continuous energy.
(Wavefunction: Ψ = Aeᵢkx, Energy eigenvalue: k²ℏ²/2m, where k can be any values)

2. To determine force constants, you need the fundamental vibrational modes of CH₄. The exact band positions of each fundamental mode is determined from its ro-vibronic spectrum, and not from its pure rotational spectrum.

3. The earth is a low temperature blackbody; it gives low temperature radiation, most of which is in the IR region. In the atmosphere of the earth, there are lots of small molecules. If there is a dipole moment change in them, they can absorb IR radiation emitted by the earth, preventing it from escaping from the earth, then increase the earth's temperature. This is called the greenhouse effect. In the case of N₂ and O₂, which are principal atmospheric gases, because there is no dipole moment change, there is no rotational or vibrational absorption spectrum. So, these gases do not contribute to the greenhouse effect.