**2016 Ch112 – problem set 6**
**Due: Thursday, Dec. 1**

## Problem 1 (2 points)

### Part 1

a. Consider the following $V^{III}$ complexes: $V(H_2O)_6^{3+}$, $VF_6^{3-}$, and $VCl_6^{3-}$ . The table below contains the energies corresponding to the two lowest spin-allowed d-d transitions ($\upsilon_1$ and $\upsilon_2$). Assign the state symbols corresponding to these two transitions and fill in the table heading with the transition.

b. Use the included Tanabe-Sugano Diagram to determine B and $\Delta_o$ and complete the table below. (Estimate $\Delta_o$/B to the nearest 0.5)

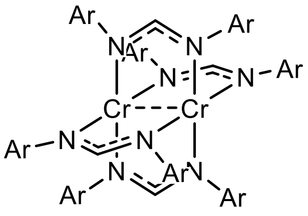
| | $\upsilon_1$ ($cm^{-1}$) | $\upsilon_2$ ($cm^{-1}$) | Ratio of $\upsilon_2/\upsilon_1$ | B (Racah Parameter) ($cm^{-1}$) | $\Delta_o$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| $V(H_2O)^{3+}$ | 17,800 | 25,700 | | | |
| $[VF_6]^{3+}$ | 15,100 | 23,600 | | | |
| $[VCl_6]^{3+}$ | 11,000 | 18,020 | | | |

c. Rationalize the observed trends in B and $\Delta_o$ values in terms of ligand properties.

### Part 2

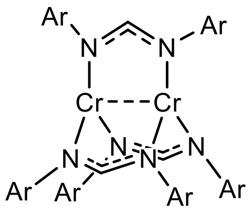
In the fourth problem set, you derived the MO diagrams for two complexes containing Cr-Cr bonds:

**A**



Ar = 2-Me-Ph
Cotton, *J. Chem Soc., Dalton Trans* (2000), 2007

**$B^-$**



Ar = 2,6-Me-Ph
Tsai, *Angew. Chem. Int. Ed.* (2008) *47*, 7250

a. Based on these MO diagrams, what is the term symbol for the ground state of A and $\mathbf{B}^-$?

b. Give the state symbols for the first excited electron configurations of these complexes (lowest energy transition between HOMO and LUMO).

c. For A and $\mathbf{B}^-$, would any transition to these excited states from the ground state be orbitally allowed?

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## Problem 2 (3 points)

### Part 1

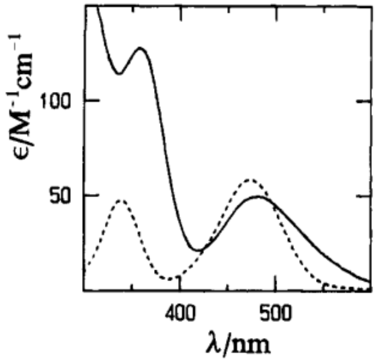

**Figure 4.** UV−visible absorbtion spectra of $[Co(NH_3)_5(CH_3)](NO_3)_2$ (—) and $[Co(NH_3)_6]Cl_3$(- - -) in 5.0 M ammonia water at 20 °C.

Below is a table with the energies and ε values for the visible d-d transitions in $[Co(NH_3)_6]^{3+}$.

| Wavelength (nm) | Energy (cm$^{-1}$) | ε (M$^{-1}$cm$^{-1}$) |
|---|---|---|
| 338 | 29585.8 | 48 |
| 474 | 21097.1 | 58 |

a. Using the appropriate Tunabe-Sugano diagram, assign these transitions, assuming they are the two lowest energy transitions from the ground state.

b. Determine the Racah parameter (B) and $\Delta_o$ for this complex.

### Part 2

Vibrations for the $CoN_6$ core of $[Co(NH_3)_6]^{3+}$ transform as the following irreducible representations in the $O_h$ point group:

$\Gamma = A_{1g} + 2T_{2u} + T_{1u} + T_{2g} + E_g$

Consider the spin-allowed transitions for the following electronic transition: $(1t_{2g})^6 \rightarrow (1t_{2g})^5(2e_g)^1$

a. Write the spin allowed transitions and demonstrate that they are Laporte forbidden through multiplication. Although the g and u characters are sufficient here to determine if the transition is allowed, perform the full multiplication (You are allowed to use the symmetry multiplication tables at the end of *Symmetry and Spectroscopy*.)

b. List any of these transitions that will increase in intensity due to vibronic coupling.

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**Part 3**

In class, we analyzed the absorption spectrum of *trans*-[Co(en)$_2$Cl$_2$]$^+$:

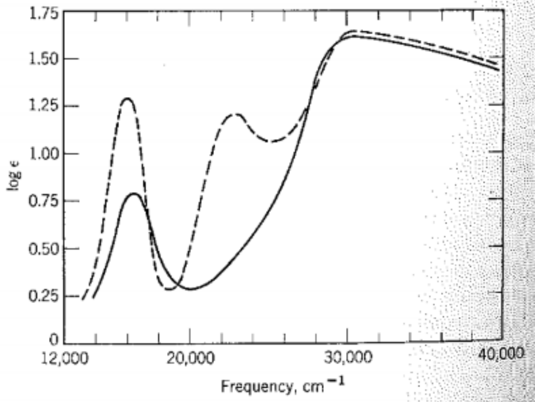
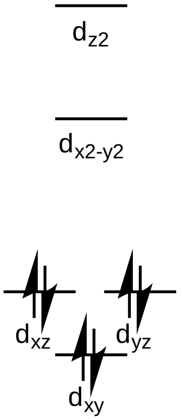


**Figure 9.13** Dichroism of *trans*-[Co(en)$_2$Cl$_2$]$^+$ after the results of Yamada et al. on *trans*-[Co(en)$_2$Cl$_2$]Cl·HCl·2H$_2$O. The full line shows the spectrum with light polarized parallel (or nearly parallel) to the Cl—Co—Cl axis, and the dashed line shows the spectrum with light polarized perpendicular to the Cl—Co—Cl axis.



This spectrum displays the 4 d-d transitions considered in-class (two are overlapping), with one displaying a dependence on the polarization of the light to be allowed by symmetry. During lecture, the qualitative splitting diagram on the right was considered for the $D_{4h}$ *trans*-[Co(en)$_2$Cl$_2$]$^+$ ion.

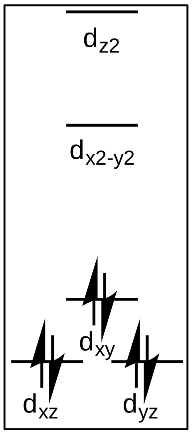
a. From your notes, assign the peak in the spectrum that changes most depending on the polarization of light.

b. Assign Mulliken symbols to the d orbitals. Denote what excited electron configuration this peak corresponds to (which excited configuration will have the appropriate state symbol for the excited state?).

c. Based on the MO diagram above, assign the transition for the lowest energy peak in the spectrum above.

d. Assuming the two highest energy transitions are coincident (indistinguishable), assign the two remaining d-d transitions (provide the excited state electron configurations, and ground state and excited state symbols).

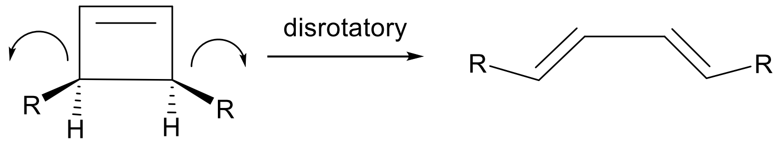
e. Can you rule out the alternative d-splitting diagram on the right with the data in the absorbance spectrum of this complex? Explain.

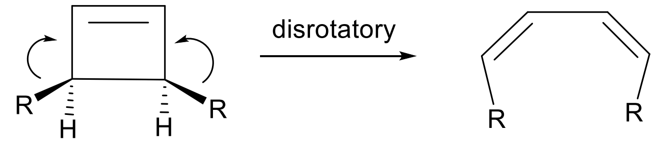


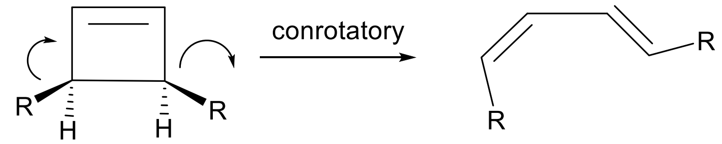
## Problem 3 (2 points)

a. Sketch the four MOs corresponding the π-system of butadiene from the basis set of the four p-orbitals perpendicular to the plane of the molecule. Rank them in order of increasing energy, and indicate which orbitals are filled.

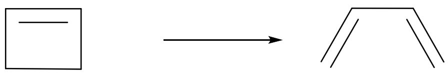
b. Consider the electrocyclic ring opening of a substituted cyclobutene, shown below. Depending on the symmetry properties of the transition state of the molecule, different products can be envisioned, two which arise from a disrotatory process, and one which arises from a conrotatory process. What is the characteristic symmetry element of each process? What is the point group corresponding to the reaction coordinate for each process? (consider R=H and the movement of atoms as the reaction proceeds)

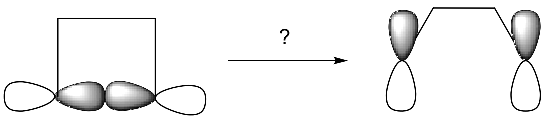




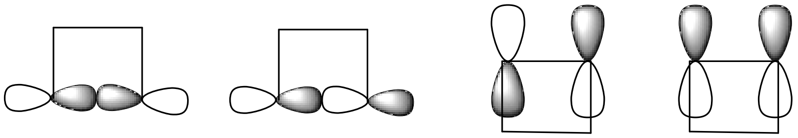


c. This electrocyclic ring-opening reaction produces two π-bonds from a π-bond and a σ-bond. For the orbital reaction scheme transforming the σ-bond, determine if a conrotatory or disrotatory process is shown below. Next, draw the product corresponding to the *opposite* process. In the point group corresponding to each process, assign the Mulliken symbol of these two products.





d. Below are sketched the two σ and π orbitals of cyclobutene (corresponding to the π-system of butadiene) that are participating in the cyclization. Label them (σ, σ*, π, π*) and order them based on their energy.

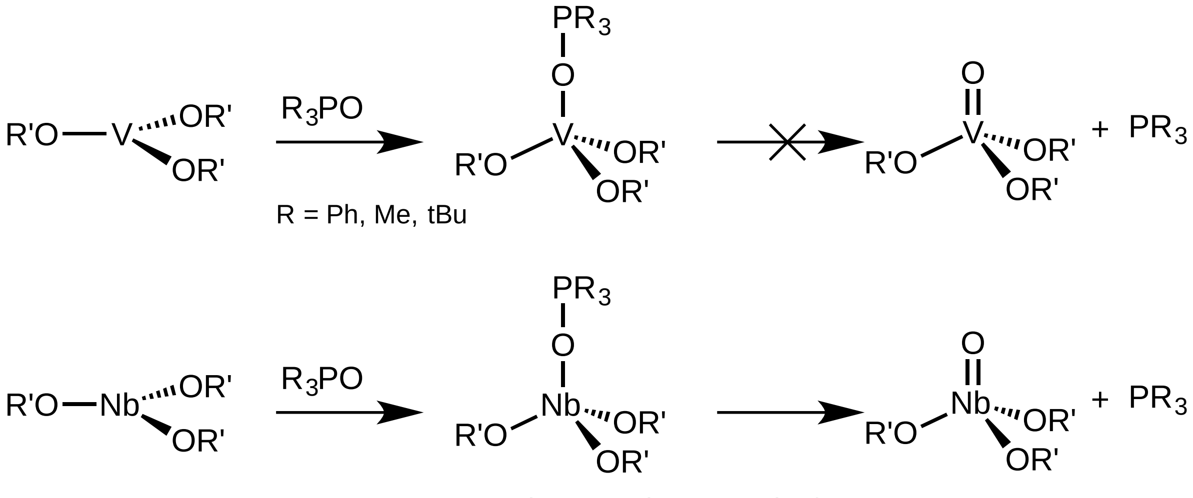


e. Draw the orbital correlation diagram for the conrotatory and disrotatory ring opening of cyclobutene. Start with the four orbitals of cyclobutene in the center of the diagram (energy order determined in part d). Correlate these orbitals to those of butadiene (determined in part a) in a disrotatory process to the left and a conroratory process to the right, making sure to order the orbitals correctly based on their energy in the starting material and product. Include Mulliken symbols in the point group of each process. Explain whether, based on this diagram, a conrotatory or disrotatory process is thermally allowed.

f. Draw the state correlation diagram for the conrotatory and disrotatory ring opening of cyclobutene. Use only three states of cyclobutene: ground state, singlet first excited state, and a higher singlet excited state that corresponds to the electron configuration of one of the low-lying states in the butadiene products (ground state or first excited state). Include electron configurations and state symbols. Explain whether, based on this diagram, a conrotatory or disrotatory process is thermally allowed. What about from the first excited state of cyclobutene?

## Problem 4 (3 points)

In class, we introduced the evaluation of a state correlation diagram toward understanding the reactivity of vanadium and niobium complexes with phosphine oxides (*Inorg. Chem.* **2003** *42*, 6204):



when R = Ph, Me <5min @ R.T.
when R = tBu no O-atom transfer after 35 days @ 85 $^{o}$C

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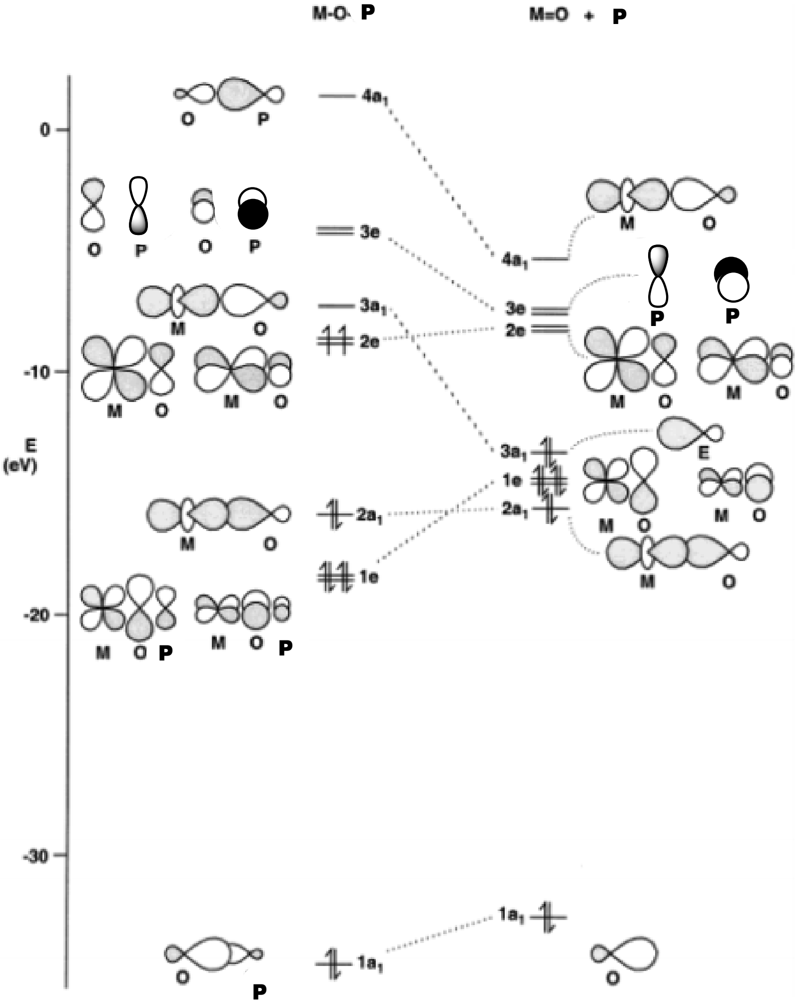
**Part 1**

a. Provide oxidation states and d electron count for the phosphine oxide adduct ((R’O)$_3$MOPR$_3$) and the metal oxo species ((R’O)$_3$MO). Assume that no electron transfer occurs upon phosphine oxide coordination compared to starting material ((R’O)$_3$M).

Below is a partial MO diagram of the starting materials and product of the oxygen atom transfer reaction investigated by the authors of this article:



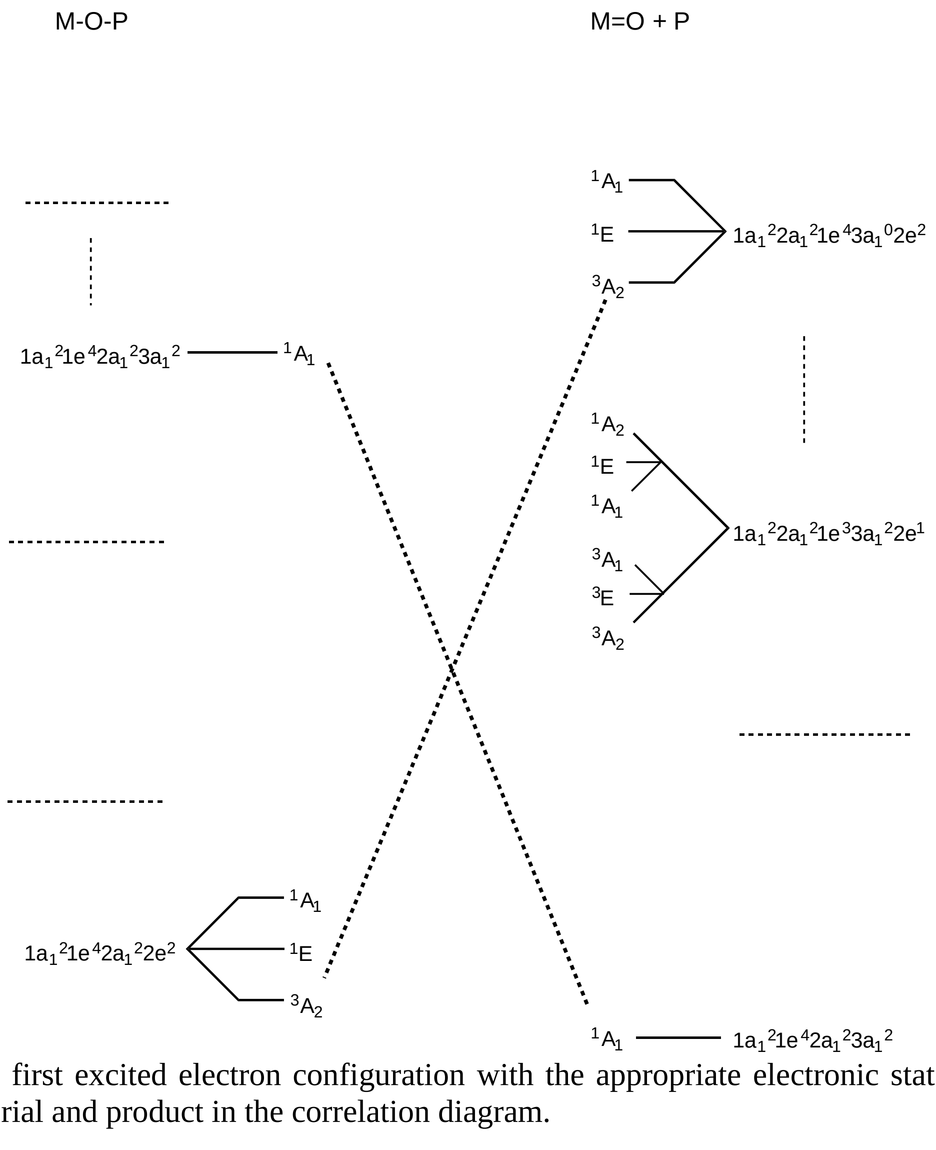
b. Highlight in the diagrams above the molecular orbitals that are “d-based” (note that some of them might not be represented). Check that the d electron count provided in point a. is in agreement. What is the nature of the metal-ligand interaction (σ, σ*, π, etc.) for these orbitals?

c. To better understand the interaction between the metal and the phosphine oxide ligand, sketch a qualitative MO diagram of H$_3$PO (as a model of R$_3$PO) in $C_{3v}$. Use 3s and 3p orbitals for phosphorous, 3 p orbitals for oxygen, and the SALCs derived from the 3 1s orbitals of the 3 H moieties as your basis set. Label with Mulliken symbols. Place the H atomic orbitals lowest and the P atomic orbitals highest. What is the nature of HOMO with respect to the P-O and P-H interactions, respectively (non-bonding, σ, σ*, π, etc.)?

d. Based on your MO diagram, and assuming that the HOMO of $H_3PO$ is involved in the interaction with the metal represented by orbital 1e of the starting material in the diagram above, are there orbital contributions on the phosphine side that are not represented? If yes, provide an MO drawing that includes these interactions.

## Part 2

Here is the mostly complete correlation diagram derived in lecture:



a. Fill in the first excited electron configuration with the appropriate electronic state(s) for the starting material and product in the correlation diagram.

So far, the diagram contains a line linking the ground state of the starting material to an excited state of the product (with same electronic configuration and term symbol) and a line linking an excited state of the starting material with the ground state of the product.

To construct the correlation diagram for the reaction under the triplet manifold, we found the lowest electron configuration of the product containing an electronic state identical to the ground state of the starting material ($^3A_2$), which ends up being the second excited electron configuration ($1a_1^2 2a_1^2 1e^3 3a_1^2 2e^1$).

b. Determine the relative energy of this electron configuration in the starting material, and fill it in one of the energy levels for the correlation diagram above, along with its electronic state(s).

c. Draw a line connecting the $^3A_2$ of the $1a_1^2 2a_1^2 1e^3 3a_1^2 2e^1$ configuration in the product to the same state and electron configuration in the starting material.

d. Use the intersection of this line with the other line connecting triplet states to determine if this type of reaction process (through triplet states) has an activation barrier associated with it.

e. Repeat this process with the $^1A_1$ states (you do not need to determine states of a new electron configuration for either side; everything you need should be on the diagram).

Intersystem crossing may occur (going from a triplet to singlet state) along the intersection of these two reaction pathways that you have drawn.

f. Clearly label the point in the reaction coordinate where intersystem crossing may occur. Is this overall process symmetry allowed or forbidden?

g. If intersystem crossing occurs, is the activation barrier lower or higher compared to the process preserving the spin state?

**Part 3**

Consider the case where the symmetry along the reaction coordinate is lowered by decreasing the M–O–P angle (bending from linear coordination at oxygen). The system is no longer $C_{3v}$ symmetric, and now the correlation diagram should be considered in the $C_s$ point group.

On the following page is an incomplete electron state correlation diagram for each geometry, to compare their relative energies. The correlation diagram on the left has been filled in as far as we filled it in during lecture.

a. Using the correlation diagram you constructed in part 2, fill in the partial correlation diagram on the left, marking the point where intersystem crossing occurs.

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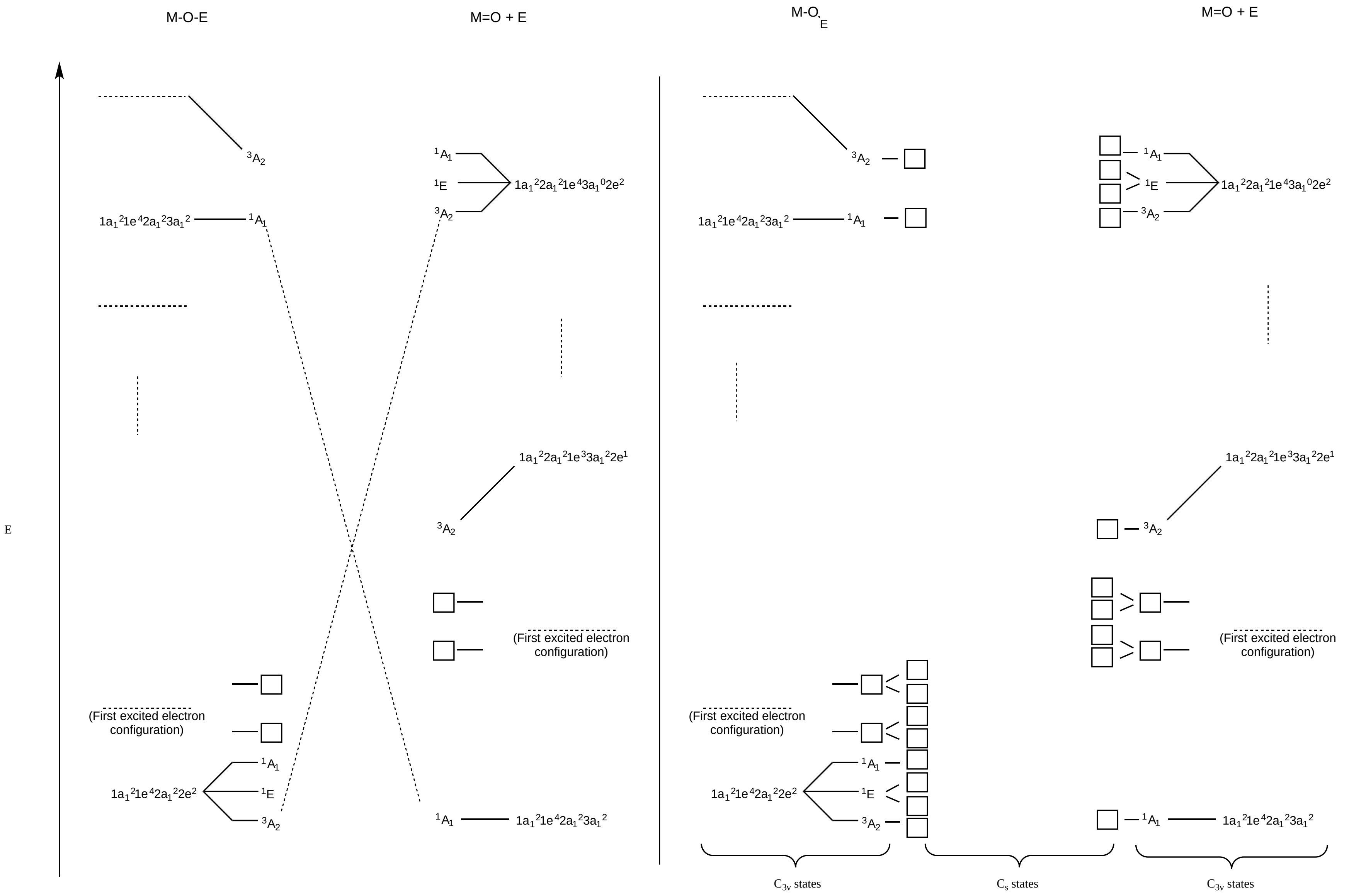


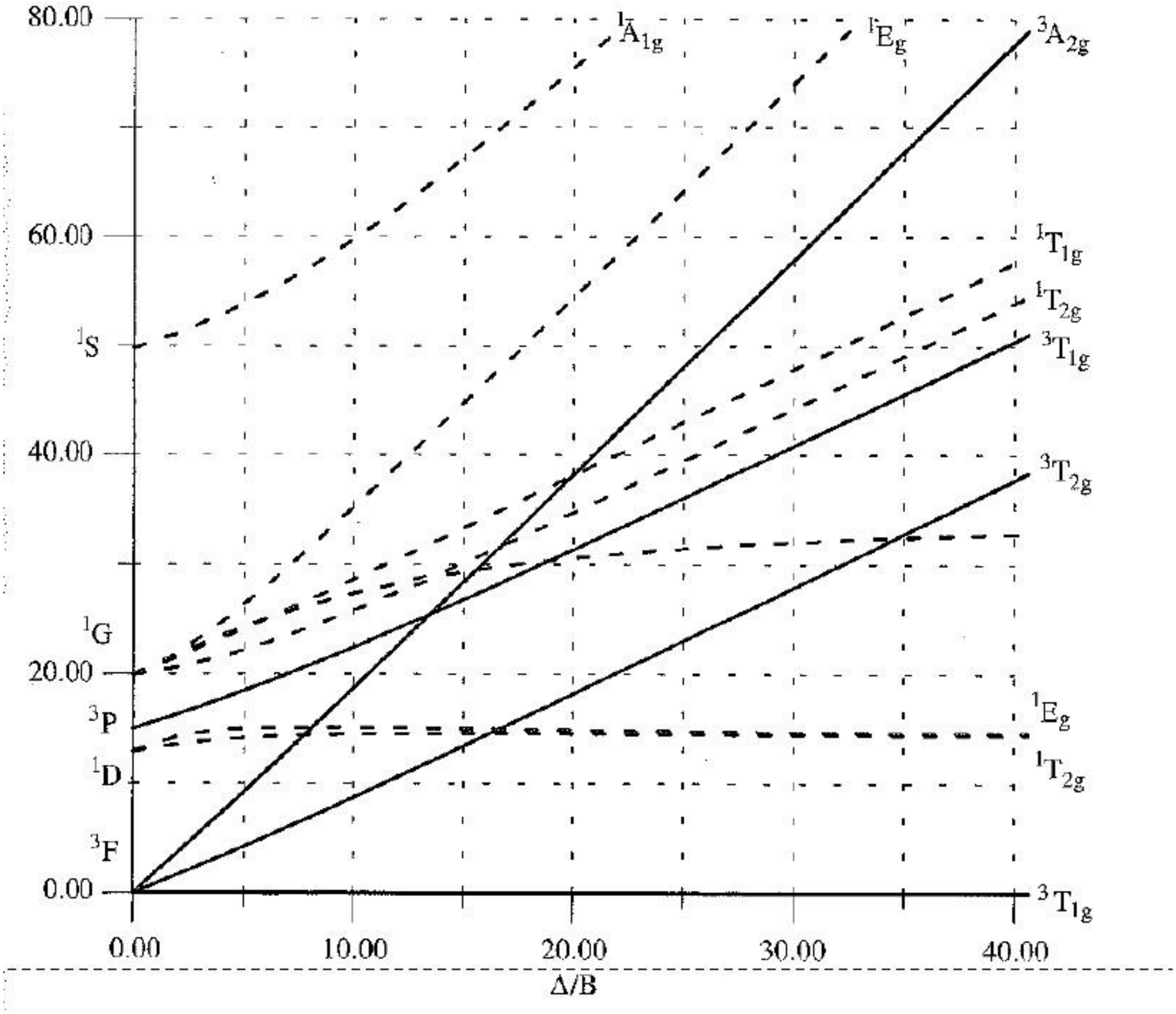
b. When going from $C_{3v}$ to $C_s$ symmetry, the term symbols of the electronic states will change to match the Mulliken symbols of the new point group. Fill in the correlation diagram on the right with the new electronic states. E states will diverge into two states in this new geometry, A' and A'' (assume A' is lower in energy). $A_1$ states will become A', and $A_2$ will become A''. Multiplicity will be conserved. (Your are not responsible for deriving these state symbols, but note that it can be done by labeling the orbitals in the new point group [assuming the bend is deviating from the z axis in $C_{3v}$ symmetry] and coming up with the states for the corresponding electron configurations).

c. With this new correlation diagram, find the reaction coordinates for the singlet and triplet manifolds following the same procedure as before. Note that the lowest electron configuration of the product containing an electronic state identical to the ground state of the starting material may be different in $C_s$ compared to $C_{3v}$. Similarly, the lowest electron configuration of the starting material containing an electronic state identical to the ground state of the product may be different in $C_s$ compared to $C_{3v}$. Determine the point of intersystem crossing.

d. Compare the activation barriers within the same spin manifolds for $C_s$ vs $C_{3v}$ reaction coordinates. (Assume that these diagrams were constructed taking into account the calculated energies, so they can be compared directly by the height of the various intersection points vs the ground states.)

e. Is the activation barrier for intersystem crossing higher with a linear geometry of the $OPR_3$ ligand, or bent?

f. Based on all this analysis, can you provide an explanation for the dependence of the sterics of the $PR_3$ group on the reactivity of the niobium complex? Why might the vanadium complex be incapable of accomplishing oxygen atom transfer?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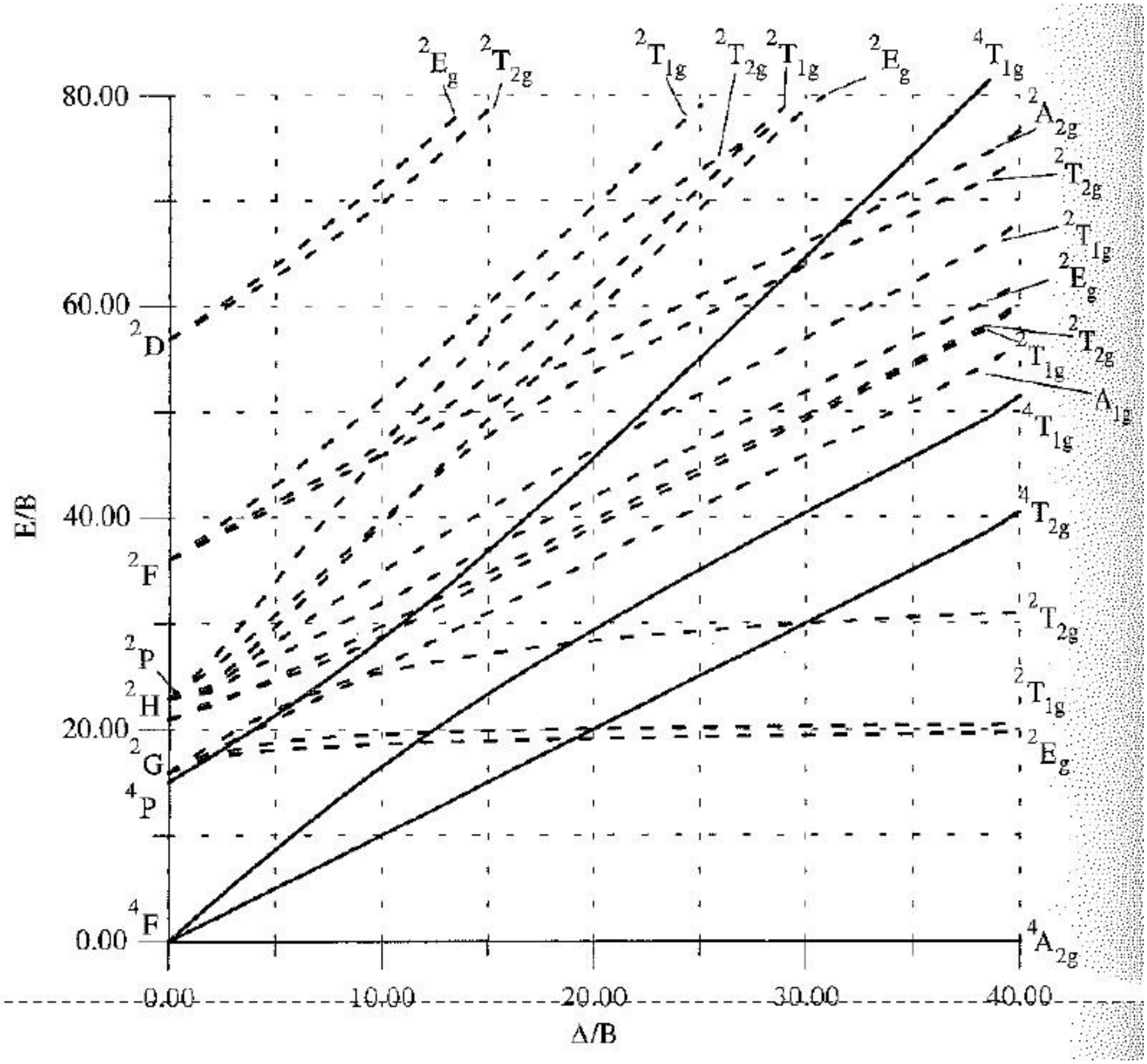
²Eg
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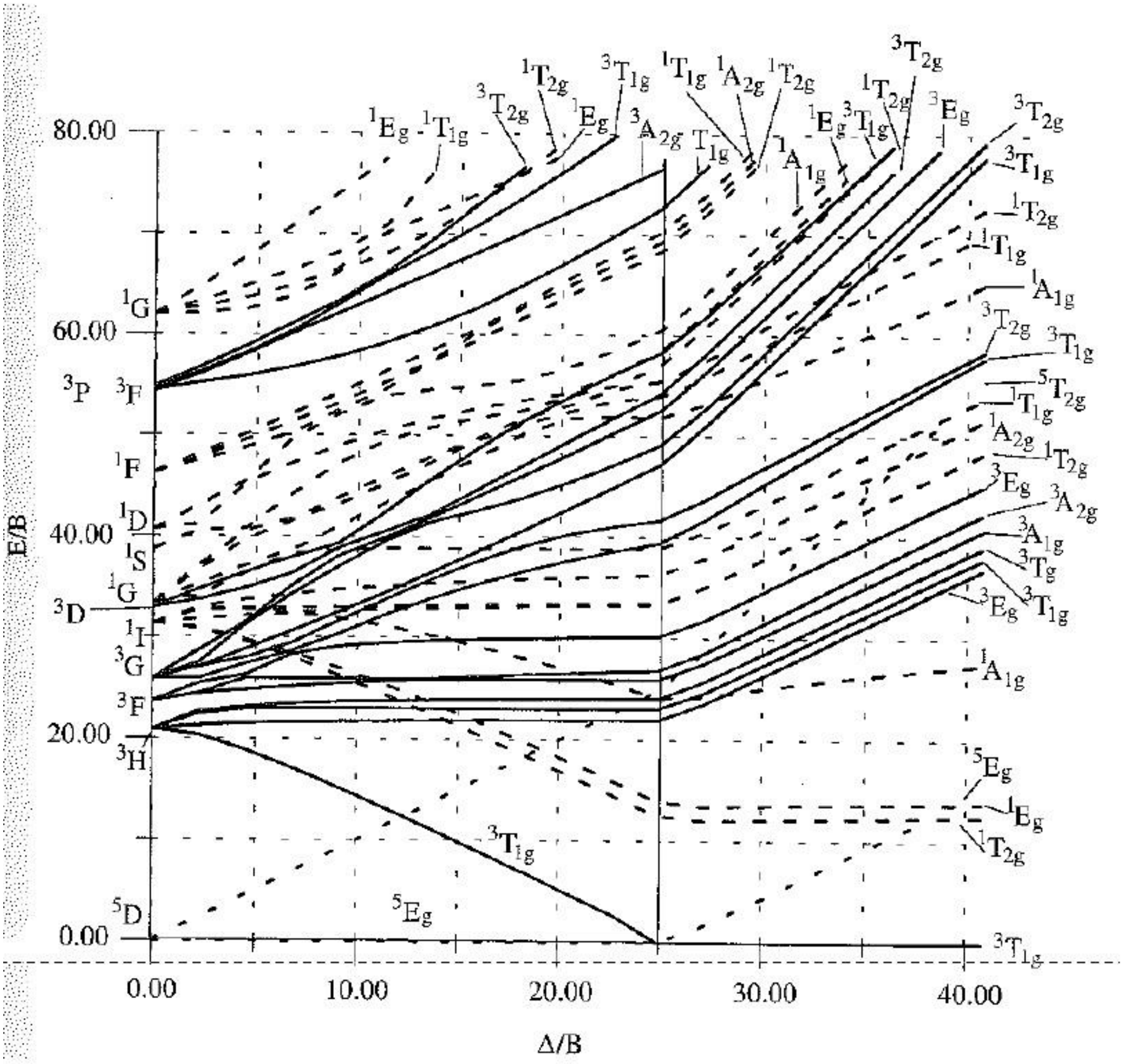

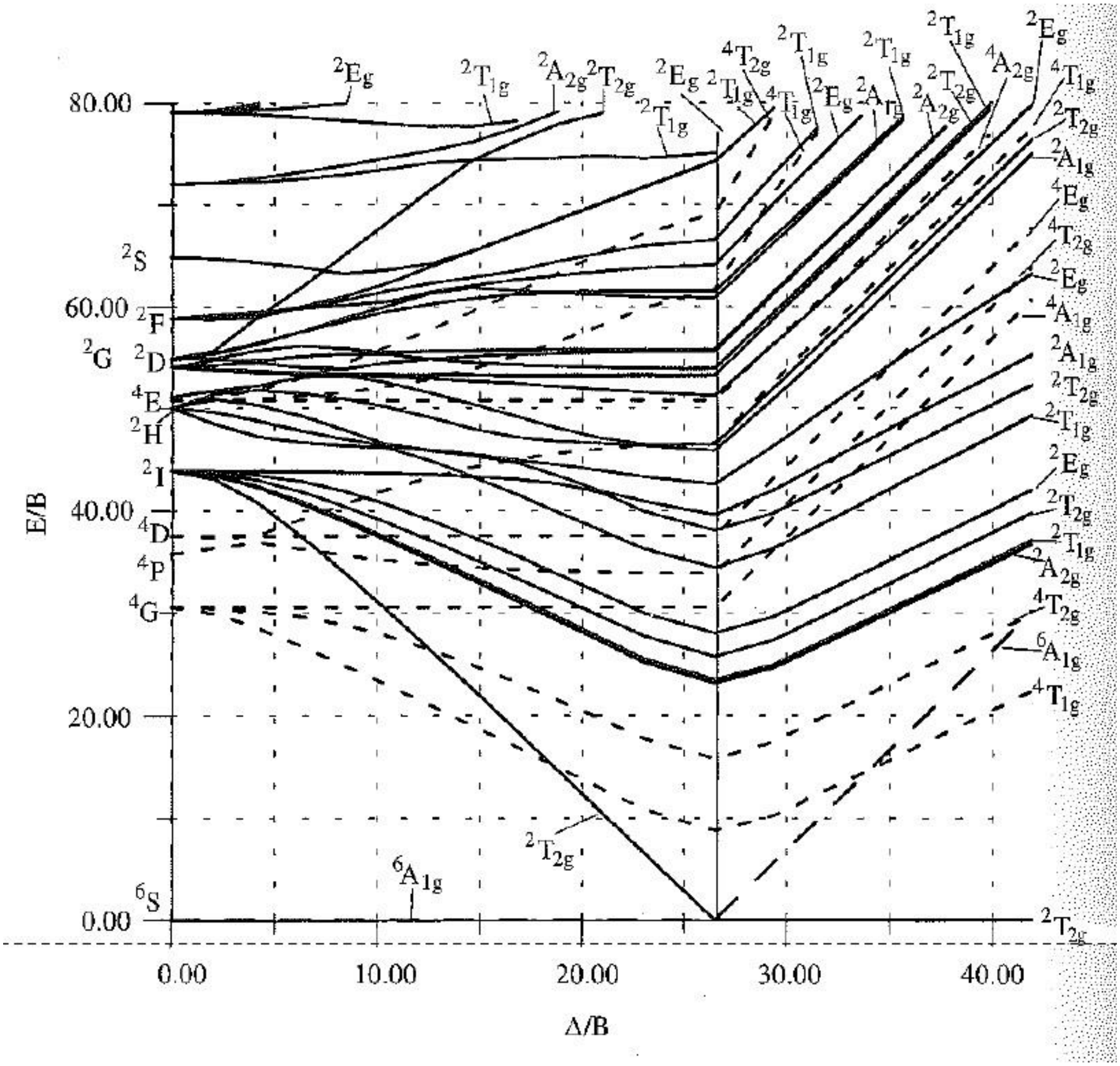
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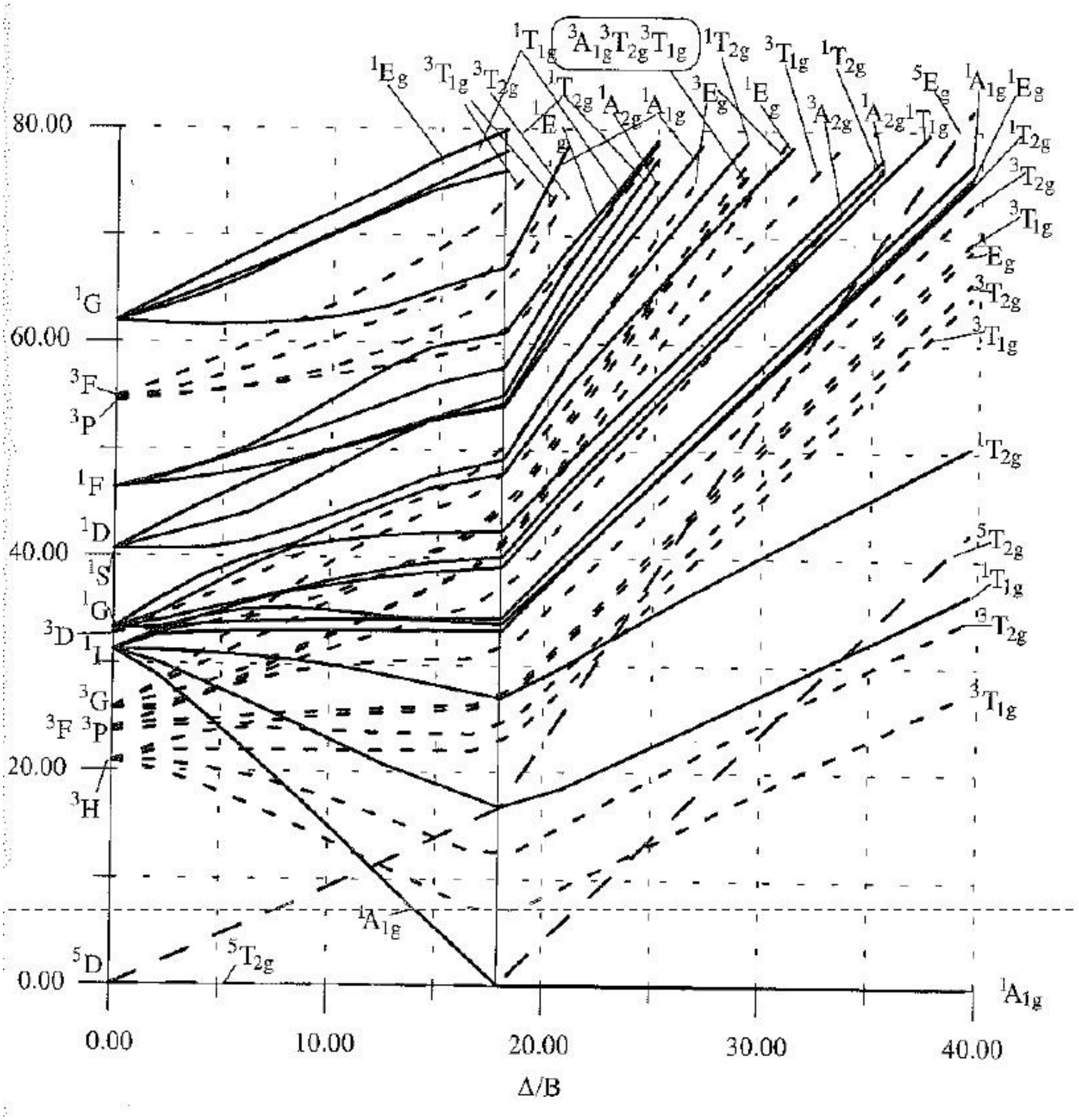
$^1T_{1g}$ $^3A_{1g}$ $^3T_{2g}$ $^3T_{1g}$ $^1T_{2g}$ $^3T_{1g}$ $^1T_{2g}$
$^1E_g$ $^3T_{1g}$ $^3T_{2g}$ $^1T_{2g}$ $^1A_{2g}$ $^1A_{1g}$ $^3E_g$ $^1E_g$ $^3A_{2g}$ $^1A_{2g}$ $^1T_{1g}$ $^5E_g$ $^1A_{1g}$ $^1E_g$
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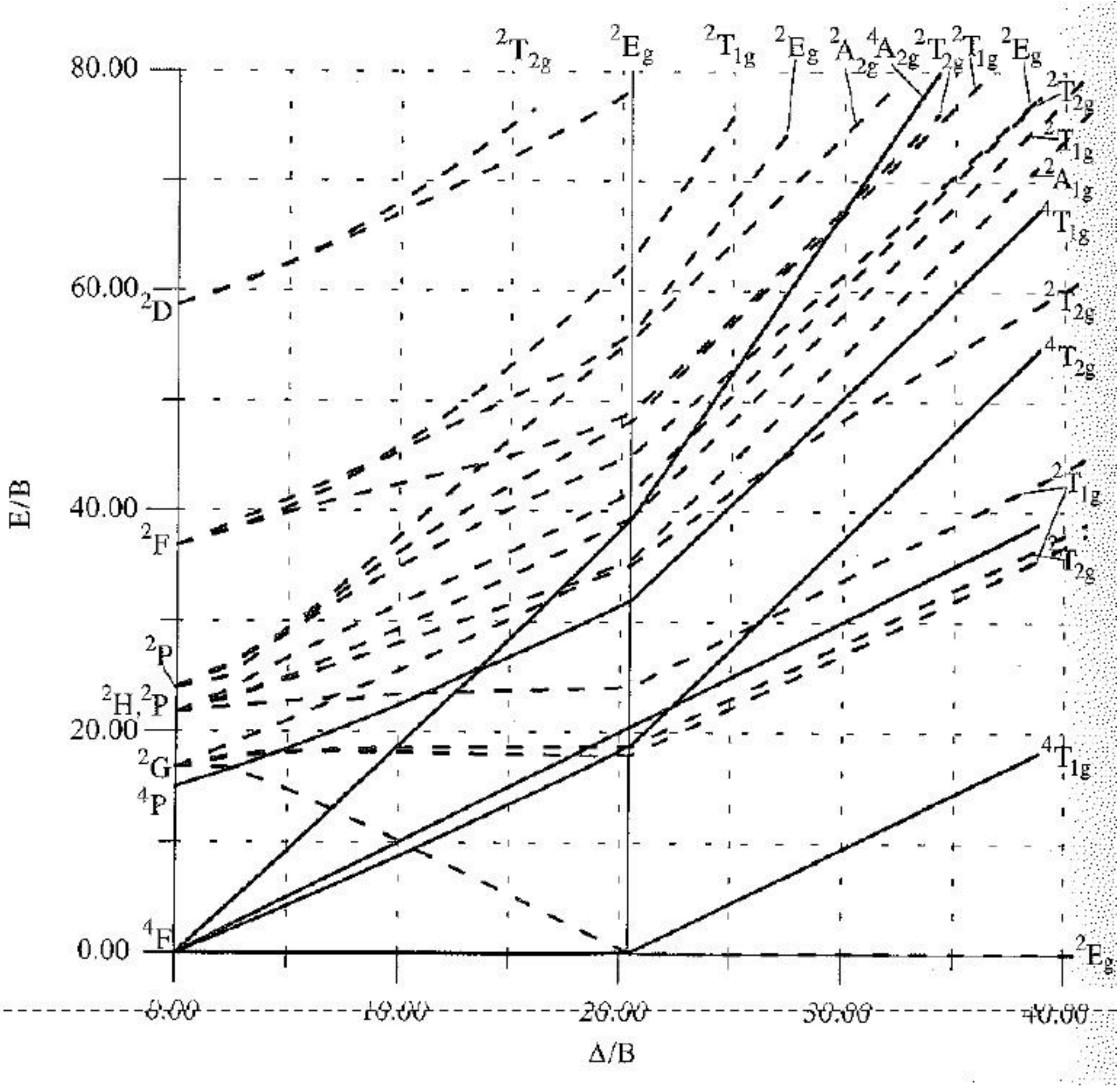

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