2017 Ch112 – problem set 6
Due: Thursday, Nov. 30th

Problem 1 (2 points)

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 (υ_1 and υ_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 Δ_o and complete the table below. (Estimate Δ_o/B to the nearest 0.5)

$V(H_2O)^{3+}$: Δ_o/B ≈ 30 matches the υ_2/υ_1 = 1.44 ratio from the T-S diagram.
This Δ_o/B ≈ 30 corresponds to a υ_1/B = 28 from the T-S diagram. Taking 17,800 cm^{-1}/28 = 640 cm^{-1} as B, and Δ_o = 640 cm^{-1} * 28 = 19,000 cm^{-1}.

$[VF_6]^{3+}$: Δ_o/B ≈ 25.
15,100 cm^{-1}/23 = 660 cm^{-1}; Δ_o = 16,500 cm^{-1}

$[VCl_6]^{3+}$: Δ_o/B ≈ 22.5.
11,000 cm^{-1}/21 = 520 cm^{-1}; Δ_o = 11,700 cm^{-1}

	υ_1 (cm^{-1}) $^3T_1 \rightarrow {}^3T_2$	υ_2 (cm^{-1}) $^3T_1 \rightarrow {}^3T_1$	Ratio of υ_2/υ_1	B (Racah Parameter) (cm^{-1})	Δ_o (cm^{-1})
$V(H_2O)^{3+}$	17,800	25,700	1.44	640	19,000
$[VF_6]^{3+}$	15,100	23,600	1.56	660	16,500
$[VCl_6]^{3+}$	11,000	18,020	1.64	520	11,700

c. Rationalize the observed trends in B and Δ_o values in terms of ligand properties.

The Racah parameter indicates covalency increasing as: Cl > H2O > F. Fluoride gives the most ionic interaction due to the high electronegativity. Chloride gives the most covalent interaction due to a combination of sigma and pi bonding, both better than in water (essentially only a sigma donor). The trend in d-splitting H2O > F > Cl, as expected from the spectrochemical series, reflects the pi donating abilities of these ligands.

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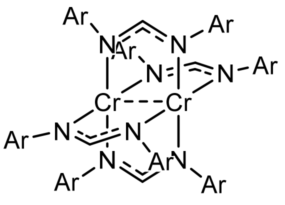
Part 2

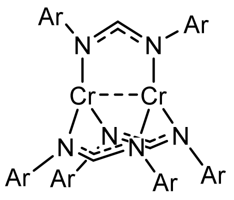
In the fourth problem set, you derived the MO diagrams for two complexes containing Cr-Cr bonds:

A



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

B$^-$



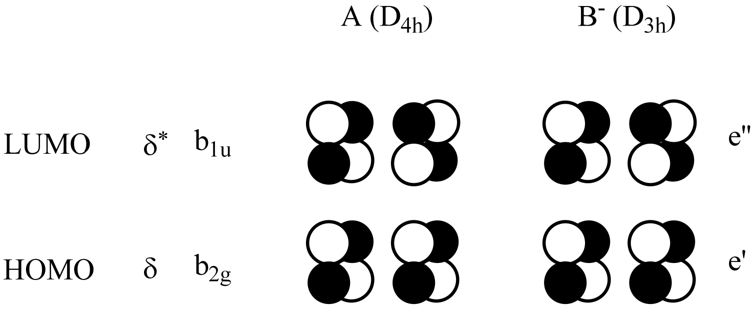
Ar = 2,6-Me-Ph
Tsai, *Angew. Chem. Int. Ed.* (2008) *47*, 7250

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

A: $^1A_{1g}$

B$^-$: $^1A_1'$

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



A: excited state configuration $(b_{2g})^1(b_{1u})^1$, term symbols $^3A_{2u}$ and $^1A_{2u}$
B$^-$: excited state configuration $(e')^3(e'')^1$, term symbols $^1A_1''$, $^1A_2''$, $^1E''$, $^3A_1''$, $^3A_2''$, $^3E''$

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

A: $A_{2u} * \begin{pmatrix} A_{2u} \\ E_u \end{pmatrix} * A_{1g} = \boldsymbol{A_{1g}} + E_g$; orbitally allowed

B$^-$: $A_1'' * \begin{pmatrix} A_2'' \\ E' \end{pmatrix} * A_1' = A_2' + E''$; orbitally forbidden

$A_2'' * \begin{pmatrix} A_2'' \\ E' \end{pmatrix} * A_1' = \boldsymbol{A_1'} + E''$; orbitally allowed

$E'' * \begin{pmatrix} A_2'' \\ E' \end{pmatrix} * A_1' = E'' + A_1'' + A_2'' + E''$; orbitally forbidden

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Problem 2 (3 points)

The d orbital splitting diagram of Potassium Tetrachloroplatinate(II) has been debated in numerous articles over the years. Absorption spectra collected with polarized light helped elucidating the d-orbital splitting of this complex. In the following problem the absorption spectra will be used to determine the possibility of a number of d-orbital splitting diagrams.

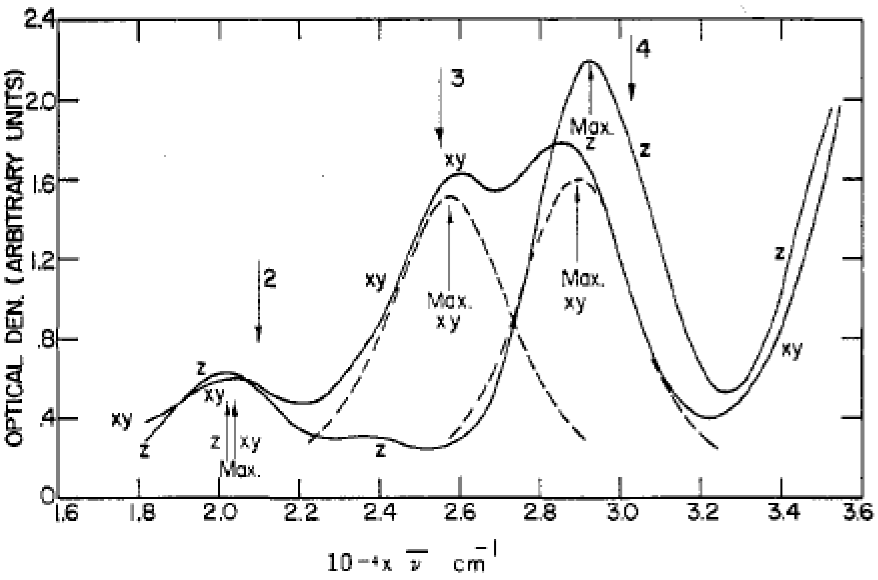
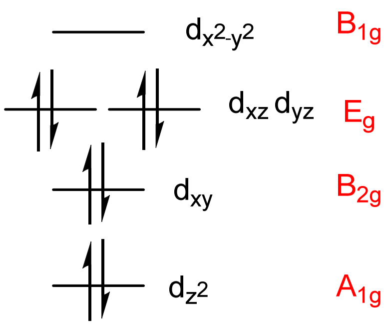


Fig. 3.—Absorption spectrum of K_2PtCl_4 crystal in polarized light. The optical density is in arbitrary units. Dashed lines indicate the Gaussian components for the x–y polarization.

a) Assign the point group of the $[PtCl_4]^{2-}$ ion.

D_{4h}

b) One of the possible MO diagrams is given below. Assign Mullikan symbols to the d-orbitals.



c) 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 for completeness. (You are allowed to use the symmetry multiplication tables at the end of *Symmetry and Spectroscopy*)

${}^1A_{1g} \rightarrow {}^1E_g$	$(1a_{1g})^2(1b_{2g})^2(1e_g)^3(1b_{1g})^1$	$E_g \begin{pmatrix} A_{2u} \\ E_u \end{pmatrix} A_{1g} = \begin{pmatrix} E_u \\ A_{1u}\ A_{2u}\ B_{1u}\ B_{2u} \end{pmatrix}$
${}^1A_{1g} \rightarrow {}^1A_{2g}$	$(1a_{1g})^2(1b_{2g})^1(1e_g)^4(1b_{1g})^1$	$A_{2g} \begin{pmatrix} A_{2u} \\ E_u \end{pmatrix} A_{1g} = \begin{pmatrix} A_{1u} \\ E_u \end{pmatrix}$
${}^1A_{1g} \rightarrow {}^1B_{1g}$	$(1a_{1g})^1(1b_{2g})^2(1e_g)^4(1b_{1g})^1$	$B_{1g} \begin{pmatrix} A_{2u} \\ E_u \end{pmatrix} A_{1g} = \begin{pmatrix} B_{2u} \\ E_u \end{pmatrix}$

None of them are allowed because they do not contain the completely symmetric irreducible representation (A_{1g}).

d) Vibrations of the $[PtCl_4]^{2-}$ ion transform as the following irreducible representations in the point group determined in part a.

$\Gamma = A_{1g} + A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_u$

Determine for each transition and light polarization if the intensity will increase due to vibronic coupling

${}^1A_{1g} \rightarrow {}^1E_g$	enhanced with xy and z polarized light
${}^1A_{1g} \rightarrow {}^1A_{2g}$	enhanced with xy polarized light
${}^1A_{1g} \rightarrow {}^1B_{1g}$	enhanced with xy and z polarized light

e) Assign transitions to the bands labeled **3** and **4** in the UV-Vis spectrum. The band labeled **2** is assigned to spin forbidden transitions and can be ignored for this problem.

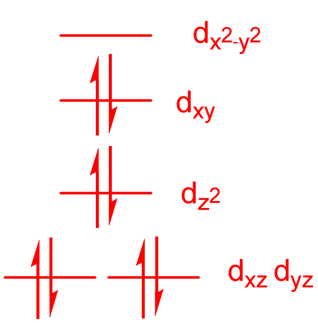
Band 3 ${}^1A_{1g} \rightarrow {}^1A_{2g}$. This transition is only enhanced with xy polarized light

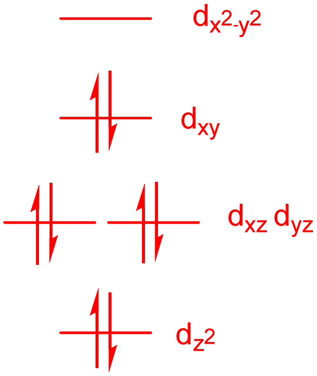
Band 4 ${}^1A_{1g} \rightarrow {}^1E_g$ or ${}^1A_{1g} \rightarrow {}^1B_{1g}$. Both transitions will give enhancement with xy and z polarized light.

f) Is the MO diagram given in part b correct? Explain.

The given MO diagram is incorrect because the lowest energy transition in the given diagram would correspond to ${}^1A_{1g} \rightarrow {}^1E_g$, which is enhanced with both xy and z polarized light. The actual lowest energy transitions is only allowed with xy polarized light.

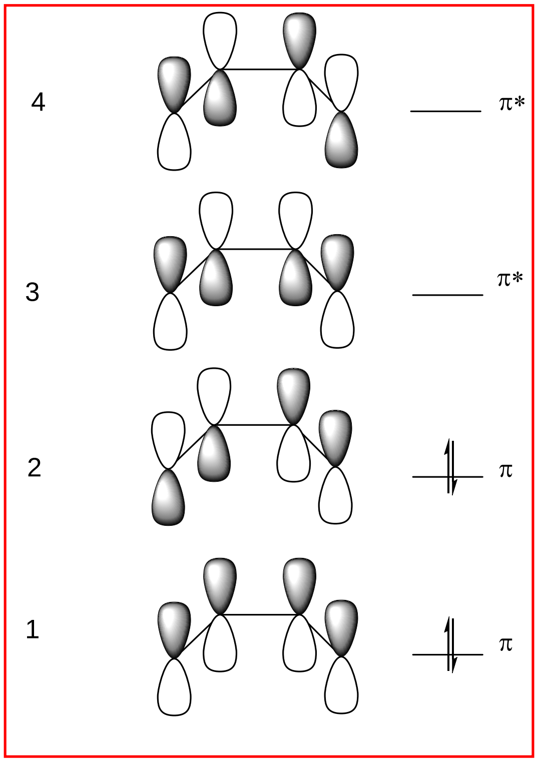
g) Propose two other MO diagrams which could give rise to the spectrum above assuming that the LUMO is d_{x2-y2}.


$d_{x^2-y^2}$
d_{xy}
d_{z^2}
d_{xz} d_{yz}

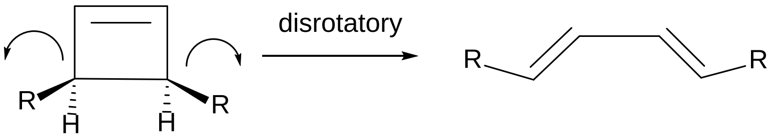

$d_{x^2-y^2}$
d_{xy}
d_{xz} d_{yz}
d_{z^2}

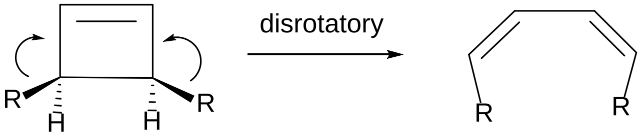
Problem 3 (2 points)

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.

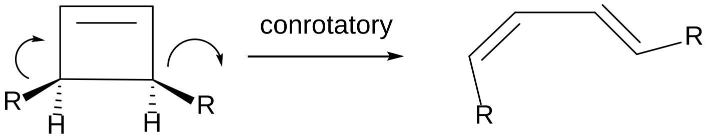


b. Consider the electrocyclic ring opening of a substituted cyclobutene, shown below. Depending on the symmetry properties of the transition state of the molecule, different products can be envisioned, two which arise from a disrotatory process, and one which arises from a conrotatory process. What is 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)



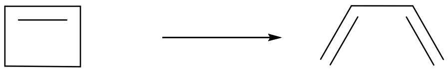


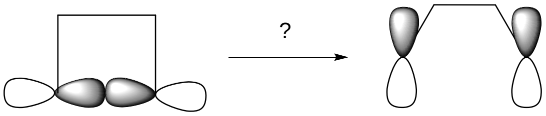
C_s



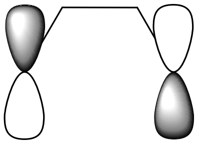
C_2

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.



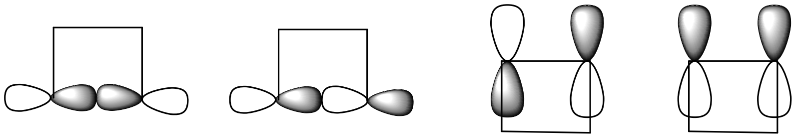


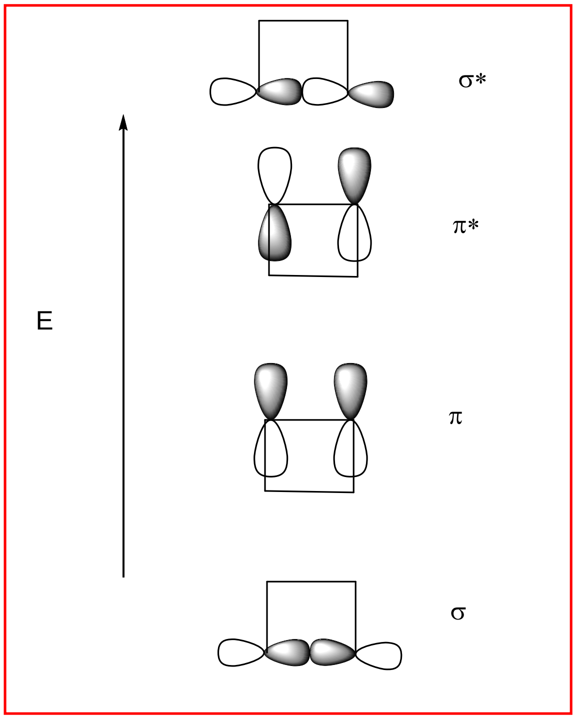
A′, disrotatory



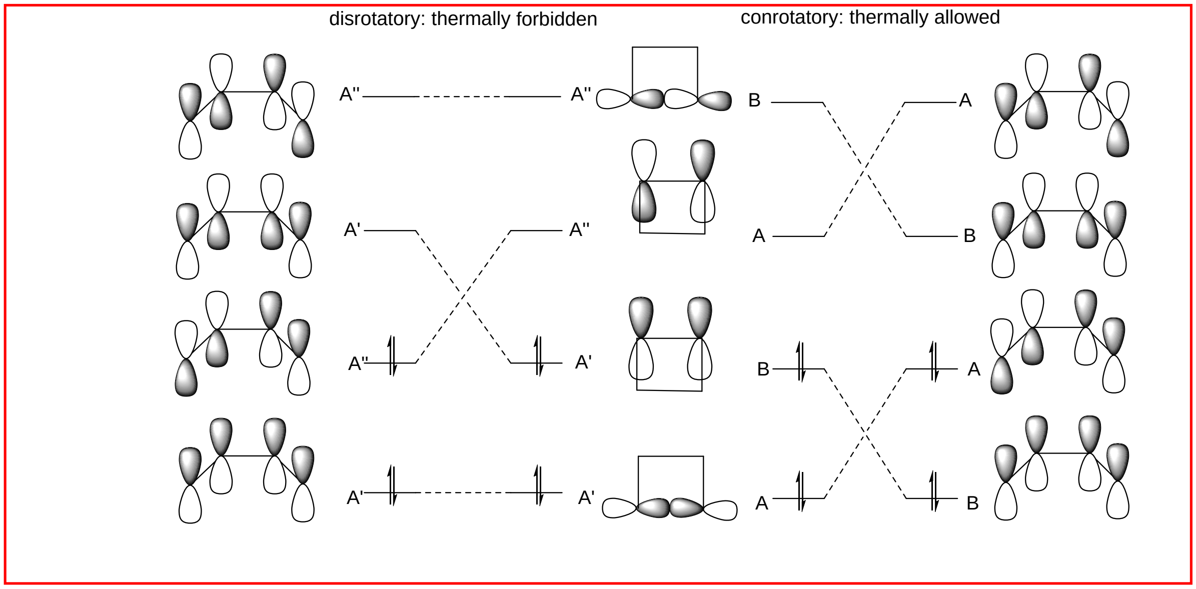
A, conrotatory

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.

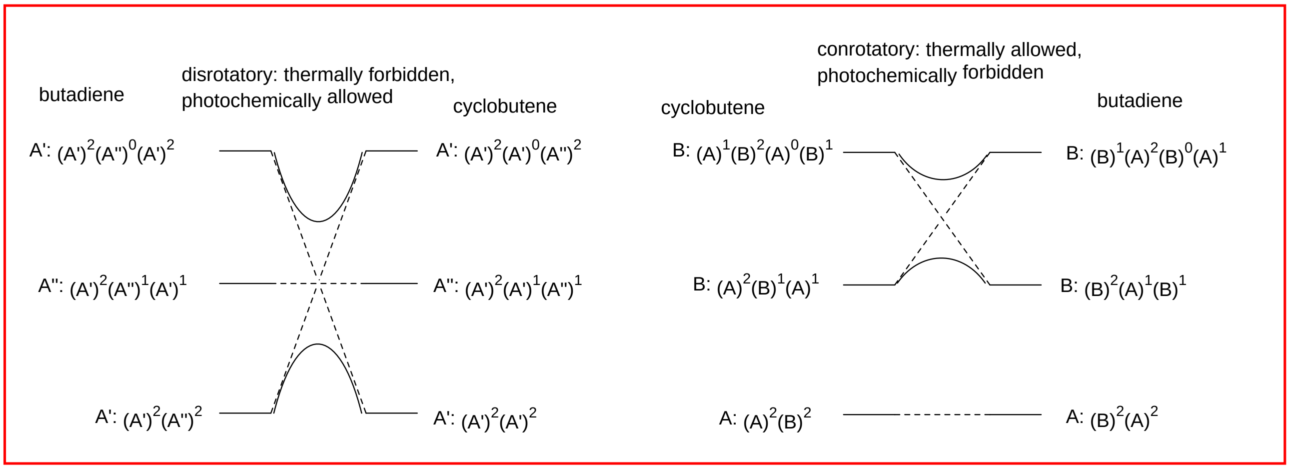




e. Draw the orbital correlation diagram for the conrotatory and disrotatory ring opening of cyclobutene. Start with the four orbitals of cyclobutene in the center of the diagram (energy order determined in part d). Correlate these orbitals to those of butadiene (determined in part a) in a disrotatory 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?



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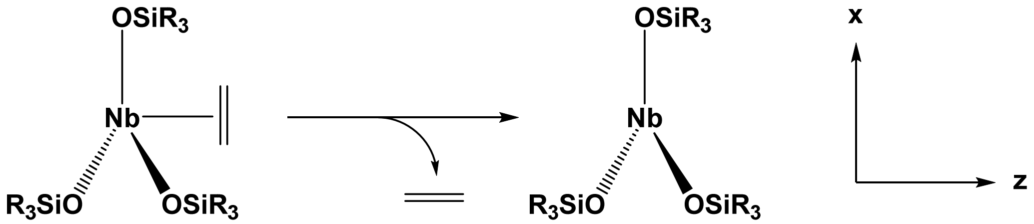
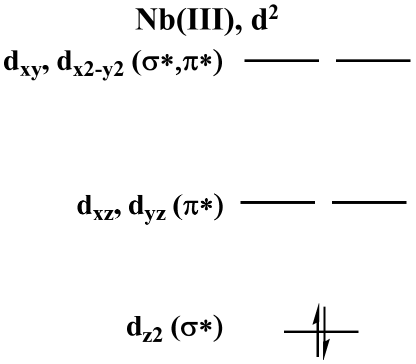
Problem 4 (3 points)

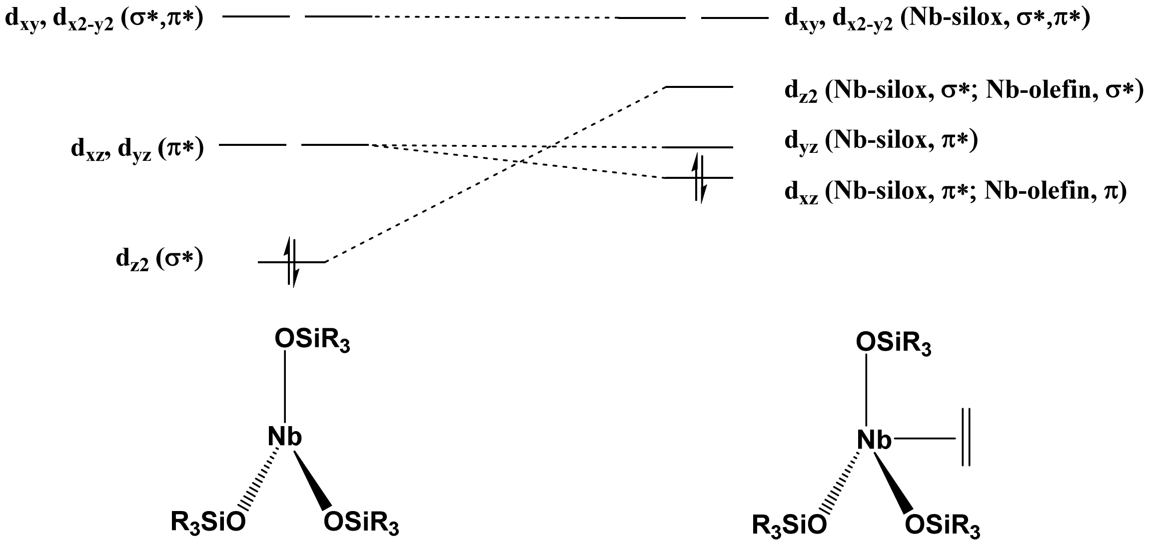
Consider the dissociation of ethylene from a niobium tris-siloxide complex.



A) Determine the niobium oxidation state and d-electron count for Nb(OSiR$_3$)$_3$. By inspection, provide the d-splitting diagram of Nb(OSiR$_3$)$_3$ taking into consideration that siloxides have two oxygen lone pairs available for π bonding. Nb(OSiR$_3$)$_3$ is diamagnetic. Label each orbital with its d-orbital parentage and the nature of the Nb-siloxide interaction. Populate with electrons.



B) Starting from the d-splitting diagram of Nb(OSiR$_3$)$_3$, provide the d-splitting diagram of Nb(OSiR$_3$)$_3$(C$_2$H$_4$). Correlate the d-orbitals in Nb(OSiR$_3$)$_3$(C$_2$H$_4$) to the d-orbitals in Nb(OSiR$_3$)$_3$, showing their relative energies. Label each orbital of the new diagram with the nature of the Nb-siloxide and Nb-ethylene interaction. Populate with electrons. Nb(OSiR$_3$)$_3$(C$_2$H$_4$) is also diamagnetic.



C) Based on your d-splitting diagrams, is the dissociation of ethylene from Nb(OSiR$_3$)$_3$(C$_2$H$_4$) orbitally allowed? Explain briefly.

The reaction is orbitally forbidden since a filled d$_{xz}$ orbital and an empty d$_{z2}$ orbital from the ethylene adduct become an empty d$_{xz}$ and a filled d$_{z2}$ orbital in the product.

D) Consider the ground state electronic configuration and the first three excited state electronic configurations of Nb(OSiR$_3$)$_3$(C$_2$H$_4$). Provide these four electronic configurations and list them in order of increasing energy [e.g. (d$_{xz}$)^1(d$_{xy}$)^1]. For the ambiguous case between 2nd and 3rd excited states, choose the configuration that maximizes spin multiplicity as the more stable configuration.

See table for part E

E) Working in the correct point group of Nb(OSiR$_3$)$_3$(C$_2$H$_4$), provide electronic state symbols for each electronic configuration from part D) and list them in order of increasing energy following Hund's rules. Be careful when assigning the Mulliken symbols of the d-orbtials in Nb(OSiR$_3$)$_3$(C$_2$H$_4$).

	Configuration	**States**
Ground state	**(d$_{xz}$)^2**	**^{1}A'**
First excited state	**(d$_{xz}$)^1(d$_{yz}$)^1**	**^{3}A'' + ^{1}A''**
Second excited state	**(d$_{xz}$)^1(d$_{z2}$)^1**	**^{3}A' + ^{1}A'**
Third excited state	**(d$_{yz}$)^2**	**^{1}A'**

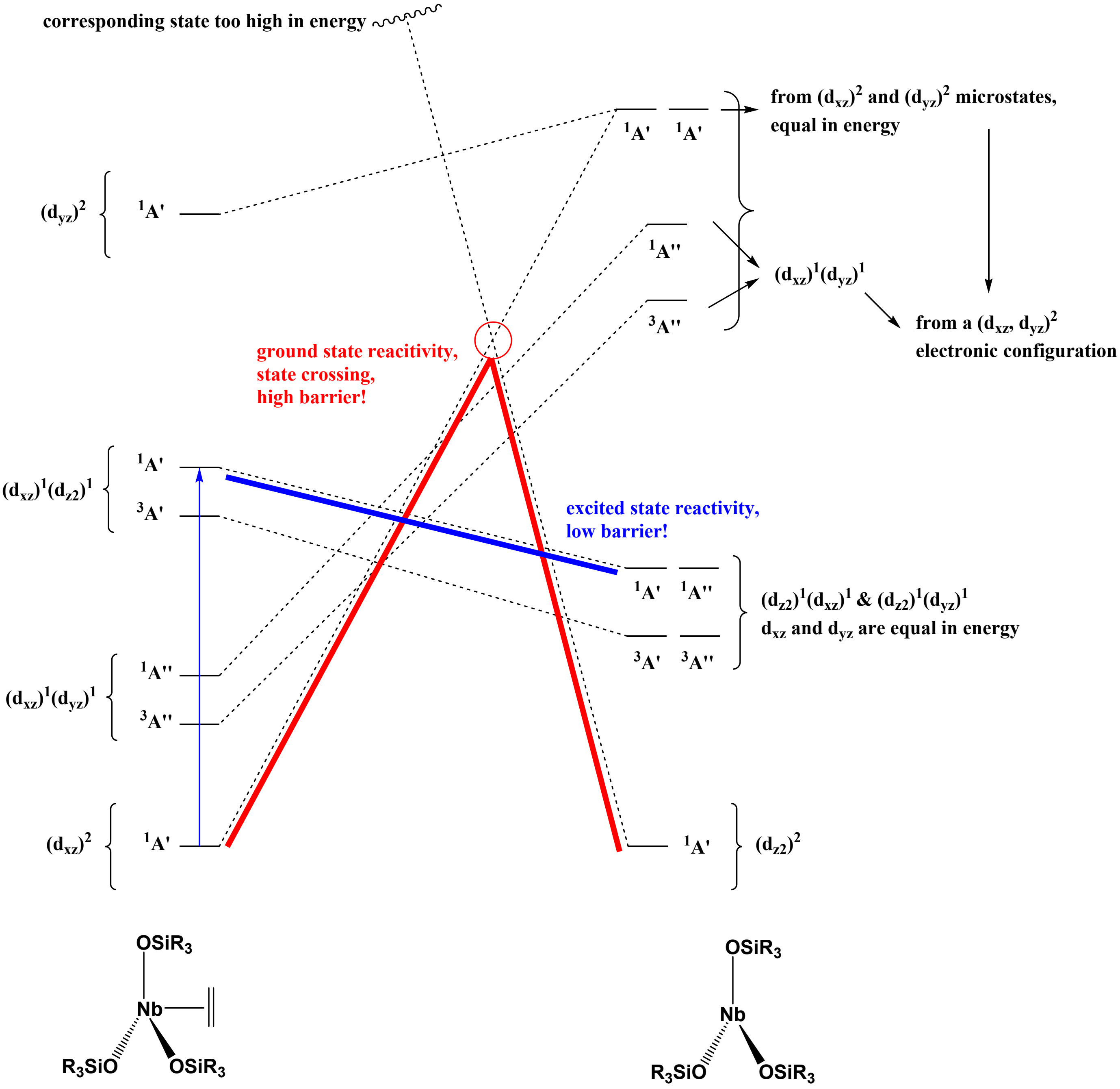
(d$_{z2}$ and d$_{xz}$ transform as A'; d$_{yz}$ transforms as A'')

F) Working in the C$_{3v}$ point group for Nb(OSiR$_3$)$_3$, provide electronic configurations for the ground state and the first two excited states (use Mulliken symbols). Provide electronic state symbols for each electronic configuration. For the ambiguous case of the second excited state, provide all possible solutions.

	Configuration	**States**
Ground state	**(d$_{z2}$)^2 → (A$_1$)^2**	**^{1}A$_1$**
First excited state	**(d$_{z2}$)^1(d$_{xz}$,d$_{yz}$)^1 → (A$_1$)^1(E)^1**	**^{3}E + ^{1}E**
Second excited state	**(d$_{xz}$,d$_{yz}$)^2 → (E)^2**	**(i) ^{3}A$_1$ + ^{1}A$_2$ + ^{1}E** **(ii) ^{1}A$_1$ + ^{3}A$_2$ + ^{1}E**

G) Express the electronic state symbols in part F) in the point group of Nb(OSiR$_3$)$_3$(C$_2$H$_4$). [Note: Mulliken symbols of orbitals in a degenerate set may differ by lowering the symmetry of the point group. Thinking about the microstates may help as well.] Correlate the electronic state of Nb(OSiR$_3$)$_3$(C$_2$H$_4$) with the electronic states of Nb(OSiR$_3$)$_3$. Not all electronic states in Nb(OSiR$_3$)$_3$ have matches, since not all excited states have been considered for Nb(OSiR$_3$)$_3$(C$_2$H$_4$). The corresponding excited states may lie well above the ones considered here.

	Configuration	**States in C_{3v}**	**States in C_S**
Ground state	$(d_{z2})^2 \rightarrow (A_1)^2$	$^1A_1$	$^1A'$
First excited state	$(d_{z2})^1(d_{xz},d_{yz})^1 \rightarrow (A_1)^1(E)^1$	$^3E + {}^1E$	$(d_{z2})^1(d_{xz})^1 \rightarrow {}^3A' + {}^1A'$ $(d_{z2})^1(d_{yz})^1 \rightarrow {}^3A'' + {}^1A''$ Effectively, $^3E \rightarrow {}^3A' + {}^3A''$ and $^1E \rightarrow {}^1A' + {}^1A''$
Second excited state	$(d_{xz},d_{yz})^2 \rightarrow (E)^2$	(i) $^3A_1 + {}^1A_2 + {}^1E$ (ii) $^1A_1 + {}^3A_2 + {}^1E$	$(d_{xz})^2 \rightarrow {}^1A'$ $(d_{yz})^2 \rightarrow {}^1A'$ $(d_{xz})^1(d_{yz})^1 \rightarrow {}^3A'' + {}^1A''$



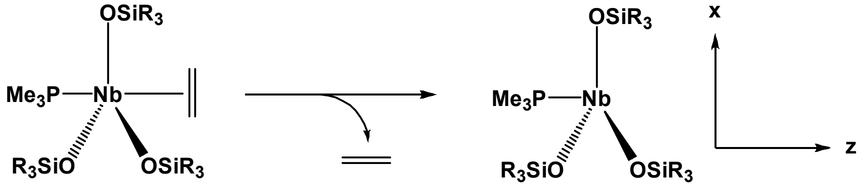
H) From the state correlation diagram obtained in part G), explain whether the reaction is symmetry allowed or forbidden. If it is forbidden, clearly indicate the point in the reaction coordinate where intersystem crossing may occur.

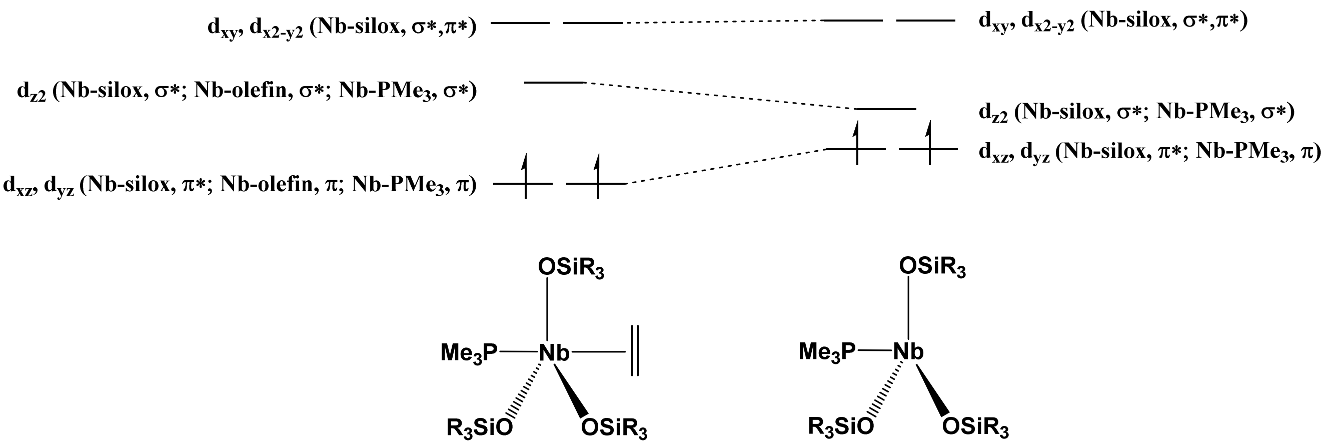
The reaction is symmetry forbidden. See correlation diagram above.

I) Comment on the feasibility of excited state reactivity from $Nb(OSiR_3)_3(C_2H_4)$. Which electronic transition from the ground state (provide initial and final electronic configurations and states) in $Nb(OSiR_3)_3(C_2H_4)$ may lead to a low-barrier dissociation of ethylene?

An electronic transition from $(d_{xz})^2 \rightarrow (d_{xz})^1(d_{z2})^1$ [$^1A' \rightarrow {}^1A'$] would result in a low-barrier dissociation of ethylene to the first excited state configuration of the product.

J) Consider binding of trimethyl phosphine in the axial position. Predict whether dissociation of ethylene would occur slower or faster. Provide both an orbital argument and an electronic state argument.





The same orbitals are populated in both the starting material and the product. Orbitally allowed. The triplet ground states of both the starting material and the product correlate.