

2018 Ch112 – problem set 6**Due: Thursday, Dec. 6th****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 (ν_1 and ν_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)

$V(H_2O)_6^{3+}$: $\Delta_o/B \approx 30$ matches the $\nu_2/\nu_1 = 1.44$ ratio from the T-S diagram.

This $\Delta_o/B \approx 30$ corresponds to a $\nu_1/B = 28$ from the T-S diagram. Taking $17,800\text{ cm}^{-1}/28 = 640\text{ cm}^{-1}$ as B, and $\Delta_o = 640\text{ cm}^{-1} * 28 = 19,000\text{ cm}^{-1}$.

$[VF_6]^{3+}$: $\Delta_o/B \approx 25$.

$15,100\text{ cm}^{-1}/23 = 660\text{ cm}^{-1}$; $\Delta_o = 16,500\text{ cm}^{-1}$

$[VCl_6]^{3+}$: $\Delta_o/B \approx 22.5$.

$11,000\text{ cm}^{-1}/21 = 520\text{ cm}^{-1}$; $\Delta_o = 11,700\text{ cm}^{-1}$

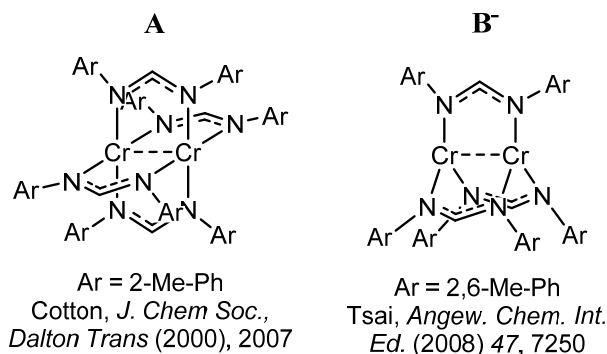
	$\nu_1\text{ (cm}^{-1}\text{)}$ ${}^3T_1 \rightarrow {}^3T_2$	$\nu_2\text{ (cm}^{-1}\text{)}$ ${}^3T_1 \rightarrow {}^3T_1$	Ratio of ν_2/ν_1	B (Racah Parameter) (cm^{-1})	Δ_o (cm^{-1})
$V(H_2O)_6^{3+}$	17,800	25,700	1.44	640	19,000
$[VF_6]^{3+}$	15,100	23,600	1.56	660	16,500
$[VCl_6]^{3+}$	11,000	18,020	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: $Cl > H_2O > F$. 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 $H_2O > F > Cl$, as expected from the spectrochemical series, reflects the pi donating abilities of these ligands.

Part 2

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

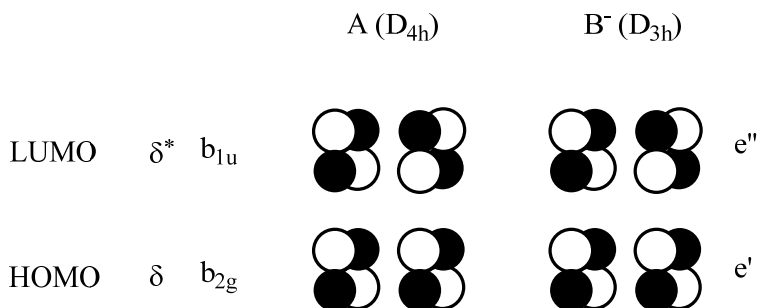


a. Based on these MO diagrams, what is the term symbol for the ground state of A and B⁻?

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

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

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

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

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.

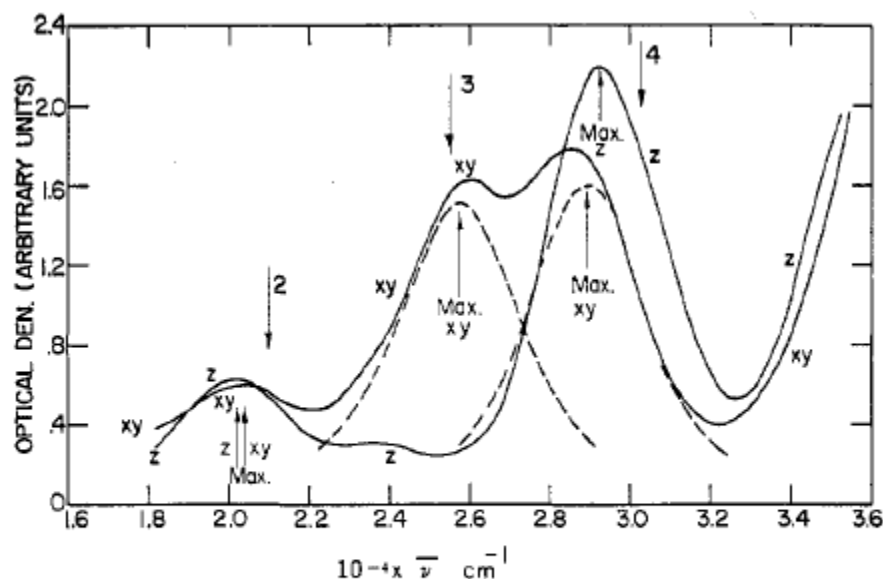
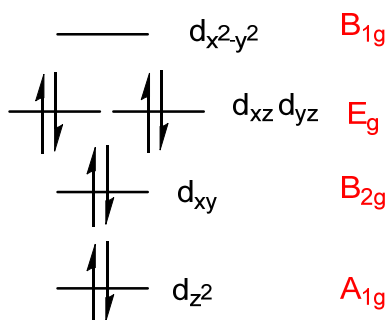


Fig. 3.—Absorption spectrum of K_2PtCl_4 crystal in polarized light. The optical density is in arbitrary units. Dashed lines indicate the Gaussian components for the x-y polarization.

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

D_{4h}

- b) One of the possible MO diagrams is given below. Assign Mulliken 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

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

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

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

- d) Vibrations of the $[\text{PtCl}_4]^{2-}$ 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

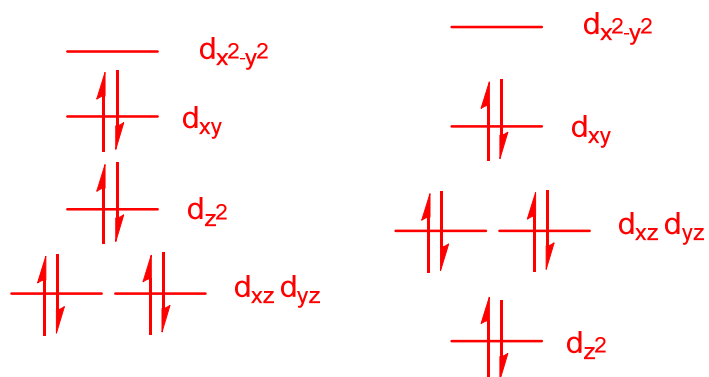
Band 4 ${}^1A_{1g} \rightarrow {}^1E_g$ or ${}^1A_{1g} \rightarrow {}^1B_{1g}$. Both transitions will give enhancement with xy and z polarized light.

- 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 $d_{x^2-y^2}$.

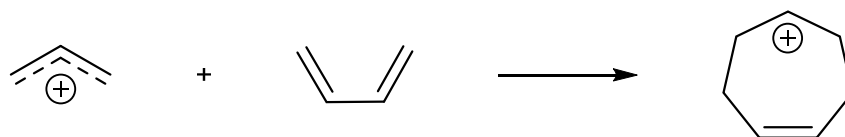
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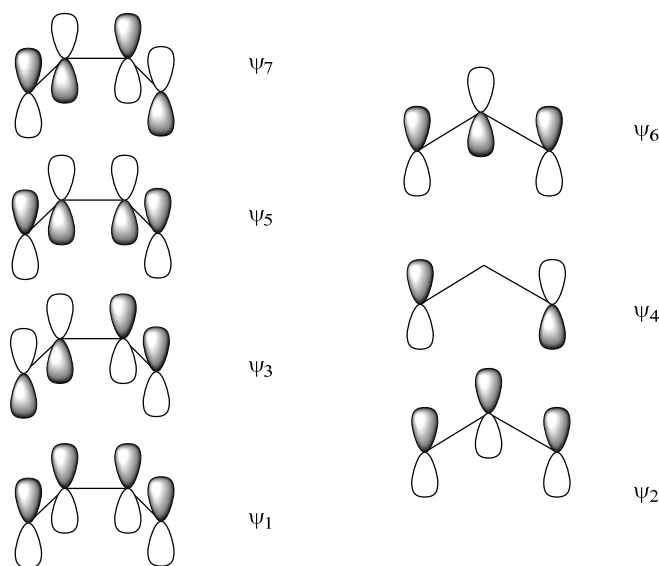
Problem 3 (2 points)

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Consider the following cycloaddition reaction.

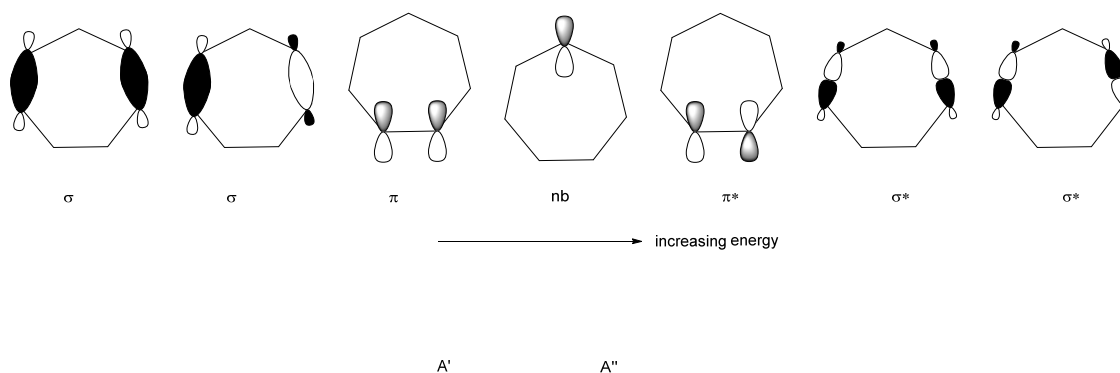


a. – c.



Energy of orbitals increase from ψ_1 to ψ_7 .

d. In forming the product, two π bonds are broken to make one new π bond and two σ bonds. Assuming that the σ orbitals are lower in energy than the π orbitals, and the σ^* orbitals are higher in energy than the π^* orbitals, sketch the seven MOs of the product and rank them in order of increasing energy. List the nature of the orbitals (σ , π , etc.).



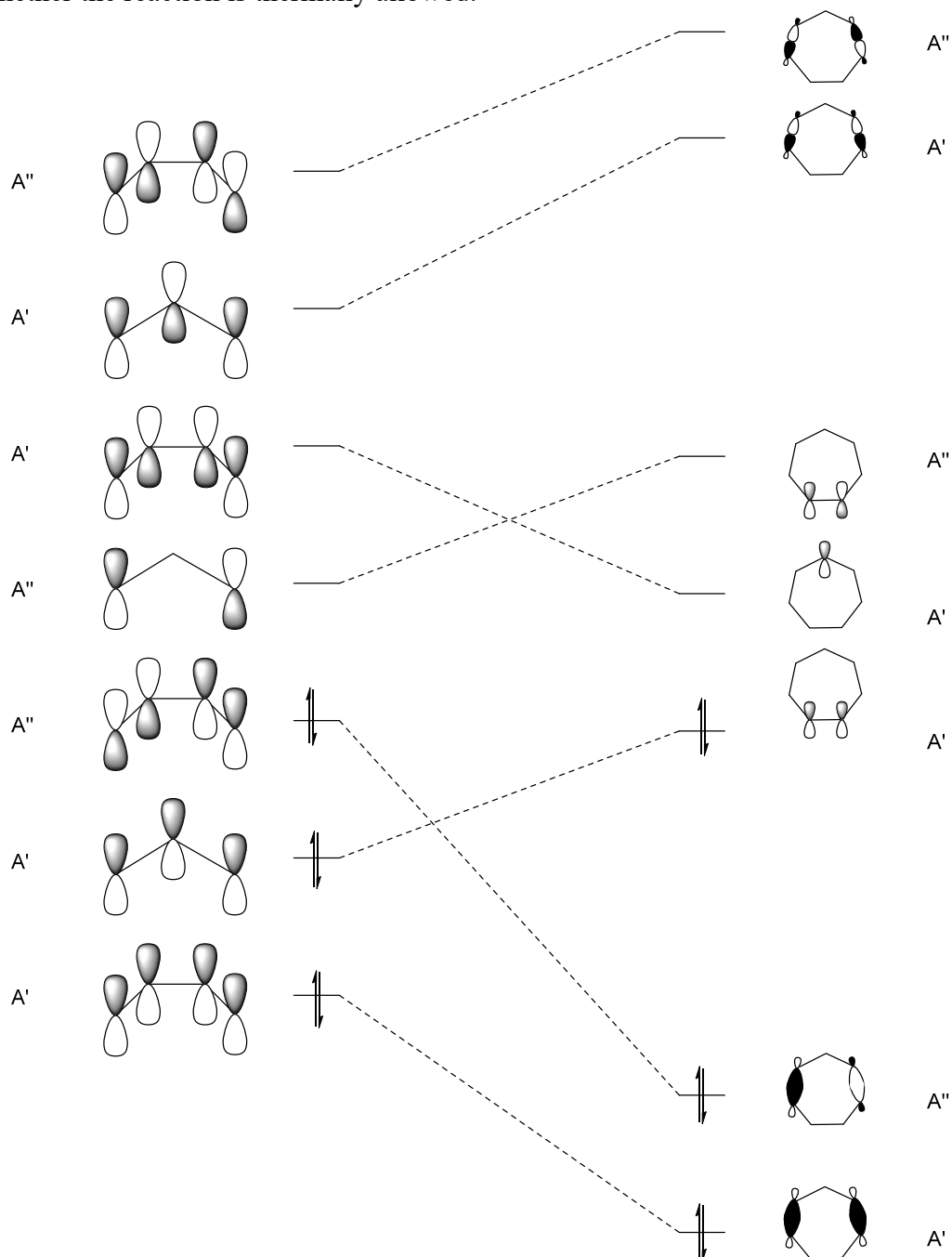
e. What characteristic symmetry element is preserved throughout the course of this reaction? In what point group should we consider this reaction?

Mirror plane, C_s

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f. Draw the orbital correlation diagram for this cycloaddition reaction. Start with the seven orbitals of the reactants on the left (energy order determined in part c) and correlate these orbitals to those of the cycloheptene cation. Include Mulliken symbols in the point group of the process. Explain, based on this diagram, whether the reaction is thermally allowed.



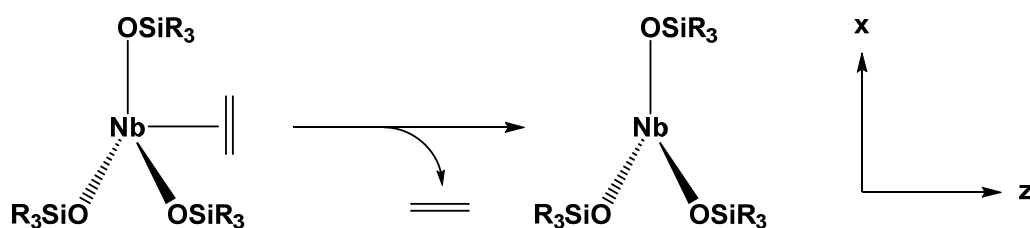
Allowed

g. Consider the cycloaddition reaction between allyl anion and butadiene. Based on your correlation diagram in part f, will this reaction be thermally allowed or forbidden?

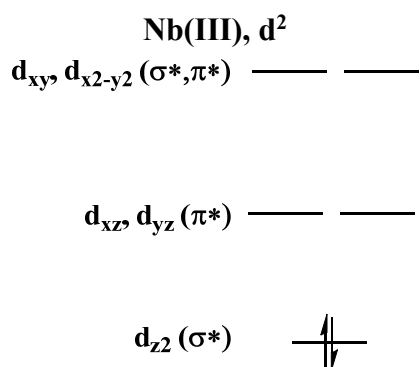
Forbidden

Problem 4 (3 points)

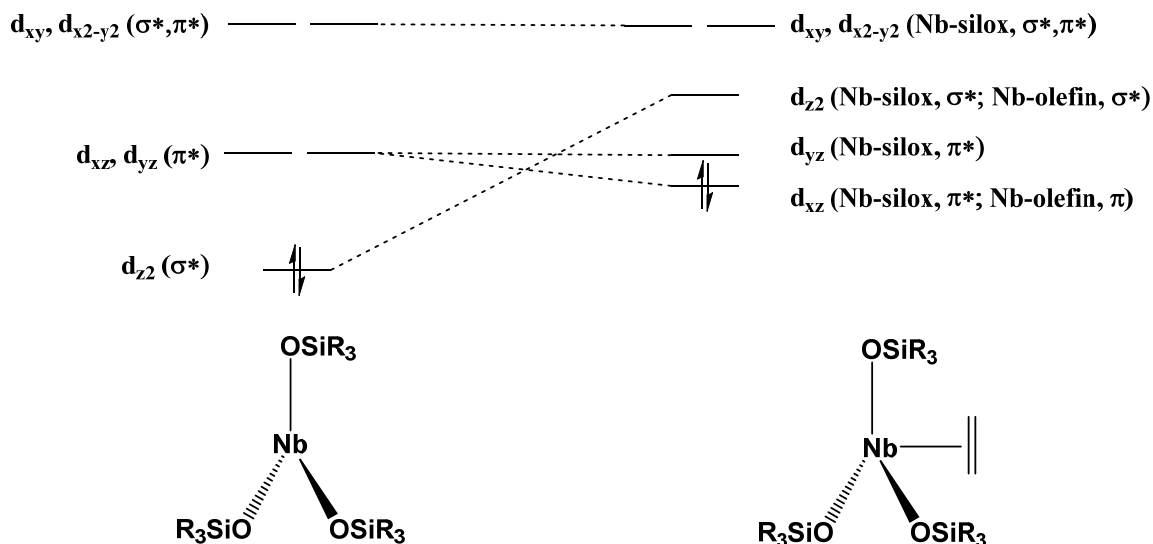
Consider the dissociation of ethylene from a niobium tris-siloxide complex.



A) Determine the niobium oxidation state and d-electron count for $\text{Nb}(\text{OSiR}_3)_3$. By inspection, provide the d-splitting diagram of $\text{Nb}(\text{OSiR}_3)_3$ taking into consideration that siloxides have two oxygen lone pairs available for π bonding. $\text{Nb}(\text{OSiR}_3)_3$ 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 $\text{Nb}(\text{OSiR}_3)_3$, provide the d-splitting diagram of $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$. Correlate the d-orbitals in $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$ to the d-orbitals in $\text{Nb}(\text{OSiR}_3)_3$, 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. $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$ is also diamagnetic.



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

The reaction is orbitally forbidden since a filled d_{xz} orbital and an empty d_{z^2} orbital from the ethylene adduct become an empty d_{xz} and a filled d_{z^2} orbital in the product.

D) Consider the ground state electronic configuration and the first three excited state electronic configurations of $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$. 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 $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$, 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-orbitals in $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$.

	Configuration	States
Ground state	$(d_{xz})^2$	$^1A'$
First excited state	$(d_{xz})^1(d_{yz})^1$	$^3A'' + ^1A''$
Second excited state	$(d_{xz})^1(d_{z^2})^1$	$^3A' + ^1A'$
Third excited state	$(d_{yz})^2$	$^1A'$

(d_{z^2} and d_{xz} transform as A' ; d_{yz} transforms as A'')

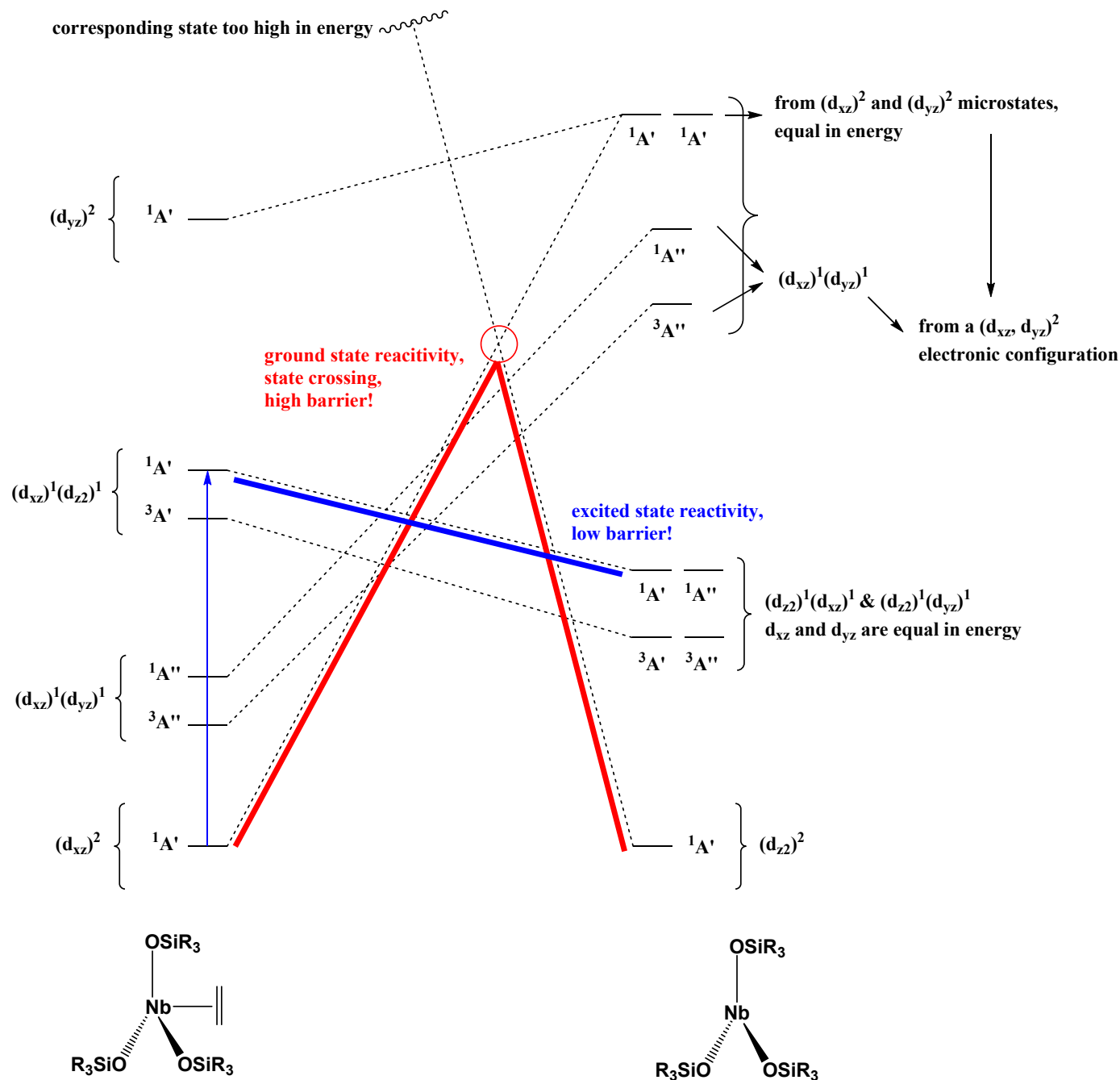
F) Working in the C_{3v} point group for $\text{Nb}(\text{OSiR}_3)_3$, provide electronic configurations for the ground state and the first two excited states (use Mulliken symbols). Provide electronic state symbols for each electronic configuration. For the ambiguous case of the second excited state,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

	Configuration	States
Ground state	$(d_{z^2})^2 \rightarrow (A_1)^2$	1A_1
First excited state	$(d_{z^2})^1(d_{xz}, d_{yz})^1 \rightarrow (A_1)^1(E)^1$	$^3E + ^1E$
Second excited state	$(d_{xz}, d_{yz})^2 \rightarrow (E)^2$	(i) $^3A_1 + ^1A_2 + ^1E$ (ii) $^1A_1 + ^3A_2 + ^1E$

G) Express the electronic state symbols in part F) in the point group of $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$. [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 $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$ with the electronic states of $\text{Nb}(\text{OSiR}_3)_3$. Not all electronic states in $\text{Nb}(\text{OSiR}_3)_3$ have matches, since not all excited states have been considered for $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$. The corresponding excited states may lie well above the ones considered here.

	Configuration	States in C_{3v}	States in C_s
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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) $^1A_1 + ^3A_2 + ^1E$	$(d_{xz})^2 \rightarrow ^1A'$ $(d_{yz})^2 \rightarrow ^1A'$ $(d_{xz})^1(d_{yz})^1 \rightarrow ^3A'' + ^1A''$



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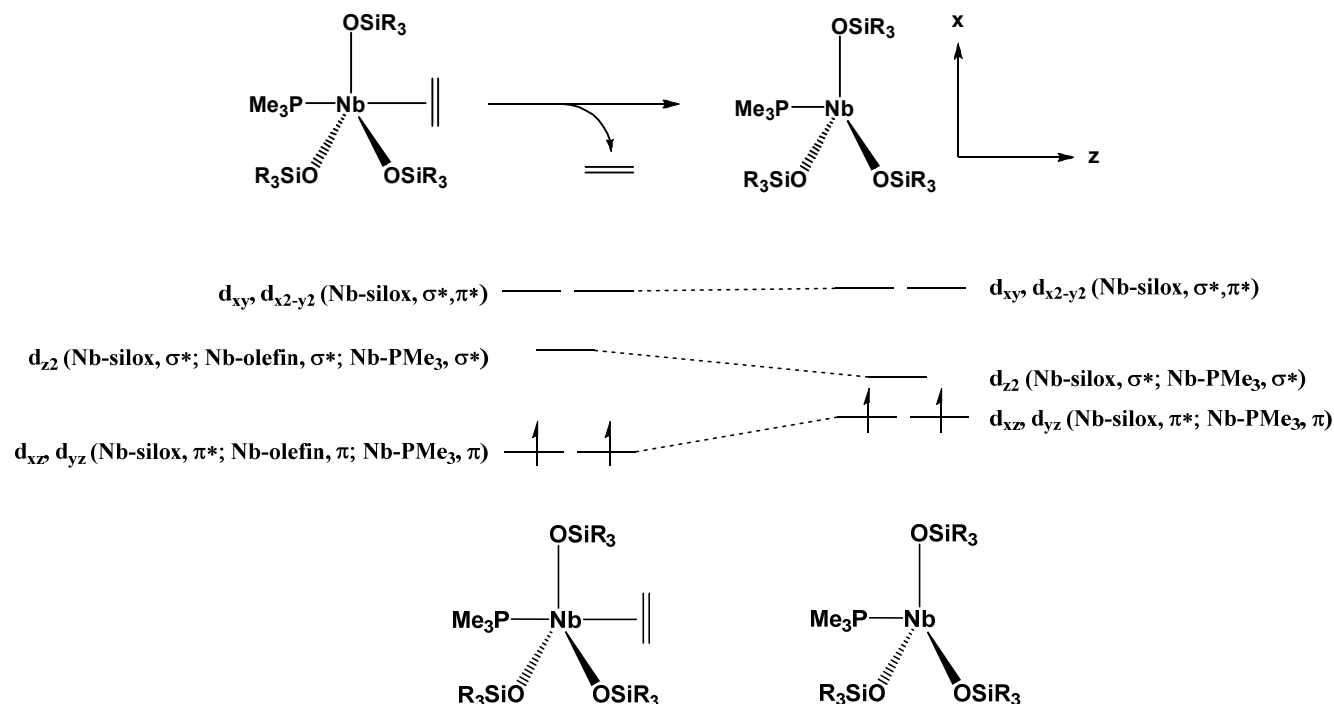
H) From the state correlation diagram obtained in part G), explain whether the reaction is symmetry allowed or forbidden. If it is forbidden, clearly indicate the point in the reaction coordinate where intersystem crossing may occur.

The reaction is symmetry forbidden. See correlation diagram above.

I) Comment on the feasibility of excited state reactivity from $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$. Which electronic transition from the ground state (provide initial and final electronic configurations and states) in $\text{Nb}(\text{OSiR}_3)_3(\text{C}_2\text{H}_4)$ may lead to a low-barrier dissociation of ethylene?

An electronic transition from $(d_{xz})^2 \rightarrow (d_{xz})^1(d_{z^2})^1$ [$^1A' \rightarrow ^1A'$] 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. Orbitaly allowed.
The triplet ground states of both the starting material and the product correlate.**