Assignment 2
Due Thursday, February 25, 2010

(1) The free-ion terms are split in an octahedral field in the manner given in this table.

Splitting of the Free-Ion terms of d^n configurations in an Octahedral Field	
Free-Ion Term	Terms in O_h
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_{1g} + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

Formulas that allow one to derive these results are given below.

$$\chi(E) = 2J + 1 \quad ; \quad \chi(i) = \pm(2J + 1)$$

$$\chi(C_\alpha) = \frac{\sin[(J + 1/2)\alpha]}{\sin(\alpha/2)}$$

$$\chi(S_\alpha) = \pm\frac{\sin[(J + 1/2)(\alpha + \pi)]}{\sin[(\alpha + \pi)/2]}$$

$$\chi(\sigma) = \pm\sin[(J + 1/2)\pi]$$

In these formulas E, C, S, σ, and i refer to the identity, proper rotation, improper rotation, reflection, and inversion operations, respectively. The angle of rotation is α. + signs apply for a *gerade* ***atomic state*** and – signs apply for an *ungerade* ***atomic state***, whether the point group under consideration has inversion symmetry or not. Examples: a ^3P state derived from either p^2 configuration ($u \times u$) or a d^2 configuration ($g \times g$) give g states. However, a ^2D state derived from a p^3 configuration ($u \times u \times u$) gives a u state, while a ^2D state derived from a d^3 configuration ($g \times g \times g$) gives a g state.
The symbol J refers to the angular momentum quantum number of the state under consideration. In the Russell-Saunders scheme, J can be replaced by L when considering a spatial wave function.

(a) Verify the results given for the D and H states.

(b) For all the states, add two more columns to the table for D_{4h} and D_{3h} point groups. (You can *sometimes* save work by choosing an appropriate subgroup.)

(2) For each of the following pairs of molecules and ions, sketch a d-orbital splitting diagram for the parent species and the substituted derivative. Draw the diagrams for each pair side-by-side and show how the orbital energies are expected to change on going from parent to derivative. (Explain your answers.)

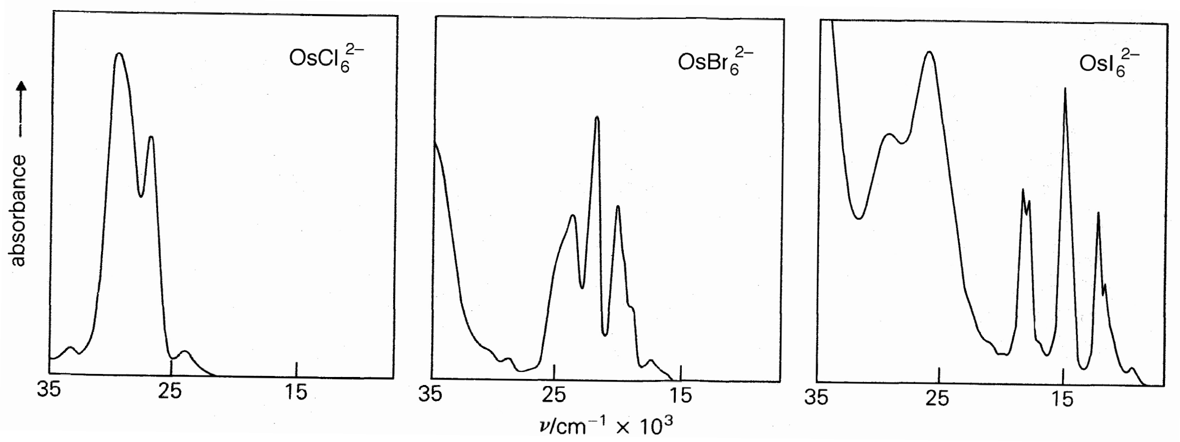
(a) $[PtCl_4]^{2-} \rightarrow$ *trans*-$PtCl_2(NH_3)_2$

(b) $[RuCl_6]^{4-} \rightarrow [Ru(CO)Cl_5]^{3-}$

(c) $[Co(NH_3)_6]^{3+} \rightarrow$ *trans*-$[Co(NH_3)_4Cl_2]^+$

(3) UV-Visible spectra of two Ni(II) amide complexes, $[Ni(DMF)_6]^{2+}$ and $[Ni(DMA)_6]^{2+}$, are shown on the penultimate page. (DMF = N,N-dimethylformamide, DMA = N,N-dimethylacetamide) Using the attached Tanabe-Sugano diagram and the spectra, calculate Δ_o (= 10 Dq) and the Racah parameters, B, for each complex. Discuss the results in terms of the nephelauxetic effect and the position of the ligands in the spectrochemical series. (Note that the energy scale is nonlinear; use the wavelength scale and convert to cm^{-1}.)

(4) Visible spectra of the OsX_6^{2-} anions are shown on the next page. Corresponding regions of the spectra of the $[Os(py)_4X_2]$ complexes are almost indistinguishable from one another. Explain these observations.



(5) This problem is intended to expose a little of the 'guts' of ligand field theory. We will calculate the energies of the triplet states of an octahedral d^8 complex. Energy expressions for two of the triplet states, the ground ${}^3A_{2g}(t_{2g}^6e_g^2)$ state and the excited ${}^3T_{2g}$ $(t_{2g}^5e_g^3)$ state, are easily obtained because they are the only triplet states with these symmetries. (Part a below.) However, the ${}^3T_{1g}(t_{2g}^5e_g^3)$ and ${}^3T_{1g}(t_{2g}^4e_g^4)$ excited states are of the same symmetry, and they mix to an extent that varies as a function of the ligand field strength. In the weak field limit, these two states descend from the free-ion ${}^3F$ and ${}^3P$ states and the energies are easily evaluated. However, the wavefunctions for the *high-field* ${}^3T_{1g}$ states can be used as a basis for the *zero-field* free-ion ${}^3F({}^3T_{1g})$ and ${}^3P({}^3T_{1g})$ states. In doing this, we take advantage of *the sum rule* (see part d): the sum of the diagonal elements of the Hamiltonian (the trace) is equal to the sum of the energies, irrespective of the basis. This means that if we were to look at the high-field problem using the atomic ${}^3F({}^3T_{1g})$ and ${}^3P({}^3T_{1g})$ wavefunctions, the wavefunctions mix to yield the molecular wavefunctions, but the *sum* of their energies is unchanged (when the ligand field mixes them, the upper state moves up exactly as much as the lower state moves down). Conversely, if we use the molecular ${}^3T_{2g}(t_{2g}^5e_g^3)$ and ${}^3T_{1g}(t_{2g}^4e_g^4)$ wavefunctions to write the *atomic* Hamiltonian, the *sum* of diagonal Hamiltonian matrix elements is equal to $E({}^3F) + E({}^3P)$.

(a) As pointed out in the preceding (and as is evident in the d^8 Tanabe-Sugano diagram), the $^3A_{2g}$ ground state and $^3T_{2g}$ excited state are the only triplet states of their respective symmetries. Consequently, you should be able to write a single-configuration wavefunction (for a $M_S = 1$ spin component) for each of these states. (This is trivial for the ground state. For the excited state, use the the 'descent in symmetry' method discussed for Co(III) and Cr(III) complexes in class.) By use of methods discussed in class, write down expressions for the energies using these wavefunctions and the formulas given at the tables attached to this homework set. Your answers should involve Racah parameter(s) and Δ_o (= 10 Dq). What is the energy *difference* between the two states?

(b) Using the tables provided, find expressions for the energies of the free-ion ^3F and ^3P states in terms of Racah parameter(s). What is the energy *difference* between the two states?

(c) Write a single-configuration wavefunction expression (for the M_S = $^3/_2$ spin component) for each of the *high-field* $^3T_{1g}$ states. (Just to save space, let's call these two states $^3T^A_{1g}$ and $^3T^B_{1g}$.) These are obtained by assuming the only configuration that contribute to these states are $t^5_{2g}e^3_g$ (for $^3T^A_{1g}$) and $t^4_{2g}e^4_g$ (for $^3T^B_{1g}$). Once again, use the 'descent in symmetry' method. Write down expressions for the energies using these wavefunctions in terms of Racah parameter(s) and Δ_o (= 10 Dq). What is the energy *difference* between the two states?

(d) When two orthogonal basis states, Ψ_p and Ψ_q, interact with each other via a matrix element H_{pq}, the appropriate secular determinant is

$$\begin{vmatrix} H_p - E & H_{pq} \\ H_{pq} & H_q - E \end{vmatrix} = 0 \text{ , which has solutions } E_\pm = \frac{H_p + H_q}{2} \pm \sqrt{\left(\frac{H_p - H_q}{2}\right)^2 + H_{pq}^2} \text{ .}$$

This has two limiting cases that are useful:

$$(i)\ H_p = H_q \text{ , for which } E_\pm = H_p \pm H_{pq} \text{ , and}$$

$$(ii)\ \left|\frac{H_p - H_q}{2}\right| \gg \left|H_{pq}\right| \text{ , } \quad \text{for which } E_\pm \to H_p \text{ or } H_q$$

Note that in every case the *sum* of the two energies is the same: $E_+ + E_- = H_p + H_q$.

Let's use this information to work out the way that the two states, $^3T^A_{1g}$ and $^3T^B_{1g}$, mix with each other over the entire range of ligand field strengths. We have already examined the high-field limit in part (c); we have two $^3T_{1g}$ states for which we know both the energies. Now, using the methods illustrated in class and the formula sheet attached on this problem set, find expressions for the free-ion ^3F and ^3P states. Starting with the energies of *high-field* $^3T^A_{1g}$ and $^3T^B_{1g}$ wavefunctions at zero field (Δ_o = 0), deduce the off-diagonal matrix element between these states that yields the correct energies of the atomic states, $E(^3F)$ and $E(^3P)$.

(e) The off-diagonal matrix element you found in part c applies at *all* ligand-field strengths, ($\Delta_o \neq 0$). Therefore, you can write a general 2 × 2 secular determinant in the basis of the molecular ${}^3T_{1g}^A(t_{2g}^5 e_g^3)$ and ${}^3T_{1g}^B(t_{2g}^4 e_g^4)$ wavefunctions that will give the energies of the ${}^3T_{1g}^A$ and ${}^3T_{1g}^B$ states for *all* ligand-field strengths. Solve the secular determinant to determine a general expression for the energies of the two states.

(f) Using a spreadsheet program, plot the energies of the three excited triplet states relative to the ground ${}^3A_{2g}$ state – on the horizontal axis, plot the energies as a function of Δ_o/B, and on the vertical axis, plot energies in units of B. In other words, plot three functions: $E({}^3T_{2g}) - E({}^3A_{2g})$, $E({}^3T_{1g}^A) - E({}^3A_{2g})$, and $E({}^3T_{1g}^B) - E({}^3A_{2g})$. Do the results look familiar?

(g) Extra Credit: The high-field wavefunctions, ${}^3T_{1g}^A(t_{2g}^5 e_g^3)$ and ${}^3T_{1g}^B(t_{2g}^4 e_g^4)$, are a combination of the atomic wavefunctions, $\Psi({}^3F)$ and $\Psi({}^3P)$:

$$\Psi({}^3T_{1g}^A) = c_{PA}\Psi({}^3P) + c_{FA}\Psi({}^3F) \quad ; \quad \Psi({}^3T_{1g}^B) = c_{FA}\Psi({}^3P) - c_{PA}\Psi({}^3F)$$

These are already constructed to be orthogonal and they must be normalized,

$$|c_{PA}|^2 + |c_{FA}|^2 = 1.$$

Find the relative ${}^3F$ and ${}^3P$ contributions to the high-field molecular states: $|c_{PA}/c_{FA}|$.

Relations Involving Coulomb and Exchange Integrals

p orbitals

definitions

$$J_{i,j} = \int \varphi_i^*(1)\varphi_j^*(2)\left(1/r_{12}\right)\varphi_i(1)\varphi_j(2)\,d\tau_1 d\tau_2;$$
$$K_{i,j} = \int \varphi_i^*(1)\varphi_j^*(2)\left(1/r_{12}\right)\varphi_i(2)\varphi_j(1)\,d\tau_1 d\tau_2$$

$$J_{0,0} = J_{z,z} = J_{x,x} = J_{y,y}$$
$$J_{1,1} = J_{-1,-1} = J_{-1,1} = \left(1/2\right)(J_{x,x} + J_{x,y})$$
$$J_{1,0} = J_{-1,0} = J_{x,y} = J_{x,z} = J_{y,z}$$
$$K_{1,-1} = K_{-1,1} = 2K_{x,y} = J_{x,x} - J_{x,y}$$
$$K_{1,0} = K_{-1,0} = K_{x,y} = K_{x,z} = K_{y,z}$$

d orbitals

$$J_{0,0} = J_{z^2,z^2}$$
$$J_{2,2} = J_{-2,-2} = J_{2,-2} = \left(1/2\right)(J_{xy,xy} + J_{x^2-y^2,xy})$$
$$J_{2,1} = J_{-2,-1} = J_{2,-1} = J_{-2,1} = J_{xy,xz}$$
$$J_{2,0} = J_{-2,0} = J_{xy,z^2}$$
$$J_{1,1} = J_{-1,-1} = J_{1,-1} = \left(1/2\right)(J_{xz,xz} + J_{xz,yz})$$
$$J_{1,0} = J_{-1,0} = J_{xz,z^2}$$
$$K_{1,-1} = 2K_{xz,yz} = J_{xz,xz} - J_{xz,yz}$$
$$K_{2,-2} = 2K_{xy,x^2-y^2} = J_{xy,xy} - J_{xy,x^2-y^2}$$
$$K_{2,1} = K_{-2,-1} = K_{xy,xz} - \int \varphi_{xz}(1)\varphi_{xy}(2)\left(1/r_{12}\right)\varphi_{yz}(1)\varphi_{x^2-y^2}(2)\,d\tau_1 d\tau_2$$
$$K_{2,-1} = K_{-2,1} = K_{xy,xz} + \int \varphi_{xz}(1)\varphi_{xy}(2)\left(1/r_{12}\right)\varphi_{yz}(1)\varphi_{x^2-y^2}(2)\,d\tau_1 d\tau_2$$
$$K_{2,0} = K_{-2,0} = K_{xy,z^2}$$
$$K_{1,0} = K_{-1,0} = K_{xz,z^2}$$

Energies of real *d* orbital integrals in terms of Racah parameters

$J_{xy,xy} = J_{xz,xz} = J_{yz,yz} = J_{z^2,z^2} = J_{x^2-y^2,x^2-y^2}$	$A + 4B + 3C$
$J_{xz,yz} = J_{xy,yz} = J_{xy,xz} = J_{x^2-y^2,yz} = J_{x^2-y^2,xz}$	$A - 2B + C$
$J_{xy,z^2} = J_{x^2-y^2,z^2}$	$A - 4B + C$
$J_{yz,z^2} = J_{xz,z^2}$	$A + 2B + C$
$J_{x^2-y^2,xy}$	$A + 4B + C$
$K_{xy,yz} = K_{xz,yz} = K_{xy,xz} = K_{x^2-y^2,yz} = K_{x^2-y^2,xz}$	$3B + C$
$K_{xy,z^2} = K_{x^2-y^2,z^2}$	$4B + C$
$K_{yz,z^2} = K_{xz,z^2}$	$B + C$
$K_{x^2-y^2,xy}$	C
$\int \varphi_{xz}(1)\varphi_{xy}(2)\left(1/r_{12}\right)\varphi_{yz}(1)\varphi_{x^2-y^2}(2)\,d\tau_1 d\tau_2$	$-3B$

For 1st-row transition metals, Racah parameters B and C have typical ranges: $B \approx 650 - 1100$ cm^{-1}, $C \approx 2400 - 5500$ cm^{-1}. (State energy differences don't involve A.)

Energies of complex *d* orbital integrals in terms of Racah parameters

$J_{0,0}$	$A+4B+3C$
$J_{2,2}=J_{-2,-2}=J_{2,-2}$	$A+4B+2C$
$J_{2,1}=J_{-2,-1}=J_{2,-1}=J_{-2,1}$	$A-2B+C$
$J_{2,0}=J_{-2,0}$	$A-4B+C$
$J_{1,1}=J_{-1,-1}=J_{1,-1}$	$A+B+2C$
$J_{1,0}=J_{-1,0}$	$A+2B+C$
$K_{1,-1}$	$6B+2C$
$K_{2,-2}$	C
$K_{2,1}=K_{-2,-1}$	$6B+C$
$K_{2,-1}=K_{-2,1}$	C
$K_{2,0}=K_{-2,0}$	$4B+C$
$K_{1,0}=K_{-1,0}$	$B+C$

The "Slater-Condon parameters" are defined by

$$F^k \equiv e^2 \int_0^\infty r_1^2 \left[\int_0^\infty r_2^2 \frac{r_<^k}{r_>^{k+1}} \left|R_{nl}(r_1)\right|^2 \left|R_{nl}(r_2)\right|^2 dr_2 \right] dr_1 \quad ; \quad \frac{r_<^k}{r_>^{k+1}} = \begin{cases} \dfrac{r_1^k}{r_2^{k+1}} & \text{if } r_2 > r_1 \\ \dfrac{r_2^k}{r_1^{k+1}} & \text{if } r_1 > r_2 \end{cases}$$

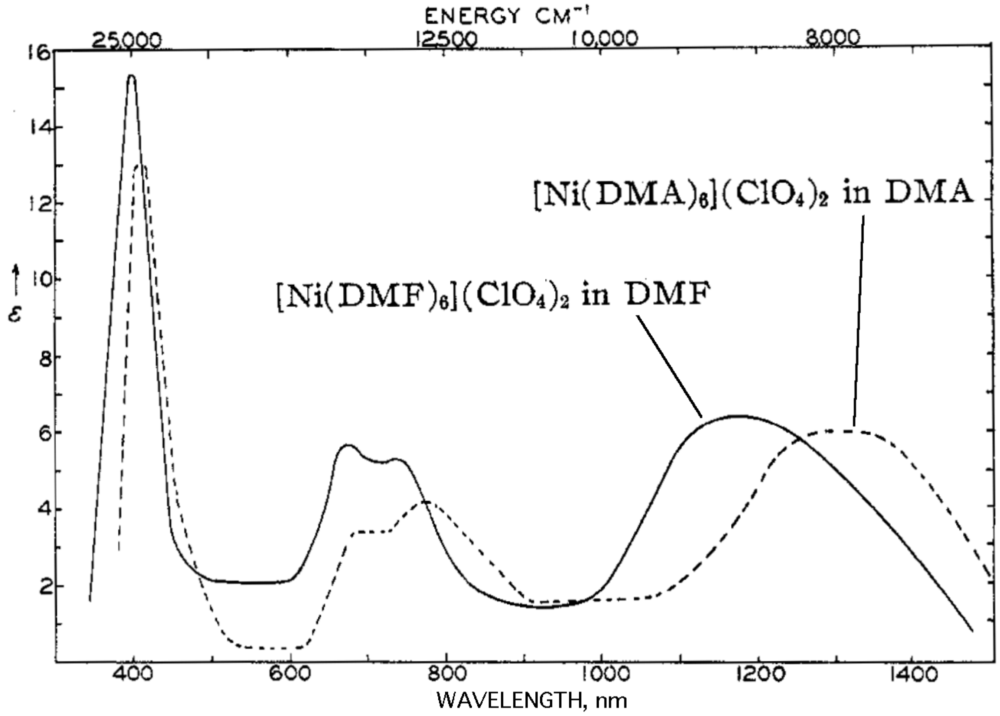
and (in the *d*-shell): $F_0 \equiv F^0$, $F_2 = \dfrac{F^2}{49}$, $F_4 = \dfrac{F^4}{441}$

The "Racah Parameters" are related to the Slater-Condon parameters by

$$A = F_0 - 49F_4$$

$$B = F_2 - 5F_4$$

$$C = 35F_4$$



The ε scale is arbitrary for the DMA complex; the peak heights are shown in true relative scale.