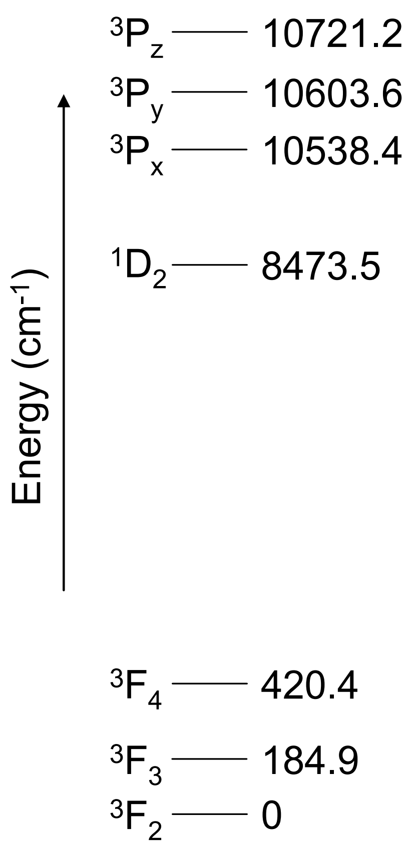
Quiz 11
CHEM 325
Spring 2009

Name: ____

An energy level diagram depicting some of the lowest energy levels for Ti^{2+} is shown below. Note that all of these levels derive from the electronic configuration [Ar] $3d^2$.



1. (4 Points) What are the values of x, y and z for the ^3P levels (i. e., the allowed J values)?

For these states $L = 1$ and $S = 1$ and the possible values of J are 2, 1 and 0. Since this configuration is less than half-filled, the state with the lowest J is lowest in energy (*since this is an excited state, this may not be strictly true, however*).

x = **0**

y = **1**

z = **2**

2. (2 Points) What causes the splitting of the electronic configuration into terms?

electron-electron interactions

3. (2 Points) What causes the splitting of the ^3P and ^3F terms?

spin orbit coupling

4. (3 Points) Why doesn't the ^1D term split into levels (i. e., why is there only $^1D_2$)?

For a ^1D term $L = 2$ and $S = 0$, and the only possible value that J can have is 2 ($|L - S| = L + S = 2$).

5. (4 Points) One of the next highest terms that isn't shown arises from the [Ar] $3d^1$ $4s^1$ configuration. What is its term symbol?

A single electron in a d orbital will have $S = 1/2$ and $L = 2$, while a single electron in an s orbital will have $S = 1/2$ and $L = 0$. Coupling the spins gives a total S or 1 and 0, while coupling the orbital angular momentum gives $L = 2$. Therefore, there are two states with the same orbital angular momentum which differ in their spin. These states are ^1D and ^3D. Of these Hund's rules places ^3D lowest (highest spin). We can then determine that spin orbit coupling will split these by J into $^3D_3$, $^3D_2$ and $^3D_1$. Since this configuration is less than half filled, the $^3D_1$ is lowest in energy.

For a ^3D state, L = 2, S = 1 and J can have values of L + S, L + S – 1, . . . |L – S|. In this case L + S = 3, L + S – 1 = 2, L + S – 2 = |L – S| = 1. Since the allowed values of J are 3, 2 and 1, the term symbols that describe these levels are $^3D_3$, $^3D_2$ and $^3D_1$.

6. (4 Points) Would the transition $^3P_2 \leftarrow {}^3F_2$ be very intense? Explain your reasoning.

For this transition $\Delta S = 0$ (since the multiplicities are the same), $\Delta L = -2$ (an F state has $L = 3$ and a P state has $L = 1$) and $\Delta J = 0$. This transition is spin allowed, orbitally forbidden and allowed in the total angular momentum change. Therefore, it is expected to be moderately intense.

7. (6 Points) At what wavelength (in nm) will the transition from the $^3F_2$ ground state to the ^3P_z excited state occur?

This transition occurs at 10721.2 cm^{-1}. We can combine the equations $\Delta E = h\nu$ (relates the energy of the transition with the frequency of the light) and $\lambda\nu = c$ to give $\Delta E = \frac{hc}{\lambda}$, with the energy in joules. To convert from joules to wavenumbers we simply divide both sides by hc to give $\Delta E\left(\text{in cm}^{-1}\right) = \frac{1}{\lambda}$, and thus $\lambda = \frac{1}{\Delta E\left(\text{in cm}^{-1}\right)}$.

$$\lambda = \frac{1}{10721.2\ \text{cm}^{-1}} = 9.32731_4 x10^{-5}\ \text{cm}\left(\frac{1\,\text{m}}{100\,\text{cm}}\right)\left(\frac{1\,\text{nm}}{1x10^{-9}\ \text{m}}\right) = 932.731\,\text{nm}$$

This transition occurs at 932.731 nm.

8. (6 Points) What is the value of the spin orbit coupling constant (in cm^{-1}) for the ^3F levels?

Use the equation $E_{spin-orbit} = \frac{Ahc}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$ with $L = 3$, $S = 1$ and any pair of the possible J values. If we divide by sides by hc, the value of A will be in cm^{-1}, which gives the equation $E_{spin-orbit} = \frac{A}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$.

$$L = 3,\ S = 1,\ J = 2:\ E_{spin-orbit} = \frac{A}{2}\left[2(2+1) - 3(3+1) - 1(1+1)\right] = -4A$$

$$L = 3,\ S = 1,\ J = 3:\ E_{spin-orbit} = \frac{A}{2}\left[3(3+1) - 3(3+1) - 1(1+1)\right] = -A$$

$$L = 3,\ S = 1,\ J = 4:\ E_{spin-orbit} = \frac{A}{2}\left[4(4+1) - 3(3+1) - 1(1+1)\right] = +3A.$$

Note that the degeneracy of each level is 2J + 1 (corresponding to the possible values of M_J), so there are 9 levels that go up by 3A, 7 levels that go down by A and 5 levels that go down by 4A. Multiplying the number of levels by their change in energy and totaling them *up gives 0 (9 x 3A + 7 x –A + 5 x –4A = 0). This will always be true and is called the Center of Gravity Rule.*

Thus the splitting between the J = 2 **and** J =3 **levels is** 3A **and the splitting between the** J = 3 **and** J = 4 **levels is** 4A**. Calculating** A **from the first pair of levels gives** A = 61.63 cm^{-1} **and between the second pair of levels** A = 58.88 cm^{-1}**, for an average value of** A **of** 60.26 cm^{-1}**.** *Note that the two calculated values are not the same, and usually aren't given when this relatively simple treatment is used. This is because there are additional effects that we have ignored which are more important for transition metals (and other heavy elements) than they are for lighter elements.*