#3 not assigned for 2015

3.

$s^1 d^1$, $m_\ell = 0$, $m_\ell = \pm 2, \pm 1, 0$

$M_L = \pm 2$ $s = 0$ $\frac{1}{2}$ M_S $1, 0, 0, -1$

$M_L = \pm 1$ $1, 0, 0, -1$

$M_L = 0$ $1, 0, 0, -1$

M_L	1	0	-1
2	X	XX	X
1	X	XX	X
0	X	XX	X
-1	X	XX	X
-2	X	XX	X

M_S

Term 1:
L=2 S=1 → ^3D

Term 2:
L=2 S=0 → ^1D

Lowest energy: ^3D

7.
a) ^2D L=2 $M_L = -2, -1, 0, 1, 2$ $S = \frac{1}{2}$ $M_S = +\frac{1}{2}, -\frac{1}{2}$

b) ^3G L=4 $M_L = -4, -3, -2, -1, 0, 1, 2, 3, 4$ S=1 $M_S = -1, 0, 1$

c) ^4F L=3 $M_L = \pm 3, \pm 2, \pm 1, 0$ $M_S = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ $S = \frac{3}{2}$

8.
a) J = $\frac{5}{2}, \frac{3}{2}$ $d^3 = < \frac{1}{2}$ full → $^2D_{3/2}$

b) d^4 J = 5, 4, 3 $< \frac{1}{2}$ full → $^3G_3$

c) ^4F d^7 J = $\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$ $> \frac{1}{2}$ full → $^4F_{9/2}$

9.
A = $\varepsilon b c$ $\varepsilon = 0.038 \ M^{-1} cm^{-1}$ A = 0.10   b = 1.00 cm

$c = \dfrac{0.10}{(0.038 \ M^{-1} cm^{-1})(1.00 \ cm)} = 2.6 \ M$

10. a) $\dfrac{1}{\lambda} = 24900 \ cm^{-1}$ $\lambda = 4.02 \times 10^{-5} cm = 402 \ nm$

$\nu = \dfrac{c}{\lambda} = c\bar{\nu} = (24,900 \ cm^{-1})(2.998 \times 10^{8} m/s) = 7.47 \times 10^{14} Hz$

b) $E = \dfrac{hc}{\lambda} = \dfrac{(6.626 \times 10^{-34} J \cdot s)(2988 \times 10^{8} m/s)}{366 \times 10^{-9} m} = 5.43 \times 10^{-19} J$

$\left(366 \ nm \left(\dfrac{1 \ cm}{1 \times 10^7 nm} \right) \right)^{-1} = 27,300 \ cm^{-1} = \bar{\nu}$

11.

a. d^8 O_h $L = max\ M_L = 2(2) + 2(1) + 2(0) + (-1) + (-2)$

$\uparrow$ $\boxed{1\ 1}$ eg $L = 3$ $S = max\ M_S = 1$

$\boxed{1\!\!1\ 1\!\!1\ 1\!\!1}$ t_{2g} $\underline{^3F}$ $(J = 4)$

b. d^5 HS $L = 0$ $S = +5/2$ $\rightarrow$ $\underline{^6S}$ $(J = 5/2)$

d^5 LS $L = 6$ $S = +\frac{1}{2}$ $\rightarrow$ $\underline{^2I}$

c. $E\left[\begin{array}{c} \boxed{1\ 1}\ -t_2 \\ \boxed{1\ 1}\ e \end{array}\right.$ $L = 2$ $S = 2$ $\rightarrow$ ^5D $(J = 0)$

d. $L = 2$ $S = +\frac{1}{2}$ ^2D $(J = 5/2)$

Ch. 11 Part B: #13, 14(a,b), 17, ~~19, 20~~, 26, 27   [a,b]

13.

$[Ni(H_2O)_6]^{2+}$ Ni^{2+} d^8
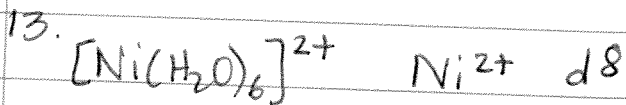
$\Delta_o \approx$ energy of lowest-energy peak in UV-vis spectrum (Fig. 11.8, p. 421)

$\Delta_o \sim 8,000 \, cm^{-1}$

Further splitting — Don't expect Jahn-Teller distortion in the ground state (d^8 = equally occupied orbitals); however, there will be unequal occupation in the excited state (when an e^- is promoted), leading to distortion & splitting.

14.

a) $[Cr(C_2O_4)_3]^{3-}$: $Cr^{3+} \Rightarrow d^3$ $\Delta_o = 17,400 \, cm^{-1}$

b) $[Ti(NCS)_6]^{3-}$: $Ti^{3+} \Rightarrow d^1$ $\Delta_o = 18,400 \, cm^{-1}$
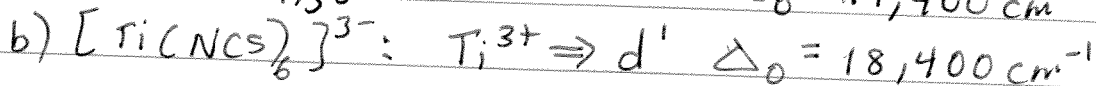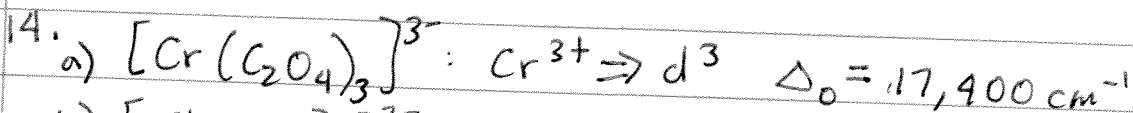
Splitting is due to Jahn-Teller distortion.

17.

M^{3+}: M=	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	(Cu	Zn)
# d e^-	0	1	2	3	4	5	6	7	8	9
Jahn-Teller?	N	Y	Y	N	Y	Y(LS)	Y (HS)	Y	N	Y

(Note that some of these 3+ metal ions are not commonly observed — Ni^{3+}, Cu^{3+}, Zn^{3+}...)

19. $[Co(NH_3)_5 X]^{2+}$ $X = Cl, Br, I$ Co^{3+} d^6 low spin

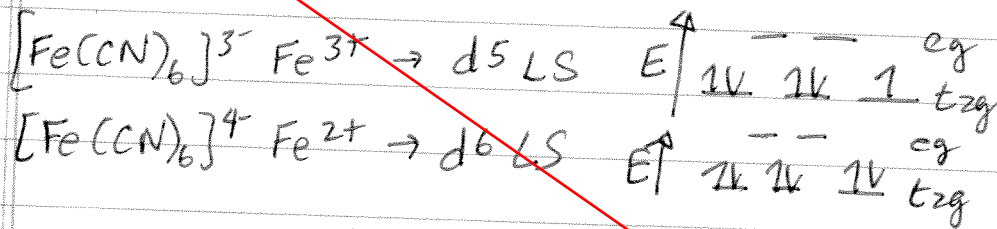E ↑   ⥮ ⥮ ⥮ t_{2g} — e_g
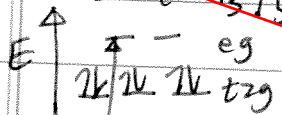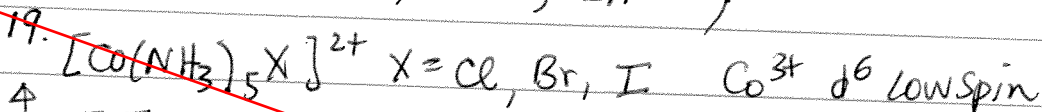
⥮ ⥮ ⥮ ⥮ ⥮ ⥮ filled L MOs

LMCT here will occur from filled L σ MOs to empty e_g orbitals on Co^{3+}. The lowest energy LMCT band will occur for the ligand with orbitals closest in E to Co d orbitals.

This should be I (5p orbitals vs. 4p or 3p).

20.

$[Fe(CN)_6]^{3-}$ 2 sets of CT bands —
$[Fe(CN)_6]^{4-}$ only 1 CT at high energy (UV)

$[Fe(CN)_6]^{3-}$ Fe^{3+} → d^5 LS $E\uparrow$ $\underline{1\downarrow}$ $\underline{1\downarrow}$ $\underline{1}$ e_g / t_{2g}

$[Fe(CN)_6]^{4-}$ Fe^{2+} → d^6 LS $E\uparrow$ $\underline{1\downarrow}$ $\underline{1\downarrow}$ $\underline{1\downarrow}$ e_g / t_{2g}

For LMCT, $[Fe(CN)_6]^{3-}$ (Fe^{3+}) can accept e^- into the t_{2g} and the e_g orbitals, giving rise to 2 CT bands. In $[Fe(CN)_6]^{4-}$ (Fe^{2+}), the t_{2g} orbitals are full; the only LMCT transition possible is into the higher energy e_g set.
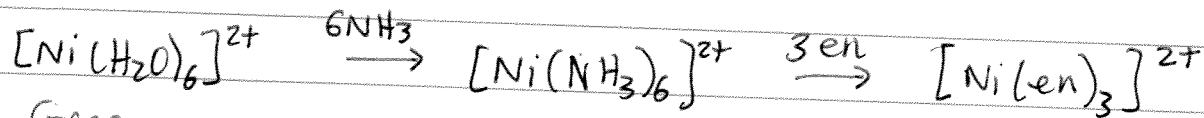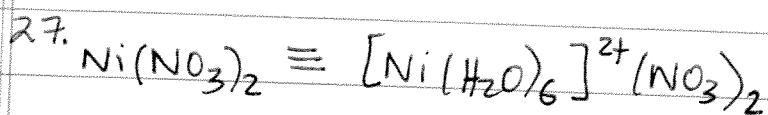
26.

a) CrO_4^{4-} MnO_4^{3-} FeO_4^{2-} RuO_4^{2-}
    Cr^{4+} Mn^{5+} Fe^{6+} Ru^{6+}
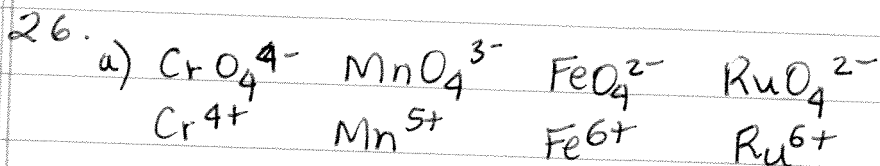
Δ_t increases from $CrO_4^{4-} < MnO_4^{3-} < FeO_4^{2-} < RuO_4^{2-}$.
Δ_t increases with increasing charge on the metal ion and with increasing size (radial extent).

b)
Since FeO_4^{2-} has the highest charge on the metal (Fe^{6+}), it should have the strongest M–O electrostatic attraction and the shortest M–O bond distance.

c) O^{2-} is a σ-donor with no empty π^* orbitals. Therefore, MLCT is very unlikely. Thus, these are probably LMCT transitions.

27. $Ni(NO_3)_2 \equiv [Ni(H_2O)_6]^{2+}(NO_3)_2$

$$[Ni(H_2O)_6]^{2+} \xrightarrow{6NH_3} [Ni(NH_3)_6]^{2+} \xrightarrow{3\,en} [Ni(en)_3]^{2+}$$

Appears: Green   Blue   Violet

Absorbs: Red   Orange   Yellow

The color of light absorbed changes from red → orange → yellow as the ligand goes from H_2O → NH_3 → en. The energy absorbed — and the size of Δ_0 — are increasing. This is consistent with the positions of the ligands in the spectrochemical series.