11.1 For each of the following configurations, construct a microstate table and reduce the table to its constituent free-ion terms. Identify the lowest-energy term for each.

a. p^3
b. p^1d^1 (as in a $4p^1$ $3d^1$ configuration)

11.2 For each of the lowest-energy (ground state) terms in **Problem 11.1**, determine the possible values of J. Which J value describes the state with the lowest energy?

11.3 An excited state of calcium has the configuration [Ar]$4s^13d^1$. For an s^1d^1 configuration, do the following:

a. Prepare a microstate table, showing each microstate.
b. Reduce the table to its free ion terms.
c. Determine the lowest-energy term.

11.4 The outer electron configuration of the element cerium is d^1f^1. For this configuration, do the following:

a. Construct a microstate table.
b. Reduce this table to its constituent free-ion terms (with labels).
c. Identify the lowest-energy term (including J value).

11.5 The nitrogen atom is an example of a valence p^3 configuration. There are five energy levels associated with this configuration, with the energies shown here.

Energies (cm^{-1})
28839.31
28838.92
19233.18
19224.46
0

a. Account for these five energy levels.
b. Using information from **Section 2.2.3** , calculate Π_c and Π_e

11.6 There is such a thing as an s^1f^1 configuration! This can occur, for example, in an excited state of a Pr^{3+} ion. For an s^1f^1 configuration, do the following:

a. Construct a microstate table, showing clearly the relevant quantum numbers of each electron in each microstate.
b. Reduce this table to its constituent free-ion terms (with labels).
c. Identify the lowest-energy term (including J value).

11.7 For each of the following free-ion terms, determine the values of L, M_L, S, and M_S:

a. $^2D(d^3)$
b. $^3G(d^4)$
c. $^4F(d^7)$

11.8 For each of the free-ion terms in **Problem 11.6** , determine the possible values of J, and decide which is the lowest in energy.
11.9 The most intense absorption band in the visible spectrum of $[Mn(H_2O)_6]^{2+}$ is at 24,900 cm^{-1} and has a molar absorptivity of 0.038 L mol^{-1} cm^{-1}. What concentration of $[Mn(H_2O)_6]^{2+}$ would be necessary to give an absorbance of 0.10 in a cell of path length 1.00 cm?
11.10

a. Determine the wavelength and frequency of 24,900 cm^{-1} light.
b. Determine the energy and frequency of 366 nm light.

11.11 Determine the ground terms for the following configurations:

a. d^8 (O^h symmetry)
b. high-spin and low-spin d^5 (O^h symmetry)
c. d^4 (T_d symmetry)
d. d^9 (D_{4h} symmetry, square-planar)

11.12 Identify the *first row* transition metal that satisfies the requirements given:

a. $[M(H_2O)_6]^{2+}$ having two unpaired electrons (list all possibilities).

b. $[M(NH_3)_6]^{3+}$ that may have splitting of spin-allowed absorption band as a consequence of distortion of excited state (provide one example).
c. $[M(H_2O)_6]^{2+}$ expected to have the palest color in aqueous solution.

11.13 The spectrum of $[Ni(H_2O)_6]^{2+}$ (**Figure 11.8**) shows three principal absorption bands, with two of the bands showing signs of further splitting. Referring to the Tanabe–Sugano diagram, estimate the value of $\boldsymbol{\Delta}_o$ Give a likely explanation for the further splitting of the spectrum.

11.14 From the following spectral data, and using Tanabe–Sugano diagrams (**Figure 11.7**), calculate $\boldsymbol{\Delta}_o$ for the following:

a. $[Cr(C_2O_4)_3]^{3-}$, which has absorption bands at 23,600 and 17,400 cm^{-1}. A third band occurs well into the ultraviolet.
b. $[Ti(NCS)_6]^{3-}$, which has an asymmetric, slightly split band at 18,400 cm^{-1}. (Also, suggest a reason for the splitting of this band.)
c. $[Ni(en)_3]^{2+}$, which has three absorption bands: 11,200, 18,350, and 29,000 cm^{-1}.
d. $[VF_6]^{3-}$, which has absorption bands at 14,800 and 23,250 cm^{-1}, plus a third band in the ultraviolet. Also calculate B for this ion.
e. The complex $VCl_3(CH_3CN)_3$, which has absorption bands at 694 and 467 nm. Calculate $\boldsymbol{\Delta}_o$ and B for this complex.

11.15 $[Co(NH_3)_6]^{2+}$ has absorption bands at 9,000 and 21,100 cm^{-1}. Calculate $\boldsymbol{\Delta}_o$ and B for this ion. (Hints: The ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition in this complex is too weak to be observed. The graph in **Figure 11.13** may be used for d^7 as well as d^2 complexes.)

11.16 Classify the following configurations as A, E, or T in complexes having O_h symmetry. Some of these configurations represent excited states.

a. $t_{2g}^4 e_g^2$
b. t_{2g}^6

c. $t_{2g}^3\ e_g^3$

d. t_{2g}^5

e. e_g

11.17 Of the first-row transition metal complexes of formula $[M(NH_3)_6]^{3+}$, which metals are predicted by the Jahn–Teller theorem to have distorted complexes?

11.18 MnO_4^- is a stronger oxidizing agent than ReO_4^-. Both ions have charge-transfer bands; however, the charge-transfer band for ReO_4^- is in the ultraviolet, whereas the corresponding band for MnO_4^- is responsible for its intensely purple color. Are the relative positions of the charge-transfer absorptions consistent with the oxidizing abilities of these ions? Explain.

11.19 The complexes $[Co(NH_3)_5X]^{2+}$(X = Cl, Br, I) have charge transfer to metal bands. Which of these complexes would you expect to have the lowest-energy charge-transfer band? Why?

11.20 $[Fe(CN)_6]^{3-}$ exhibits two sets of charge-transfer absorptions, one of lower intensity in the visible region of the spectrum, and one of higher intensity in the ultraviolet. $[Fe(CN)_6]^{4-}$, however, shows only the high-intensity charge transfer in the ultraviolet. Explain.

11.21 The complexes $[Cr(O)Cl_5]^{2-}$ and $[Mo(O)Cl_5]^{2-}$ have C_{4v} symmetry.

a. Use the angular overlap approach (**Chapter 10**) to estimate the relative energies of the *d* orbitals in these complexes.

b. Using the C_{4v} character table, determine the symmetry labels (labels of irreducible representations) of these orbitals.

c. The $^2B_2 \rightarrow {}^2E$ transition occurs at 12,900 cm^{-1} for $[Cr(O)Cl_5]^{2-}$ and at 14,400 cm^{-1} for $[Mo(O)Cl_5]^{2-}$. Account for the higher energy for this transition in the molybdenum complex. (See W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, John Wiley & Sons, New York, 1988, pp. 33–35.)

11.22 For the isoelectronic series $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)x_6]^+$, would you expect the energy of metal to ligand charge-transfer bands to increase or decrease with increasing charge on the complex? Why? (See K. Pierloot, J. Verhulst, P. Verbeke, L. G. Vanquickenborne, *Inorg. Chem*., **1989**, *28*, 3059.)

11.23 The compound *trans*-(*o*-phen)$_2$ (NCS)$_2$ has a magnetic moment of 0.65 Bohr magneton at 80 K, increasing with temperature to 5.2 Bohr magnetons at 300 K.

a. Assuming a spin-only magnetic moment, calculate the number of unpaired electrons at these two temperatures.
b. How can the increase in magnetic moment with temperature be explained? (Hint: There is also a significant change in the UV-visible spectrum with temperature.)

11.24 The absorption spectrum of the linear ion NiO_2^{2-} has bands attributed to *d–d* transitions at approximately 9,000 and 16,000 cm^{-1}.

a. Using the angular overlap model (**Chapter 10**), predict the expected splitting pattern of the *d* orbitals of nickel in this ion.
b. Account for the two absorption bands.
c. Calculate the approximate value of e_σ and e_π (See M. A. Hitchman, H. Stratemeier, R. Hoppe, *Inorg. Chem*., **1988**, *27*, 2506.)

11.25 The electronic absorption spectra of a series of complexes of formula $Re(CO)_3(L)(DBSQ)$ [DBSQ = 3,5-di*tert*-butyl-1,2-benzosemiquinone] show a single maximum in the visible spectrum. The absorption maxima for three of these complexes in benzene solution are shown; typical molar absorptivities are in the range of 5,000 to 6,000 L mol^{-1} cm^{-1}.

L	***V**max*, **cm^{-1}**
$P(OPh)_3$	18,250
PPh_3	17,300
NEt_3	16,670

Are these bands more likely due to charge transfer to metal or charge transfer to ligand? Explain briefly. (See F. Hartl, A. Vlcek, Jr., *Inorg. Chem*., **1996**, *35*, 1257.)

11.26 The d^2 ions CrO_4^{4-}, MnO_4^{3-}, FeO_4^{2-}, and RuO_4^{2-} have been reported.

a. Which of these has the largest value of Δ_t? Which has the smallest? Explain briefly.
b. Of the first three, which ion has the shortest metal–oxygen bond distance? Explain briefly.
c. The charge-transfer transitions for the first three complexes occur at 43,000, 33,000, and 21,000 cm^{-1}, respectively. Are these more likely to be ligand-to-metal or metal-to-ligand charge-transfer transitions? Explain briefly. (See T. C. Brunhold, U. Güdel, *Inorg. Chem.*, **1997**, *36*, 2084.)

11.27 An aqueous solution of $Ni(NO_3)_2$ is green. Addition of aqueous NH_3 causes the color of the solution to change to blue. If ethylenediamine is added to the green solution, the color changes to violet. Account for the colors of these complexes. Are they consistent with the expected positions of these ligands in the spectrochemical series?

11.28 The pertechnetate ion, TcO_4^-, is often used to introduce the radioactive Tc into compounds, some of which are used as medical tracers. Unlike the isoelectronic, vividly purple permanganate ion, pertechnetate is very pale red.

a. Describe the most likely absorption that gives rise to colors in these ions. In addition to a written description, your answer should include an energy-level sketch showing how *d* orbitals on the metals interact with oxide orbitals to form molecular orbitals.
b. Suggest why TcO_4^- is red but MnO_4^- is purple.
c. The manganate ion, MnO_4^{2-}, is green. On the basis of your answers to a and b, provide an explanation for this color.

11.29 A 2.00×10^{-4} M solution of $Fe(S_2CNEt_2)_3$ ($Et = C_2H_5$) in $CHCl_3$ at 25° C has absorption bands at 350 nm (A = 2.34), 514 nm (A = 0.532), 590 nm (A = 0.370), and 1540 nm (A = 0.0016).

a. Calculate the molar absorptivity for this compound at each wavelength.
b. Are these bands more likely due to *d*–*d* transitions or charge-transfer transitions? Explain.

11.30 Use the following spectral data to find the term symbols for the ground and excited states of each species, and calculate Δ_o and the Racah parameter, *B*, for each.

Species	Absorption Bands (cm^{-1})		
$[Ni(H_2O)_6]^{2+}$	8,500	15,400	26,000
$[Ni(NH_3)_6]^{2+}$	10,750	17,500	28,200
$[Ni(OS(CH_3)_2)_6]^{2+}$	7,728	12,970	24,038
$[Ni(dma)_6]^{2+}$	7,576	12,738	23,809

11.31 For compounds $[Co(bipy)_3]^{2+}$ and $[Co(NH_3)_6]^{2+}$, do the following:

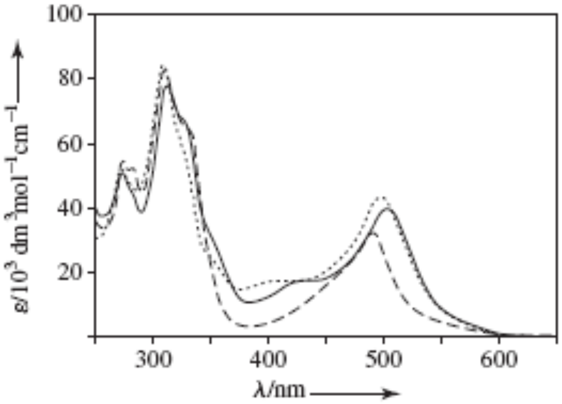
a. Find the ground-state term symbol.
b. Use the Tanabe–Sugano diagram to identify the predicted spectral bands.
c. Calculate the ligand field stabilization energy.
d. Do you expect broad or narrow absorption bands in the visible and UV regions?
e. Sketch an MO energy level diagram for each.

	$v_1(cm^{-1})$	$v_3(cm^{-1})$
$[Co(bipy)_3]^{2+}$	11,300	22,000
$[Co(NH_3)_6]^{3-}$	9,000	21,100

11.32 In the complexes $FeL(SC_6H_5)$ and $NiL(SC_6H_5)$, where L = hydrotris(3,5-diisopropylpyrazolylborate) $HB(3,5\text{-i-}Pr_2pz)_3^-$, strong charge-transfer bands were observed in the regions 28,000 to 32,500 and 20,100 to 30,000 cm^{-1}, respectively. Were these more likely LMCT or MLCT bands? Explain, taking into account the relative energies of the metal orbitals in these complexes. (See S. I. Gorelsky, L. Basumallick, J. Vura-Weis, R. Sarangi, K. O. Hodgson, B. Hedman, K. Fujisawa, E. I. Solomon, *Inorg. Chem.*, **2005**, *44*, 4947.)

11.33 Various models for the iron hydrogenase active site covalently linked to a ruthenium photosensitizer have been synthesized as candidates for light-driven proton reduction. A prototype for this class of complexes features a phenylacetylene linker between the iron and ruthenium portions of the molecule (S.

Ott, M. Borgström, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström, L. Sun, *Inorg. Chem.*, **2004**, *43*, 4683). Sketch the target complex. Provide three reasons for inclusion of the phenylacetylene linker, and assign the two most intense bands in its electronic absorption spectrum (solid line in spectrum). Briefly explain why this complex is unable to induce proton reduction.



11.34 The complex in **Figure 11.18** successfully induces photoinduced proton reduction, but with very low activities. Provide two reasons why using naphthalene monoimide dithiolates as the linker between the photosensitizer and the active site for proton reduction was considered desirable. What spectral argument was used to reason that the ground state zinc porphyrin moiety does not interact electronically with the diiron portion of this complex?