Problems:

1) Determine all the vibrations present in CO_2 and N_2O. Sketch the vibrational motions. In the IR spectrum of CO_2 two intense peaks occur at 667 and 2349 cm^{-1}. How would you assign them in the proper symmetry group for a linear molecule? For N_2O three intense IR absorptions occur at 598, 1285, and 2224 cm^{-1}. How would you assign these vibrations? (Hint: CO_2 and N_2O are isoelectronic and closely analogous) Nitrous oxide is 310 times as effective as CO_2 as a greenhouse gas. Suggest one possible reason why.

2) How many infra red and Raman active vibrations would you expect to see for $Mn_2(CO)_{10}$ in the C-O stretching frequency region of the spectra if it were a) eclipsed or b) staggered with respect to rotation around the metal-metal bond axis. Could you tell the two geometries apart from the vibrational spectroscopic data? If you don't know the structure, based on a C_4 principal axis, then look it up in an inorganic text.

3) How would you expect the IR absorptions for the S-O stretches (1030 - 1140 cm^{-1}) in the sulfate ion to differ for it as a counter ion, as in $[Co(NH_3)_6][SO_4]$, versus when it binds as a monodentate ligand as in $[Co(NH_3)_5(SO_4)][Br]$?

4) Would you be able to distinguish all possible geometric isomers of the trigonal bipyramidal complex $Fe(CO)_3(PPh_3)_2$ with a combination of infra red and Raman spectroscopy? Explain your reasoning.

5) How might you use vibrational spectroscopy to determine whether an oxalate complex $M(C_2O_4)_2$ was planar or nonplanar (plane of bound oxalate ligands at right angles)?

Answers to Problems:

1) CO_2 a $\square_g^+$ symmetric stretch, a doubly degenerate $\square_u$ bending vibration and a $\square_u^+$ antisymmetric stretch account for the 3N-5 = 4 vibrational degrees of freedom. Only $\square_u^+$ and $\square_u$ are IR allowed. The high frequency vibration (2349 cm^{-1}) is the stretch and the low frequency is the bend (667 cm^{-1}), since bending deformations always require less energy than stretches. N_2O has a $\square^+$ symmetric stretch (1285 cm^{-1}), a $\square^+$ asymmetric stretch (2224 cm^{-1}), and a $\square$ bending vibration (598 cm^{-1}). The assignments are by analogy to carbon dioxide. Although the N=O and N=N stretches are different, due to the similar bonding (isoelectronic with CO_2) and similar masses and bond strengths the two $\square^+$ stretches mix strongly to yield normal modes very similar to those of CO_2. Nitrous oxide is a stronger greenhouse gas than CO_2 because 1) it has more allowed IR absorptions; 2) it absorbs in the water-CO_2 IR window; 3) it exhibits a greater change in dipole moment in its vibrations; 4) there are many more combination and overtone vibrations that fall in the IR window. Other important considerations include atmospheric residence times.

2) In eclipsed D_{4h} symmetry the axial CO groups span $a_{1g} + a_{2u}$ and the equatorial groups $a_{1g} + b_{1g} + a_{2u} + b_{2u} + e_g + e_u$. Since the IR active vibrations are a_{2u} and e_u, while the Raman active vibrations are a_{1g}, b_{1g}, b_{2g}, and e_g then there should be 3 absorptions in the IR spectrum and 4 in the Raman spectrum.

For the staggered D_{4d} geometry the axial CO stretches are $a_1 + b_2$ and the equatorial stretches are $a_1 + b_2 + e_1 + e_2 + e_3$. Transitions from the ground state to e_1 and b_2 vibrations are IR allowed, while a_1, e_2, and e_3 should have Raman intensity. Thus there should be 3 IR absorptions and 4 in the Raman. Neither technique alone could distinguish between the two possible structures. It might be possible to use the coincidence of the b_2 to both the IR and Raman spectra for the D_{4d} case to distinguish it from the D_{4h} isomer where there should be no coincidence between the IR and Raman spectra.

3) Refer back to 10.4 in your text. There is one IR sulfate absorption (T_2) expected if the ion is not coordinated and 2 (a_1 + e) IR absorptions if bound. Note the M-O-S mode is at low frequency and not in the 1030-1140 cm^{-1} region.

4) There are three possible isomers, trans phosphines D_{3h}, one phosphine axial and one equatorial is C_s symmetry, and the isomer with both phosphines equatorial is C_{2v}. In D_{3h} the CO stretches transform like a_1' and e'. Both are allowed in the Raman spectrum, but only the e' stretch is IR allowed. In C_s the CO stretches transform like 2a' + a'', while in C_{2v} they are $2a_1 + b_1$. Unfortunately, in the lower symmetry point groups all three stretches are allowed in both the IR and Raman, so vibrational spectroscopy can only be used to distinguish the D_{3h} isomer from the other two.

5) The planar structure is of D_{2h} symmetry and the nonplanar structure is of D_{2d} symmetry. Only the 4 C=O stretches at high frequency need be considered. The representation spanned by them are:

$D_{2h} = a_g + b_{1g} + b_{2u} + b_{3u}$ with the 2 g vibrations being Raman active and the 2 u vibrations are IR active. There are no common peaks in the IR and Raman due to the inversion center.

$D_{2d} = a_1 + b_2 + e$ with all 3 Raman allowed, but only b_2 and e are IR allowed.

2) You should obtain $4a_1 + a_2 + 2b_1 + 2b_2$. Three of these are characteristic of the CF_2 fragment and another three (of the same symmetry, except $b_1 \to b_2$) of the CCl_2 fragment. These correspond to an a_1 symmetric stretch, a b_1 (or b_2) antisymmetric stretch, and an a_1 deformation vibration. The remaining a_2, b_1, and b_2 vibrations correspond to a torsional motion around the unique axis, and complex rocking of the CF_2 and CCl_2 groups with respect to the whole molecule. All except a_2 are IR active.

3) Additional peaks of reasonable intensity arise from combination and overtone bands. The presence of these additional peaks results in an enhanced greenhouse effect for the molecule and magnifies the difference between CO_2 and N_2O The peaks and assignments are:

1167 ~ 2 x 598

1868 ~ 1285 + 598

2461 ~ 1285 + 2 x 598

2563 ~ 2 x 1285

2798 ~2224 + 598

3366 ~ 2224 + 2 x 598

3481 ~ 2224 + 1285

4420 ~ 2 x 2224

4735 ~ 2224 + 2 x 1285

4) The lowest one electron transition is $e_{2g} \dashrightarrow a_{1g}$. This $e_{2g}^3 a_{1g}^1$ configuration will generate the ${}^1E_{2g}$ excited state. This is dipole forbidden, as the ground state is ${}^1A_{1g}$, but will be vibronically allowed by coupling with a vibration of symmetry such that the direct product $E_{2g} \bullet \mathrm{vib} \bullet a_{2u}$ or $E_{2g} \bullet \mathrm{vib} \bullet e_{1u}$contains the totally symmetric representation. This will occur for vibrations of e_{2u} and e_{1u} symmetry. The skeletal vibrations of ferrocene include two e_{1u} vibrations corresponding to a ring tilt and a metal-ring slip (p391 of Nakamoto). Thus, this transition is vibronically allowed. The next promotion $e_{2g} \dashrightarrow a_{2u}$, gives rise to the excited singlet state ${}^1E_{2u}$. This is not dipole allowed either. The next $e_{2g} \dashrightarrow e_{1u}$ promotion yields ${}^1E_{2u}$ and ${}^1E_{1u}$ states. The transition ${}^1A_{1g} \dashrightarrow {}^1E_{1u}$ is dipole allowed with x,y polarization.

5) The ferrocinium cation has a hole in the e_{2g} orbital, which would yield a ${}^2E_{2g}$ ground state. This is forbidden by the Jahn-Teller distortion and should distort from D_{5d} symmetry along the a_{2g} or e_{1g} normal modes. The e_{1g} ring tilt is one possibility.