

**FINAL PROBLEM SET**  
**CHEMISTRY 250B**  
**DUE APR 18, 2008**  
**DELIVERED APR 23, 2008**

SILVIO LEVY

**1a.** Assign the formal oxidation states of vanadate, chromate, and permanganate and give their  $d$  electron counts.

**Solution:** Vanadate: +5; Chromate: +6; Permanganate: +7. The  $d$  electron count is 0 in each case, so all these ions are diamagnetic.

**1b.** Out of the following list, pick the type(s) of spectroscopy that would not be helpful for studying the properties of permanganate: electronic absorption, circular dichroism, electron paramagnetic resonance, infrared, Raman.

**Solution:** EPR is not useful because there are no unpaired electrons. CD is not useful because the ion (and the crystal) is not chiral.

**1c.** Provide the energy of  $\Delta_t$  for permanganate.

**Solution:**  $\Delta_t$  is the tetrahedral crystal field splitting, between the doubly degenerate  $e$  orbital and the triply degenerate  $t_2$  orbital. In the diagram provided, these orbitals are labeled  $1e$  and  $2t_2$ , and their separation is approximately  $8,000 \text{ cm}^{-1}$ . Hence  $\Delta_t \approx 8,000 \text{ cm}^{-1}$ .

**1d.** Describe the type of electronic transition that gives rise to the color of permanganate.

**Solution:** It's a charge-transfer interaction (LMCT). In the excited state, electronic charge is transferred from the ligand to the metal, momentarily reducing it.

**1e.** The MO scheme for vanadate looks very similar to permanganate, although the former is colorless whereas the latter is purple-colored. Provide a brief explanation for this fact.

**Solution:** In vanadate, the same charge-transfer band is present but it appears in the ultraviolet, due to larger energy separation. (The greater nuclear charge of Mn relative to V means that the bond length is shorter.)

**2a.** How many IR- and Raman-active CO bands would you predict for the  $D_{3d}$  form, and what are their symmetry labels? (Hint, do normal coordinate analysis on axial and equatorial CO ligands separately).

We first consider the axial CO's. There are two stretch normal modes for the axial CO bonds, just as in  $\text{CO}_2$ : the symmetric and asymmetric stretches. The former is Raman active and the latter is IR active.

To justify this rigorously, we form the reducible representation associated with the system of axial CO's; in the usual ordering of the symmetry element classes ( $E, 2C_3, 3C_2, i, 2S_6, 3\sigma_d$ ) this representation  $\Gamma$  has coefficients 2, 2, 0, 0, 0, 2. Hence  $\Gamma = A_{1g} + A_{2u}$ . The symmetric stretch belongs to the  $A_{1g}$  representation, which is that of  $x^2 + y^2$  and  $z^2$ , so it's Raman active; no linear polynomial belongs to this representation, so the mode is not IR active. Conversely, the asymmetric stretch belongs to  $A_{2u}$  which is the mode of  $z$  and of no quadratic polynomial. Hence the mode is IR active but not Raman active. (In general, for a molecule with a center of symmetry, no mode can be both IR and Raman active.)

Now moving to the equatorial CO's, we see that the reducible representation  $\Gamma$  has coefficients 6, 0, 0, 0, 0, 2. Hence  $\Gamma = E_g + E_u + A_{1g} + A_{2u}$ . Consulting the character table (page 7 of the loose insert to Cotton) we see that  $E_g$  and  $A_{1g}$  are Raman active and  $A_{2g}$  is IR active, while  $E_u$  and  $A_{2u}$  are IR active.

Since each  $E$  representation accounts for 2 normal modes, there is a total of 4 IR active modes and 4 Raman active modes.

**2b.** *Would the  $C_{2v}$  form have a greater, a fewer, or the same number of CO-derived vibrational bands as the  $D_{3d}$  form? Provide your reasoning.*

**Solution:** The  $C_{2v}$  form have more bands, because of lower symmetry. Specifically, considering all the CO's together, the reducible representation has coefficients 8, 0, 2, 2, and so  $\Gamma = 3A_1 + A_2 + 2B_1 + 2B_2$ . All the modes are Raman active (character table, page 4 of the loose insert to Cotton) and all but one mode is IR active (the exception is the  $A_2$  mode).

**3a.** *Work by Gray, Holm, Davison, and others on nickel dithiolenes in the 1960s showed some of the first examples of non-innocent ligand behavior in metal complexes. As discussed in class, the application of EPR spectroscopy was key to this realization. Provide some alternative experiments that could be used to establish this idea.*

**3b.** *Is a molecule in its excited state a better, worse, or similar oxidant compared to when its in its ground state? What about as a reductant? Give your reasoning.*

**Solution:** A molecule in its excited state is a better reductant and a poorer oxidant than the same molecule on the ground state. The reason is this: as a reductant, the molecule must lose an electron, and the energy required for this is less if the molecule is in an excited state than if it is in the ground state. Conversely, as an oxidant, the molecule will gain an electron.

**3c.** *Explain the differences between the terms fluorescence, phosphorescence, and luminescence.*

**Solution:** Fluorescence: a photon is absorbed placing the molecule in an excited electronic state; the molecule very quickly decays back to the ground state emitting a photon with a longer wavelength (the difference in energy being lost as heat).

Phosphorescence: a photon is absorbed placing the molecule in an excited electronic state; the molecule transitions to a state (usually a triplet state for diamagnetic species) from which the transition to the ground state is spin-forbidden, and therefore takes a macroscopic amount of time to occur (lifetimes greater than say  $10^{-5}$  sec).

Luminescence refers to any non-thermal emission of electromagnetic radiation. It also can refer specifically to chemoluminescence, where a chemical reaction produces a molecule in an excited state, when then decays to the ground state by emitting a photon.

**3d.** *Place the following spectroscopic techniques in order from lowest energy electromagnetic radiation to highest: electronic absorption, electronic emission, circular dichroism/magnetic circular dichroism, electron paramagnetic resonance, infrared, Raman, X-ray absorption, Mössbauer*

**Solution:** EPR (microwave); infrared; MCD (near infrared, visible); electronic absorption (vis, near UV); electronic emission (near to far UV); CD (vis to far UV); X-ray absorption (and XMCD, X-ray magnetic circular dichroism); Mössbauer (gamma rays).