5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
5.76 Modern Topics in Physical Chemistry
Spring, 1996

Problem Set #2

DUE: At Noon on March 18

Look at the table of data on CO and CO^+. Use those data and the atomic orbital energies

		IE(nℓ)/cm^{-1}
C	2s	124,613
C	2p	90,878
O	2s	229,675
O	2p	109,837

to set up an MO diagram for CO.

A. The "valence orbitals" are 3σ, 4σ, 5σ, 6σ, 1π, 2π. Use the atomic orbital and CO, CO^+ spectroscopic data to estimate each of the valence molecular orbital energies (in cm^{-1}) relative to a zero of energy at CO^+ $X^2\Sigma^+$ v = 0, J = 0. To do this you will have to "assign" several observed Λ-S states to low-lying configurations.

B. Use your MO diagram, interpreted by perturbation theory, to describe each MO as localized more on C or on O.

C. Use your MO diagram to <u>predict</u> and <u>describe</u> the lowest energy electronic transition observable in absorption for CO. Is the transition red or blue degraded? What are the symmetries of the upper and lower states? Is there more than one electronic transition in contention for your predicted lowest energy absorption transition? If so, how could you distinguish the two possibilities?

D. Compare the energy of the highest filled and lowest empty MO in the CO ground state to the "work function" of typical metals (3–6eV = 24,000 – 48,000 cm^{-1}). What does this imply about which end of CO will bind to the metal and what will happen to the vibrational frequency when CO chemisorbs on a metal?

E. Obtain RKR and Franck-Condon programs from Robert LeRoy's web site. Compute the Franck-Condon factors for the transition you predicted to be the lowest energy electronic transition. Use the molecular constants from the data table provided. Calculate the Franck-Condon factors for $0 \le v'' \le 9$, $0 \le v' \le 19$. You may need a value for the Dunham constant Y_{00}

$$Y_{00} = \frac{B_e}{4} + \frac{(\alpha_e)(\omega_e)}{12B_e} + \frac{\alpha_e^2\omega_e^2}{144B_e^3} - \frac{\omega_e x_e}{4}.$$