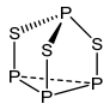
3.3: Exam 3

1. **(29 pts)** The simplest stable phosphorous sulfide, tetraphosphourous trisulfide, P_4S_3 is shown below. The bands observed in the IR and Raman spectra of P_4S_3 in gas phase, melt and solution are listed.

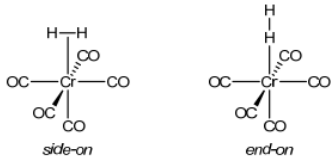


Infrared Data: ν / cm^{-1}	**Gas (550 °C)**	**Raman Data: Δ / cm^{-1} Melt (250 °C) CS_2 (25 °C)**	
		142	
184		187	
218	221	218	223
286	292	287	291
339	347	339	343
414	420	420	423
438	446	440	444

a. **(20 pts)** Determine the normal modes of vibration for P_4S_3 and how they transform.

b. **(9 pts)** Which are Raman and IR active?

2. **(41 pts)** A molecular orbital analysis of transition metal dihydrogen complexes provides critical insight into the bonding interactions between metals and hydrogen and established an elegant framework in which the reactivity between H_2 and transition metal complexes can be interpreted.



a. **(10 pts)** Construct the molecular orbital diagram of a side-on bonded $Cr(CO)_5(H_2)$ from group fragment orbitals.

b. **(6 pts)** Pictorially illustrate the σ and π interactions that stabilize the formation of the dihydrogen complex.

c. **(15 pts)** These interactions can effectively be used to rationalize several aspects of TM dihydrogen chemistry. In this regard, explain the following observations:

i. **(5 pts)** d^6 metals appear to form the most stable TM dihydrogen complexes

ii. **(5 pts)** many TM dihydrogen complexes synthesized to date have ancillary π-accepting ligands

iii. **(5 pts)** first row transition metals stabilize dihydrogen compounds while third row metals tend to promote dihydride compounds

d. **(10 pts)** Construct the MO diagram for an end-on bonded H_2 complex; and explain why (using the end- and side-on MO diagrams) end-on complexes are not favored energetically relative to side-on complexes.

3. **(30 pts)** The nitrogen chemistry of early transition metals was established with the preparation of the Ti complexes from the Bercaw group at Caltech during the mid-1970s. One of the compounds is shown below. Construct the qualitative molecular orbital diagram for the dinuclear titanium complex from the frontier orbitals of the bent Cp_2Ti fragment (in C_{2v} symmetry) and the appropriate frontier molecular orbitals of nitrogen. Label the MO with appropriate symmetry labels, identify the nature of the bond (i.e., σ, σ*, π, π*) and fill up the MO with the appropriate number of electrons.