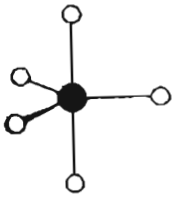
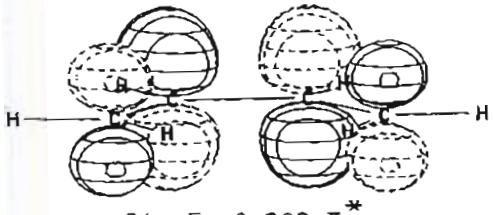
CHEM*3870 Molecular Spectroscopy
Problem Set 4
(Answers will be discussed during Week 12.)

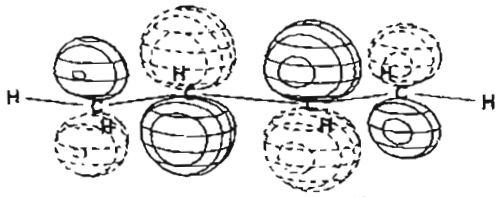
1. Determine the number and symmetries of the vibrational modes of PCl_5. Determine the contributions of bond stretches to the various vibrational modes. Determine the spectral activity of each mode. Give examples of combination bands which would be (a) infrared active and (b) Raman active.



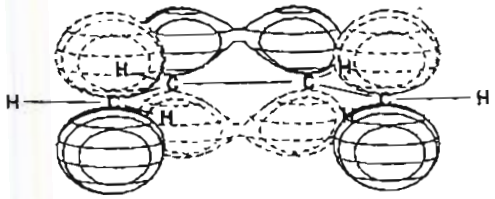
2. Compare the electronic spectra of cis- and trans-butadioene. Consider the two highest occupied and two lowest unoccupied π molecular orbitals. Determine the orbitally allowed electric dipole transitions and the polarization of each transition. Determine whether any orbitally forbidden electric dipole transitions may be vibronically allowed.



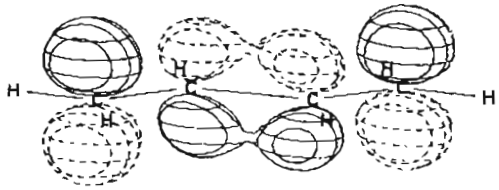
$2A_2$ E= 0.289 π^*_4



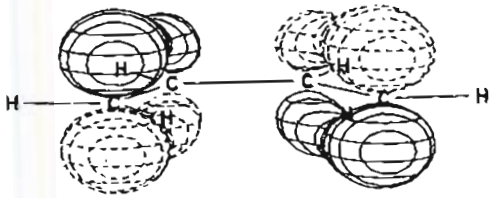
$2B_g$ E= 0.283 π^*_4



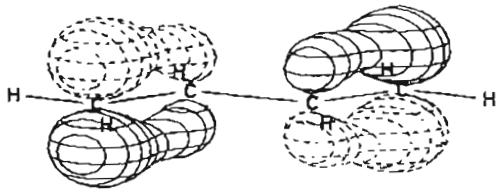
$2B_1$ E= 0.120 π^*_3



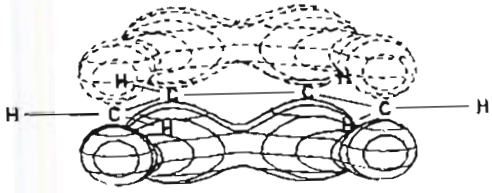
$2A_u$ E= 0.127 π^*_3



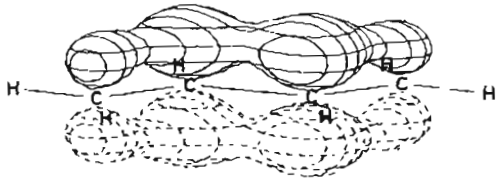
$1A_2$ E=-0.354 π_2



$1B_g$ E=-0.358 π_2



$1B_1$ E=-0.477 π_1



$1A_u$ E=-0.477 π_1