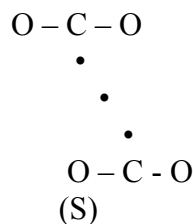
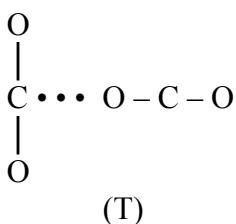


**Chem 343 Homework #2**  
**Assigned 11-Sep-07**  
**Due 20-Sep-07**

1. If you were developing a potential to do simulations of CO<sub>2</sub>, you would want to start by parameterizing the potential to the results of *ab initio* calculations on (CO<sub>2</sub>)<sub>2</sub>.

Among the possible structures are the slipped and T structures.



Let's assume rigid monomers.

- (a) Optimize the geometry of CO<sub>2</sub> at the MP2/aug-cc-pVDZ level of theory.
- (b) Optimize the T and S forms of (CO<sub>2</sub>)<sub>2</sub> at the MP2/aug-cc-pVDZ level of theory with fixed monomer geometries. What are the binding energies of the T and S structures with and without corrections for BSSE?
- (c) Using the geometries from step (b), do MP2/aug-cc-pVTZ(-f) and mP2/aug-cc-pVTZ calculations. How do your results change?
- (d) Estimate the complete basis set (CBS) limit binding energies. Comment on the relative importance of electrostatics, dispersion, and polarization for the interaction energies.
2. (a) Calculate the singlet excitation spectra of ethylene and benzene using the CIS method and the 3-21G and 6-31+G(d) basis sets.
- (b) Assign (*i.e.*, give the energy and symmetry/degeneracy) of all  $\pi \rightarrow \pi^*$  singly excited states.
- (c) Are all the  $\pi \rightarrow \pi^*$  valence states of benzene below the Rydberg states?
- (d) The lowest  $\pi \rightarrow \pi^*$  excited state of benzene is dipole forbidden. Why is it seen experimentally?
- (e) What is the energy gap between the  $\pi \rightarrow \pi^*$  singlet and triplet states of ethylene (use the 3-21G basis set).