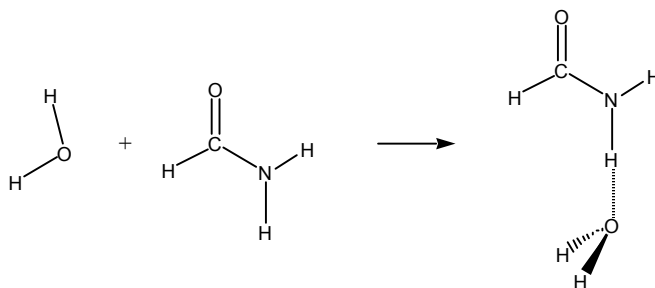


## Project V

Chemistry 5021/8021, Computational Chemistry, Spring, 2005

Assigned: April 27, 2005. Due: May 9, 2005

- 1 Use the CIS method to estimate the  $S_0 \rightarrow S_1$  excitation energy for acetone in the gas phase. You should do a full optimization at the HF/6-31G\* level, followed by single-point CIS calculations to obtain the transition energy. How would a polar protic solvent, such as water, affect the excitation energy to cause spectral shifts? You can explain it qualitatively, by examining, i.e., computing, relevant partial charges and dipole moments. Alternatively, you may want to use the polarizable continuum solvation model to determine quantitatively the solvatochromic shifts.
- 2 Returning to the same problem in Project IV, compute the interaction energy for the following complex using **three** different DFT methods with the 6-31G\* basis set. Make sure to use at least one hybrid method, and one without HF exchange. You decide what to choose for the third one since it is essentially anyone's game in making these decisions. As before, tabulate total energies in a.u. upto 5 decimal digits, and interaction energies in kcal/mol upto one decimal point. Compare the computation (CPU) time with HF calculations.



- 3 Construct an energy profile for the dissociation of CH<sub>4</sub> into CH<sub>3</sub> + H radicals using RHF/6-31G\*, UHF/6-31G\*, B3LYP/6-31G\*, and MP2/6-31G\* optimizations. Comment on your results and findings.