1.   Let's return to valine, which we examined in Problem Set 1. Early in the 20th century, Clough, Lutz, and Jirgensons found that if one added strong acid to an aqueous solution of a D-amino acid, thereby protonating it, the optical rotation measured for that amino acid became either *less* positive or, if the original rotation was negative, *more* negative. Conversely, if the optical rotation became *more* positive (or less negative), the amino acid was L. Let's see if valine obeys the CLJ rule.

To do that, optimize the three conformers of zwitterionic D-valine, and of protonated D-valine (you may ignore rotational isomerism of the carboxyl group once protonated—simply choose one oxygen to protonate for each zwitterionic rotamer case); do your work at the M06/6-311+G(d,p) level employing the SMD aqueous solvation model. Next, for each optimized rotamer, compute the optical rotation at the same level of theory. You will need the keywords `polar=optrot` and `cphf=rdfreq` for this calculation. Specify a frequency of 0.07732, which corresponds to measuring the optical rotation at the sodium D line, 589.3 nm.

In a neat and readable table (or tables), report the energies for all of your zwitterionic and protonated species, and then report the Boltzmann averaged molar rotations. Note that G09 reports the *specific* rotation. To convert your specific rotations to molar rotations, multiply by the molecular weight of the compound and divide by 100.

Do you predict valine to follow the CLJ rule? Experimentally, D-valine *is* observed to follow the CLJ rule, and the molar rotations of the zwitterion and cation are measured as –6.6 and –33.1 deg cm^2 $dmol^{-1}$ (the units are identical to those you'll get from converting G09's output as instructed above). How does the selected level do? If there are discrepancies, what steps might be taken that might be expected to improve agreement with experiment?

2.   Mixing $Ag(CN)_2$ and $Ni(CO)_4$ in chloroform under a CO atmosphere, you isolate a solid precipitate that microanalysis and mass spectroscopy indicate to be $NiC_4N_2O_2$. A ^{13}C NMR spectrum of the precipitate in chloroform with $Ni(CO)_4$ added as an internal standard shows a strong peak 6.6 ppm upfield from $Ni(CO)_4$ and a much smaller peak 8.4 ppm upfield from $Ni(CO)_4$. There is also a very strong peak 84 ppm upfield from $Ni(CO)_4$. An IR spectrum of the precipitate in a KBr pellet shows a strong absorption at 2154 cm^{-1} and very weak absorptions/shoulders at 2143, 2170, and 2188 cm^{-1}.

After three recrystallizations from diisopropyl ether, your solid is composed of beautifully twinned light orange crystals. NMR and IR spectra of the recrystallized solid show only the strong peaks noted above, and none of the weak ones.

An ultraviolet spectrum of the recrystallized solid in freon (who knew it would be soluble?) shows absorptions at 310 and 333 nm.

Here are the questions:

a. What is the structure of the molecules in the recrystallized solid? In a narrative fashion, describe in some detail how you came to your conclusion. Note that achieving 100% confidence can be very much more expensive than 99% confidence. It is perfectly OK to be satisfied with 99%.

b. To what electronic transitions do the two peaks in the UV spectrum correspond (show pictures of the orbitals)? Based on the nature of these transitions, how might you expect the geometries of the first and second excited states to differ from the ground state (don't do an excited-state geometry optimization, just infer from the orbitals).

3.   Consider the two pairs of isomeric iminium ions below that were studied in the last problem set. Our gas phase results were *not* consistent with the exocyclic double bond isomer **2** being more stable than **1**. Let's revisit the problem, as well as the question of activation free energies, using a continuum solvent model, in conjunction with possible explicit water catalysis for the tautomerization reactions.

| **1** | **2** | **3** | **4** |
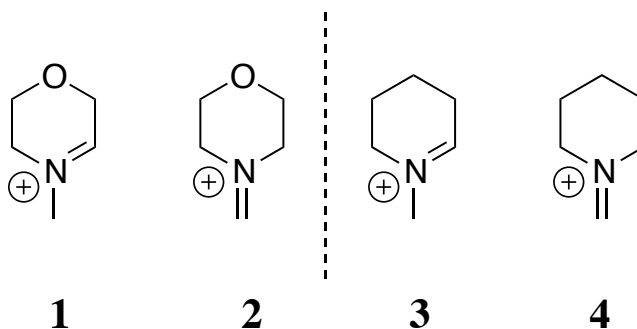
Reoptimize the minima, and proton-transfer transition-state structures, both with and without water catalysis, at the M06-2X/6-31+G(d,p) levels using the SMD aqueous continuum model. Do frequency calculations to determine thermal contributions to the 298 K free energy at that same level. Finally, do single-point calculations at the SMD/M06-2X/6-311+G(2df,2p) level

and add thermal contributions from the lower level to these electronic energies to get a best estimate of the free energy in solution.

Re-noting that it is observed that refluxing **1** in aqueous solution leads to **2**, is that consistent with these most recent calculations? If a significant change is observed compared to your earlier gas-phase results (you are welcome to refer to the answer key to Problem Set 2, should you need to), rationalize the effect of solvation. Finally, by how much does water catalysis lower the free energy of activation in the two systems? Note that you will need to pay careful attention to standard-state corrections for solutes, especially when including water as a solute.