Experiment 16
Supplemental Computational Exercise

The increased accuracy of computational methods and the speed of modern micro-chips has made computational studies an essential requirement of nearly any peer-reviewed publication. The simplest way to employ computational methods is through comparison of experimental data to computed data. This includes structure analysis (bond length and bond angle comparisons), and spectroscopic analysis (IR, Raman, NMR).

Since we are collecting IR data on the molybdenum carbonyl compound, you will also compute an infrared spectrum and make a comparison to your experimental results.

To compute a reasonably accurate infrared spectrum of your carbonyl compound you will need to employ a fairly high level of theory (in this case *ab-initio* or "first principles"). This essentially means a long computational time—hours rather than minutes. The main reason why we must use such a high level of theory is that the available semi-empirical methods do not include data for transition metals—most empirical methods are designed for problems involving organic compounds.

You will perform the computational analysis in two parts. **First optimize the geometry** of the molybdenum carbonyl complex at the HF (Hartree Fock) level of theory (or DFT), using the **LanL2DZ** basis set (this is one of only a few basis sets which includes data for the transition metals—most basis sets stop at argon). The time needed to complete the optimization will depend on the computer/processor you use. A minimum of 11 hours is expected, but most computers on campus will probably require closer to 1-2 days (because of limited memory). The DFT level of theory may require slightly greater computation time but is expected to give more accurate results. **Once the optimization is complete, do a frequency calculation using the optimized structure as the input**, employing the same level of theory and basis set used in the optimization. A minimum of 1 hr is required for completion of this computation.

Compare your computed IR spectrum to the experimental solution spectrum. You will likely note some significant differences because the computation does not include intermolecular interactions and solvent effects. Specifically, the calculation is for a "gas phase" spectrum, while the experimental spectrum is solution phase. While it is possible to account for solvent effects and intermolecular interactions in the computation, the methods are not especially simple or reliable at this time. A better comparison might be to obtain a solid state IR spectrum. If you have time I encourage you to do so.

Computational chemists usually scale their results using a scaling factor computed for a set of "standard" molecules (the need for a scaling factor is a consequence of a bias in the computational method). The scaling factor for the HF level of theory using the LanL2DZ basis set is 0.900 (± 0.058). [For more details see NIST's Computational Chemistry Comparison and Benchmark Database (http://srdata.nist.gov/cccbdb/).] Does scaling improve the match between your computed and experimental spectra?

Questions:

1. Compare the computed and "experimental" angles (determined from the CO intensities as outlined in your lab text), following the C-Mo-C angle.

2. Discuss the accuracy of the computation.