Experiment 4: Molecular Modeling
(Part II: Metal-Carbonyl Complex)

Molecular Vibrations in Metal-Carbonyl Complexes: [1,3,5-$C_6H_3(CH_3)_3$]Mo(CO)$_3$

As you know, infrared spectroscopy is a common technique used to characterize organic and inorganic compounds. Molecular vibrations that involve changes in the molecular dipole moment are detected as absorptions in the infrared region of the electromagnetic spectrum. Characteristic frequency ranges have been tabulated for a wide variety of functional groups and are routinely used in the identification of synthetic products.

Carbonyls – formally C-triple-bond-O groups – are ubiquitous ligands in organometallic chemistry and key functional groups for characterization of many transition-metal compounds. Terminal C-O groups (bound to single metal atoms) typically exhibit vibrations in the 1850-2125 cm^{-1} range, a relatively "empty" region of the spectrum. The exact frequencies of these vibrations are very sensitive to molecular geometry, and therefore provide further insight into product structure. In Experiment 6, you aimed to synthesize the organometallic compound [1,3,5-$C_6H_3(CH_3)_3$]Mo(CO)$_3$, relying on the distinctness of C-O vibrations to identify your product and investigate its geometry. Today, you will calculate and view the IR spectrum of this compound and predict the frequencies of its IR-active C-O stretches.

1. Open a **New** builder window and choose the **Inorganic** model kit. Select molybdenum from the periodic table and choose a tetrahedral connection geometry; click **Insert** and click to place the fragment in the workspace. Attach three carbonyl groups to the metal by choosing **carbon monoxide** from the **Ligands** pull-down menu; then, attach a **benzene Ligand**. (Make sure that your metal center is coordinated to all six carbons of the benzene ring.) Finally, add methyl groups to alternating carbons of the benzene ring to form mesitylene.

2. When you have finished building the compound, click on the **Minimize** button to perform the molecular-mechanics geometry optimization. **Save** the structure.

3. You will now improve on the molecular-mechanics geometry optimization using the **semi-empirical PM3** method, which is parameterized especially to determine equilibrium geometries of transition-metal complexes. Under **Setup**, select **Calculations** and check the appropriate boxes to determine the geometry of a neutral compound with no unpaired electrons. Be sure to calculate the **IR** spectrum. When you're finished, click **Submit**.

4. When the task is complete, you will likely see that the optimized geometry of the complex is at least slightly different from the one you initially built. Print the optimized geometry, viewed in **Ball and Wire** rendering. Orient the molecule so that its various bond angles are as clear to the viewer as possible.

5. Determine the three OC-Mo-CO bond angles (i.e., angles between the metal and the **carbonyl** carbons) in your optimized structure. Click the **Measure Angle** button; then, highlight three desired atoms. The measured angle is displayed in an output box in the lower right corner of the screen. Repeat for the other two OC-Mo-Co angles. Record these values. (If you have not done so yet, you will soon calculate bond angles for your synthetic product based on your measured IR spectrum. In your formal report for Experiment 6, you will need to compare these experimental versus theoretical results.)

6. Display the calculated IR spectrum and list of vibrational frequencies (as you did for the borane—amine adduct). How many vibrations are there in your list of frequencies? How many should there be for this molecule?

7. Go through the listed vibrations and find those that involve motions of the CO groups. Diagram each of the CO stretches you find and specify its calculated frequency. How many C-O peaks are predicted to appear in the IR spectrum of your synthesized product?

8. Use Group Theory to predict the IR-active C-O stretches for this molecule (number of stretches and their symmetries); show all your work. How many bands does this analysis predict in the C-O region of the IR spectrum?

9. Based on your Group-Theory analysis, provide symmetry labels for each of the stretches you diagrammed in #7 above. (Also, revisit your answer to #7 to be sure it is consistent with your Group-Theory-based prediction.)

To be turned in:
- Printout of your optimized geometry after PM3 calculations, labeled with measured OC-Mo-CO angles
- Answers to Questions 6-9.

Recall: The informal report described above (i.e., printout, answers to questions) and the formal report for Experiment 6 (incorporating modeling results) are due on Wednesday, March 28th.