

Experiment 7

Supplemental Computational Exercise

The objective of this exercise is to determine the most stable isomer of tetrachlorobis(dimethylsulfoxide) tin(IV) through comparison of computational results to the actual experimental data.

To minimize computational time you will perform calculations at a relatively low level of theory (semiempirical). The method was chosen primarily for speed of computation, thus the results must only be considered of qualitative value. We will use the computations to assess the relative stability of a set of tetrachlorobis(dimethylsulfoxide) tin(IV) linkage and geometrical isomers and to compute the IR spectra. Your computational assessment should aid in interpreting the experimental (IR) data.

Background

Experimental Dimethylsulfoxide (DMSO) can coordinate metal ions through either the sulfur or the oxygen. Both linkage isomers are known for a variety of metal complexes. In this case you will identify the most stable isomer based on IR analysis. Two different coordination geometries are also possible (*cis* vs *trans*). This computational study will aid in determining which is the most stable configuration and in interpreting the experimental IR spectrum.

Computational Semi-empirical methods have generally been developed primarily for the study of organic molecules. Semi-empirical methods are derived from and based on a limited set of experimental data. The “empirical” portion provides the necessary data to approximate reasonable solutions to the Schrodinger equation. The result is that computations can be fairly fast on very large molecules while still providing some very good, albeit qualitative results. Of course this works best if there are significant similarities between the molecule of interest and the parameterization set. The caveat is that not all atoms have parameters available, most notably heavier elements, including the transition metals.

Procedure

In your notebook take a moment to consider steric and electronic effects and any experimental data, and make a prediction regarding the most stable $[\text{SnCl}_4((\text{OS}(\text{CH}_3)_2)_2)]$ isomer. Briefly explain the logic behind your choice.

Using the Gaussian computational chemistry package construct models of the four geometrical and linkage isomers of $[\text{SnCl}_4((\text{OS}(\text{CH}_3)_2)_2)]$ and perform an Opt+Freq calculation on each isomer using the PM3 semi-empirical method. (Opt stands for optimization; Freq stand for frequency). When the calculation is complete open the Gaussian output file (called a log file) and then click on the Results menu to obtain a summary of the computational results. Successful location of a stationary minimum on the potential energy surface (which is searched when the geometry optimization is performed) is indicated by ZERO imaginary frequencies. In addition scroll through the log file to verify that the optimization (properly) converged.

Optimizations should proceed well (no errors) with the trans isomers. If your optimization fails there is likely something wrong with your original structure—try redrawing it and redoing the optimization or restart the optimization from a slightly different configuration. If your calculations continue to fail see your instructor.

Optimization of the cis-isomers appear to have a greater tendency to fail. For those optimizations, try restarting the calculation from a slightly different geometrical configuration. If the calculations continue to fail take a look at the last structure (before failure) and suggest a plausible reason for the failure.

Record the total energy of each of the isomers. Energies are typically given in hartrees: 1 hartree = 1 a.u. = 627.5095 kcal/mole = 2625.5 kJ/mol. Determine the most stable isomer from these energies. Was this result expected? Rationalize the outcome.

What the software does: Starting with the structure you provided, Gaussian iteratively determines the optimum (lowest energy) conformation followed by a frequency calculation, which generates spectral parameters as well as thermodynamic data.

Once you have determined the most stable isomer reload the computational results of that isomer and view the IR spectrum (vibrations). Attempt to identify the S=O stretch by animating each vibration and looking for significant S-O displacement. The S=O stretch occurs between 900-1160 cm^{-1} in a number of S or O bonded transition metal complexes of DMSO (see the instructors copy “Infrared and Raman Spectra of Inorganic and Coordination Compounds” by Kazuo Nakamoto for more information). The S-O stretch of free DMSO is reportedly at 1055 cm^{-1} (J. Phys. Chem., 64, 1534,1960). Compare the computed spectrum for the most stable isomer with the computed spectrum of the corresponding sulfur or oxygen linkage isomer. Are the S-O vibrations different? Do they differ from free DMSO? Explain.

Finally compare the experimental spectrum with the computed spectrum of the most stable isomer. Record all major vibrations in your notebook and print a hardcopy of the computed spectrum. Attempt to match the major vibrations of the computed spectrum with those of the experimental spectrum.

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 PM3 level of theory is reportedly 0.974 (± 0.08), though one should be cautioned that 17% of the frequencies in the standard set are still in error by more than 20% after scaling. [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?