## **Computational Chemistry**

(Last Revision: September 1, 2022)

## • ABSTRACT:

The student will use the Gaussian 16W/Gaussview 6 computational package to calculate molecular properties. You will calculate the isomerization energy for butadiene with density functional theory, calculate *ab initio* potential energy curves for the HCl molecule, and determine the structure of a molecule of your choosing.

• TEXT REFERENCE:

"Experiments in Physical Chemistry", Garland, Nibler, and Shoemaker, Eighth Ed., McGraw-Hill, 2009, pp. 70-71; 82-85.

- OTHER REFERENCES:
- GENERAL DESCRIPTION AND THEORY:

We may use computational methods to predict molecular properties. In the first part of this "experiment", you will calculate the potential energy curve for the HCl molecule using the unrestricted Hartree-Fock method, the Møller-Plesset second-order perturbation method, and a density functional method (B3LYP) with the aug-cc-pvdz basis set. Your report for this section will include a graphical comparison of the Morse potential and the ab initio potentials. In the second part, you will calculate the energies of the *cis* and *trans* conformers of butadiene using the B3LYP method. In the third part, you will determine the structure and vibrational spectrum of a molecule of your choosing.

• EQUIPMENT:

The computer laboratory computers running Gaussian 16W/Gaussview 6.

• CHEMICALS:

None.

• LABORATORY PROCEDURE:

**Part 1**: Open Gaussview 6 and build an HCl molecule. The first job will be a scan, using the unrestricted Hartree-Fock (UHF) method, using the aug-cc-pvdz basis set. This will calculate the HF energy of the HCl molecule as a function of bond length. Once the job is complete, the output file will have a list of bond

lengths and energies (in Hartrees). Optimize (calculating the force matrix always) the geometry starting with a bond length that matches that of the lowest observed energy in the preceding calculation. Run this program, which will determine the optimal geometry for the molecule and generate a vibrational spectrum. Take the optimized geometry and perform a frequency (anharmonic) calculation. The output files should be saved as HF HClpot.out, HF HCl opt.out, and HF HClfreq.out, respectively. Repeat these with the B3LYP method and the Møller-Plesset method, using the same basis set.

**Part 2**: Use Gaussview to build a rough model of a butadiene backbone. Add hydrogens and optimize the geometry using the b3lyp method and the 6/311++g(d,p) basis set. Calculate the vibrational spectrum to verify the optimization. Select the four carbon atoms and rotate the torsion angle by 180 degrees. Reoptimize, and calculate the vibrational spectrum for this conformer.

**Part 3:** Build a molecule of your choosing and optimize the geometry using the b3lyp method and the 6/311++g(d,p) basis set. Calculate the vibrational spectrum to verify the optimization.

• CALCULATIONS:

Plot the HCl potentials (energy in kJ/mole versus bond length in picometers) from your calculations. On the same graph, plot the Morse potential for HCl using the parameters found on page 70 of the text. Compare the equilibrium separations and vibrational frequencies with the literature values.

Determine the isomerization energy for butadiene by taking the difference in enthalpy between the two conformers. Compare the enthalpy of isomerization obtained in your calculation with that found in the literature.

Give a one-paragraph description of the properties found for your chosen molecule.

Your report will be emailed to the instructor no later than the due date.

• LITERATURE VALUES: