General Chemistry Lab
Molecular Modeling

PURPOSE

The objectives of this experiment are

- To learn how to use molecular modeling software, a commonly used tool in chemical research and industry.
- To examine the structures of a number of simple molecules to search for common factors affecting molecular structure.

PROCEDURE

There are a variety of software programs available to perform molecular modeling experiments; we will use a program called WebMO. First, you will learn how to build molecules, analyze bond lengths, analyze bond angles, analyze torsion angles and visualize your results. You will then use these skills to perform analyses on a series of small molecules.

PART I- INTRODUCTION TO THE WEBMO INTERFACE AND BASIC INSTRUCTIONS

What is WebMO?

WebMO is a web-based interface for computational chemistry programs that allows a user to log into a server that houses computational chemistry software via a web browser. The WebMO interface allows you to build molecules, setup/run state-of-the-art chemical calculations, and visualize the output of those programs. The WebMO server at SUNY Oneonta is currently configured to use the programs MOPAC2009 (semi-empirical), GAMESS (*ab initio* and semi-empirical), Gaussian09 (*ab initio* and semi-empirical), and TINKER (molecular mechanics). This laboratory exercise will introduce you to a small sampling of the different types of calculations that can be done. Links to full program documentation and an in-development SUNY Oneonta computational chemistry wiki can be found at http://irene.oneonta.edu.

Getting to WebMO:

The easy way:

- Go to http://irene.oneonta.edu and click on the WebMO link.

The lots-of-typing way:

- Go to http://137.141.16.193/~webmo/cgi-bin/webmo/login.cgi

Logging on to the WebMO Server:

Username= Your Oneonta username (i.e. the beginning of your email address)
Temporary Password= chemstudent

Notes:

- Passwords are case sensitive.
- Please change your password when you log in for the first time.
- When you log in, the page that appears is the Job Manager. Whenever you want to log out, select Logout at the top of the screen on the next page. If you have been viewing your results, just select Return to Job Manager and then log out.

To Change Your Password:

- Log on to the WebMO server.
- From the Utilities tab at the top of the window, select Edit Profile. Enter your new password.
- If you wish to change the email address linked to your WebMO account, select the Preferences tab on the screen where you changed your password and enter your preferred email address.

How to Build Molecules and Measure Bond Lengths and Angles

When you log on, the screen that appears is the Job Manager. Every calculation that you run (called a "job") will appear in this list. To begin building a molecule, select New Job. The molecule-building screen appears. A series of icons, or buttons, is on the left-hand side. The function of each appears if you hover the cursor over it.

Investigate the function of each button and record it on your report sheet in Table I.1.

Building a Molecule: You will first build a molecule of water, which you will return to in later parts of this lab. Click on the periodic table icon and select the element oxygen. Click anywhere on the screen and a red "oxygen atom" will appear. Next, select the periodic table again and pick hydrogen. Click on the screen near the oxygen atom and a small white "hydrogen atom" appears. To create bond between the hydrogen and the oxygen, click on one of the two atoms and drag the mouse to the other atom while holding down the left mouse button.[1] Click on the screen again and another hydrogen atom will appear. Create a bond between this atom and the oxygen. Select the rotate button to leave the "build" mode. Hold the left mouse button down and move the mouse to rotate the molecule. Try this with the translate and zoom buttons, as well, to examine all of the ways that you can view your three-dimensional model of water.

[1] To create a double-bond between two atoms, simply click on one of the atoms a second time and drag to the other atom to create a second bond.

Correcting the geometry of your molecule quickly: You now have a model of a water molecule, but the geometry of your model is probably quite different from that of a real water molecule. *Every time you build a molecule you must optimize the geometry*. You can do this quickly, by selecting either the paintbrush () or wrench () buttons (Comprehensive Cleanup Using Idealized Geometry or Mechanics). Click on one and then the other and observe what happens to your model.

Measuring bond lengths and angles: To measure a bond length, click on the adjust button (). In this mode, if you click on an atom, the charge and hybridization of that atom will appear in the status bar[2] at the bottom of the drawing window. To see the bond length for a bond, click on one of the atoms involved in the bond, then hold the shift key down and click on the other. The bond length now appears at the bottom. To view the bond angle, simply hold the shift key down and click on a third atom, which will define the angle. To return to the mode where you can move the molecule around, click on the rotate button ().

Measure the bond lengths and angles of your water molecule for both of the "quick" geometry optimization methods described above and record them in Table I.2 of your report sheet.

Correcting the geometry of your molecule with a semi-empirical[3] calculation: To run a more thorough calculation to correct your model's geometry, click on the right arrow at the bottom of the window (). This begins a series of windows where you can specify details of a calculation. Select "Gaussian" as the computational engine and click the right arrow again. On the next screen, you can type any name you want into the "Job Name" box. Choose a name that will help you remember what the calculation is (for example, you could call this job "water optimization"). For the Calculation type, select "Geometry optimization" from the pull-down menu. Leave the theory, charge, and multiplicity options at their default values. Click on the right arrow to start the calculation. The "Job Manager" screen appears. Whenever you run a calculation, it will appear in this list and is available for review any time you log on to the server. If you have a job that is still running, you can select "New Job" and work on another molecule while you wait.

---

[2] The status bar at the bottom of the viewing window will show the current mode (view, select, etc.) and other information (e.g. bond length, bond angle, which type of viewing mode you are in).

[3]There are different theories/methods for calculating molecular properties, each with its own strengths and weaknesses. Semi-empirical techniques work well for determining molecular geometries.

Viewing the results of your calculations: To view the results of a calculation, start from the Job Manager window and click on either the job name or the view icon (🔎) that appears in the "Actions" column for that job. The screen that appears looks like the molecule-building window with the molecule of interest displayed. Scroll down the browser screen to view tabulated results for your calculation. Different tables will appear depending on the type of calculation. Many of these will have a view icon (🔎) at the top of the table. Clicking on this will display the result of interest superimposed on the molecular model in the window above. For example, if you click on the view icon in the Partial Charges table, partial charge values will appear on the atoms (Fig. 1), or if you click on the icon next to the dipole moment value, the dipole moment appears as a to-scale vector (Fig. 2). If you ever want to save the image on your screen, go to the File menu and select "Save Image."

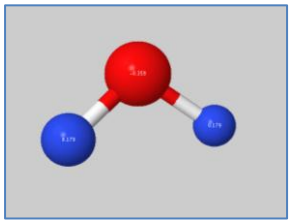

Figure 1- Partial charges in a water molecule

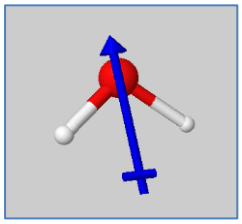

Figure 2- The dipole moment of water

When the calculated property involves multiple conformations of the molecule, the animate icon will be displayed ( ). Clicking on this icon will show a movie of the different conformations.

Build and optimize the geometry of the molecules needed for the following exercises, including one of your own choosing, as listed in the table below. NOTE: YOU DO NOT NEED TO ADD HYROGEN ATOMS INDIVIDUALLY. Begin optimization of your initial model using the Idealized Geometry tool (, this will add the H's), then run a Gaussian calculation to complete the optimization. Enter the bond lengths and angle for water into Table I.2.

Molecules to build:

H_2O	PF_5	CH_3Cl	CH_3NH_2	CH_3CN
CO_2	SF_6	CH_3Br	CH_3CH_3	CH_2O
BF_3	NH_3	CH_3OH	CH_2CH_2	CH_2ClCH_2Cl[4]
CH_4	CH_3F	CF_3OH	CHCH	Your choice

[4] Build this molecule with the *Cl* atoms on opposite sides (one "up" and one "down").

PART II- WHAT CONTROLS BOND LENGTH?

Many factors can influence the length of a chemical bond. In this exercise, you will examine several of the main determinants of bond length by examining a series of related compounds.

Complete Table II.1, using your optimized models to measure bond lengths, as described in Part I. From your results, deduce the main factors that influence bond length.

PART III- WHAT CONTROLS BOND ANGLE?

We have learned that the angle between two bonds depends mainly on electron-pair geometry of the central atom, which in turn depends on the number of structurally important electron pairs on the central atom.

Draw the Lewis structures for the molecules in Tables III.1 and III.2 and measure the indicated bond angles using WebMO.

PART IV- TORSION ANGLES

When a series of atoms are connected together, their relative positions are referred to as a conformation. A torsion angle (also called a dihedral angle), which is defined by four atoms, describes the twisting of one part of the molecule with respect to another (Fig. 3). The easiest way to observe this is to examine atoms bonded to adjacent central atoms and see if they line up (they are *eclipsed*) or seem to avoid each other (they are *staggered*).

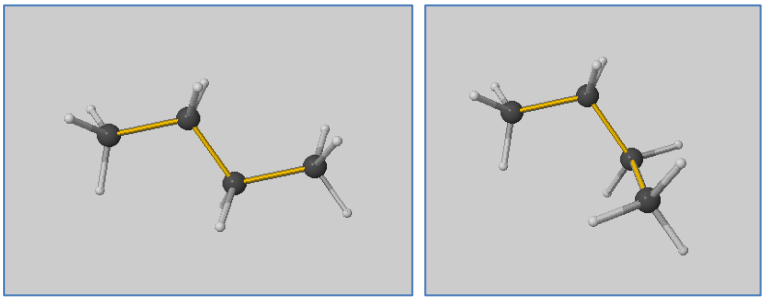

Figure 3- Torsion angle, shown in yellow, with two different values

There are two factors that might control how one fragment of a molecule will twist with respect to another fragment- steric hindrance and bonding. Steric hindrance comes about when atoms get in each other's way and take up space. The result is that atoms are arranged in order to avoid other atoms to which they are not bonded. Bonding control of conformation comes about when certain types of bonds require a particular orientation of the atoms involved. The most common and important of these are *pi* bonds.

View your molecular models of CH_3CH_3, CH_2CH_2, and CH_2ClCH_2Cl. Record the value for the torsion angles indicated in Table IV.1 and describe the relative positions of the atoms. Perform a coordinate scan for CH_2ClCH_2Cl as described below and use your results to help answer questions IV.3 and IV.4.

A coordinate scan is a calculation in which you step through many possible conformations and calculate properties of the molecule in each conformation (energy, for example). To examine the Cl-C-C-Cl torsion in CH_2ClCH_2Cl, open your optimized model and select "New Job Using This Geometry" at the bottom of the viewing window. When a new window with your molecule appears, select the adjust tool ( ). Shift-click to select the four atoms that define the dihedral angle. In the *Adjust* menu, select "Scan Coordinate." Set the "Start" value to 180, the "Stop" value to -180, and the "# Steps" to 36. Leave the default value for "Type" (which is optimized). This will run calculation for a complete rotation about that dihedral angle in 10-degree increments. Click on OK to close this window. Your dihedral angle of interest should be highlighted yellow. Next, click on the right arrow ( ) to continue the calculation setup. Select Gaussian as the calculation engine and click on the right arrow. Give your job an appropriate name (e.g., dichloroethane scan), leave the rest of the settings as their default values, and click the right arrow to run the calculation.

PART V- PARTIAL CHARGES AND MOLECULAR DIPOLES

Recall that you can view the partial charges and the molecular dipole for your model within WebMO by viewing your model and scrolling down to the partial charge table. The dipole is listed above this table. To view the direction of the dipole, click on the view icon ( ). When describing the direction of the dipole, make sure to indicate which way the dipole points (the "points to" end is the negative end of the dipole). For example, the dipole for ethanol (Fig. 4) might be described thus: *the dipole makes a roughly -30° angle to the carbon-carbon bond, points toward the oxygen, and has a magnitude of 1.561 Debeye*.

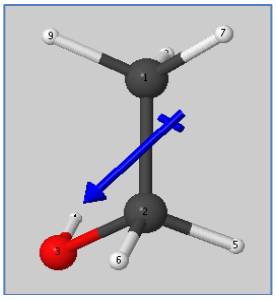

Figure 4- Molecular dipole of ethanol

Complete table V.1 by drawing the Lewis structures and entering the values indicated in the table. Measure the charges and dipole moment for the molecule you designed in Part I.

PART VI- MOLECULAR VIBRATIONS

How to calculate the vibrations in a molecule:

1. Open the geometry-optimized model for a molecule.
2. Select "New Job Using This Geometry" at the bottom of the builder window.
3. Click on the right arrow. Select Gaussian as a calculation engine then click the right arrow again.
4. Enter an appropriate name for the job (e.g., "water vibrations").
5. Select "Vibrational Frequencies" from the Calculation pull-down menu. Leave all other values as they appear. Click the right arrow to start the calculation.

Vibrations Results:

1. Select the appropriate job from the Job Manager window. Scroll down to the "Vibrational Modes" table.
2. Animate each vibration by clicking on the  icon. Determine whether the mode is a bend (sometimes called a scissor), a symmetric stretch (each side of the molecule moves in the same way), or an asymmetric stretch (both sides of the molecule move differently).[5]

Calculate and examine the vibrations for H_2O and CO_2. Record the frequency of each vibration in the appropriate box in Table VI.1 for both molecules. Describe the difference in motion between the two bending modes for carbon dioxide.

Calculate the vibrations for CH_4, C_2H_2, C_2H_4, and C_2H_6. Record the nuber of vibrational modes for each on your report form.

[5] If you have trouble viewing a vibration, sometimes selecting "Reset Viewer" (right above the status bar at the bottom) or going to the Job Manager and reselecting the molecule of interest helps.