Molecular Modeling Part 1-
Molecular Structure and Vibrations

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**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 gain an understanding of the greenhouse effect via an examination of the structures and vibrations of greenhouse and non-greenhouse gases.

**Introduction**

The greenhouse effect is the phenomenon responsible for maintaining an average global temperature capable of sustaining life on Earth. Atmospheric gases create this effect by allowing higher frequency infrared radiation (IR) to pass through and reach the planet's surface, but absorbing the lower frequency infrared radiation that gets reflected back. These gases "trap" heat by then reemitting some of the absorbed IR energy back toward the surface.

What determines whether a molecule can absorb IR? That is the central question of this exercise. The answer lies in the intramolecular motion of molecules- how bonds will bend, stretch, or wiggle. When such motions change the distribution of positive and negative charges, a molecule becomes capable of absorbing IR. This occurs when the frequency of the change in charge distribution matches the frequency of the infrared radiation.

Computational chemistry, also called molecular modeling, is a branch of chemistry that combines our knowledge of chemistry, physics, and mathematics to produce computer models of molecules. These models can be used to predict or understand molecular properties. There is a great variety of molecular modeling software; we will use a program called ***WebMO***. You will learn how to build molecules, measure bond lengths and angles, calculate vibrations and visualize your results. These techniques will then be applied to the examination of various atmospheric gases in order to discern patterns common to those considered "greenhouse gases."

**Getting to WebMO:** Go to <http://irene.oneonta.edu> and click on the ***WebMO*** link.

**How to log on:**

Username = Provided by your instructor

Password = chemstudent

**Part I- The Shape of Molecules**

***Basic Instructions for Building a Molecule (a specific example follows):***

1. Once you have logged on, the Job Manager screen will appear. Every time you build a molecule and run a calculation on it (called a "job"), it 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.
2. Click on the Periodic Table icon (). To select an element, click on its symbol in the table.
3. Next, click in the main window to add an atom of the selected element.
4. To add another atom of the same type, click in the window again (no need to reselect it in the Periodic Table).

To add another atom of a *different* element, reopen the Periodic Table (), select the desired element, and click in the window to create the atom.

1. To create a bond between two atoms, click on the first atom involved in the bond and drag to the other atom. (To create a double bond, click and drag a second time. For a triple bond, repeat the click and drag a third time.)
2. Continue to build your molecule until all of the non-hydrogen atoms have been added. There is no need to add hydrogens, the program will do that for you in the next step.
3. Once you have added and connected all of the atoms in your molecule, you need to "fix" the geometry of your molecular model. Click on the paintbrush icon (). This will add hydrogens and provide a reasonably correct shape for your molecule.
4. To finish correcting the geometry of your model, click on the right arrow at the bottom of the window (). Select "Mopac" as the computational engine and click the right arrow again.
5. 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 but make sure to include your initials at the beginning so that you can easily identify your jobs (you are sharing the WebMO account with other students). For the Calculation type, select "Geometry optimization" from the pull-down menu. Leave all other options at their default values. Click on the right arrow to start the calculation.
6. 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.

***Viewing the Results of a Job:***

1. Once the "status" of your job appears as Complete in the Job Manager window, click on either the Job Name or the view icon () to view your results.
2. Your molecular model appears in the window. You can rotate your model by holding the left mouse button down and moving the mouse.
3. 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[[1]](#footnote-1) 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 a 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 ().

***Building the Carbon Dioxide Molecule:***

1. Log on and select select New Job.
2. Click on the Periodic Table icon Table () and select carbon (C). Click once in the building window. A gray carbon atom should appear.
3. Click on the Periodic Table again. This time, select oxygen (O). Click in the building window to one side of the carbon. A red oxygen atom should appear. Place another oxygen atom on the other side of the carbon.
4. Click on the carbon and, while holding the mouse button down, drag to one of the oxygens. A line representing a single bond will appear. Click and drag between the same two atoms a second time to create a double bond (Fig. 1). Next, connect the carbon to the other oxygen with a double bond.



Figure 1- Carbon doubly bonded to one oxygen. To complete

the CO2 model, bonds must be made to the other oxygen atom.

1. Click on the paintbrush icon. Then click on the right arrow.
2. Select Mopac and click on the right arrow.
3. Give your job a name that begins with your initials (e.g., KRG-CO2 opt). Select "Geometry Optimization" from the Calculation pull-down menu and click on the right arrow.
4. When your job is complete, click on the job name to view the molecule. Click and drag to rotate.
5. Measure the bond lengths: Click on the adjust button (). Next, click on one of the oxygen atoms. Hold down the shift key and click on the carbon. The bond length will appear at the bottom of the screen. Record this length in your data table.
6. Measure the bond angle: Hold down the shift key and click on the second oxygen (all three atoms should be highlighted). Record the bond angle that appears at the bottom of the screen.
7. Once you have finished recording the bond lengths and angles in CO2, click on "Job Manager" on the left hand side of the screen.

***Build and Measure the Properties of Other Atmospheric Gases***

1. Draw the Lewis structures for the molecules H2O, N2, O2, O3, and CH4 in your data table. Have your instructor check them for correctness before you continue.
2. Following the Basic Instructions described above, build H2O, N2, O2, O3, and CH4. Record the bond lengths and angles in your data table. *IMPORTANT NOTE FOR OZONE (O3):* DO NOT use the paintbrush tool to clean up the ozone geometry. After adding the bonds, right-click on each atom. A pull-down menu will appear. For the two atoms involved in the double bond, select “sp2” from this menu. For the one oxygen atom that is only involved in a single bond, select “sp3”. After doing this, click the right arrow and proceed to set up the geometry optimization calculation. The remainder of the procedure is the same as it is for the other molecules.

**Part II- Molecular Vibrations and the Greenhouse Effect**

***How to calculate the vibrations in a molecule:***

1. From the Job Manager screen, select a molecule by clicking on its job name.
2. Select "New Job Using This Geometry" at the bottom of the builder window.
3. Click on the right arrow. Select Mopac as a calculation engine then click the right arrow again.
4. Enter an appropriate name for the job (e.g., "KG- CO2 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.

***Viewing Vibrations Results:***

1. Select the 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).[[2]](#footnote-2)
3. Record the frequency of the each vibration (from the table) and its description (bend, symmetric stretch, etc.) in your data table. Repeat for all of the molecules you have built.
4. To view the IR spectrum of your molecule, scroll down to the table of vibrational frequencies and click on the view icon () next to "IR spectrum".

**Molecular Modeling Data Table**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Molecule Name** | **Formula** | **Lewis Structure****(with lone pairs)** | **Bond Length** | **Bond Angle** | **Vibrational Modes****(label bend, symm. stretch, asymm. stretch)** |
| carbon dioxide | CO2 | co2_lewis.tiff | C=O : | O=C=O : |  |
| water | H2O |  | H-O : | H-O-H : |  |
| nitrogen | N2 |  |  : |  |  |
| oxygen | O2 |  | O-O : |  |  |
| ozone[[3]](#footnote-3) | O3 |  | O-O :O=O : | O-O=O : |  |
| methane | CH4 |  | C-H : | H-C-H : |  |

**Experiment 4 Questions**

Look for trends recorded in the data table and answer the following questions. Reading the article "Life in the Greenhouse" may help (from *ChemMatters-* October 2003 issue).

1. Carbon dioxide is the best-known greenhouse gas. There are several ways this molecule can move, called "vibrational modes" (symmetric stretch, asymmetric stretch, in-plane bend, out-of-plane bend). Are all of these modes capable of absorbing infrared radiation? If no, describe the difference between the modes that can absorb IR and those that don't.
2. Which of the other gases studied would you consider "greenhouse gases"? Explain why in terms of the molecular vibrations in each molecule.
3. According to your data, which greenhouse gas studied in this experiment absorbs the highest energy IR? (*Hint: Remember the higher the frequency and the smaller the wavelength, the higher the energy of the radiation. WebMO reports vibrational frequencies in wave numbers, or 1/. Thus, the bigger the wave number, the bigger the energy*.)
4. According to your data, which greenhouse gas studied in this experiment absorbs the lowest energy IR?
1. 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). [↑](#footnote-ref-1)
2. 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. [↑](#footnote-ref-2)
3. When building ozone, do NOT use the paintbrush tool. See instructions on page 5 for this molecule. [↑](#footnote-ref-3)