

## CHEM 208

## Lab 1: Computer Modeling and Simulations

Please report all confusions and errors to Chem208 staff or Kathy Durkin.

In this set of exercises you will use a computer to visualize and examine several important concepts in X-ray crystallography. These include visualization of unit cells, Miller planes, space groups and diffraction patterns. You will also learn how to display molecular structures and how to use the Cambridge Structural Database.

Login to *granite* or *methane* as *chem208*. Open a unix shell window if one does not open automatically. Change the directory to *user1*, *user2*, or *user3*. (We will give you the password)

**Cerius2** is an excellent program for structure manipulation and visualization. Start the program by typing **cerius2** (be patient) in a terminal window. Typically, two windows will appear. The **Cerius2 Models** window displays the graphical model(s) you are currently working on and the **Visualizer** window is used to control the input and program functions. Several modules are available from within **Cerius2**. Make sure that module **BUILDERS** is selected. This should be the header above the options on the right-hand side of the **Visualizer** window.

### Exercise 1. Examination of Miller planes.

In this exercise you will examine the relationship of various sets of Miller planes to the crystal lattice.

1. The unit cell parameters for the unit used in this exercise are stored in a file called **emptycell.msi**. To import this cell, select **Load Model** from the **File** menu (at the top of the **Visualizer** window). Select **MSI** in the **File Format** menu (part of the **Load Model** dialog box). Select **emptycell.msi**. Click on **Load** to import the cell. An empty unit cell will appear in the **Cerius2 Models** window.

The cell can be rotated by holding down the *right* mouse button and moving the mouse. Holding down the *center* mouse button allows you to move the cell up-down and left-right. Holding down both the *right* and *center* buttons allows scaling of the cell on the screen.

2. You can now expand the view to include a block of 2 x 2 x 2 unit cells.

Click on the **Visualization** tab to open a **Crystal Visualization** window. Change the values in each of the three **Crystal Cell Display Range** windows to "2". Press **ENTER** and examine the output. You can also choose to work with a larger block by requesting more unit cells in any of the three directions.

3. You will now generate several sets of Miller planes and examine their relationship to the three crystal axes.
  - a) In the **Crystal Visualization** window enter 0, 0, 1 for the **Miller Plane Display** indices. Now *check* the **Show Miller Plane** box. Examine the Miller planes by rotating the model. What is the relationship between the (0 0 1) planes and the  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  vectors?  
Now examine the (0 1 0) and the (1 0 0) planes. Answer the question in (a).
  - b) Examine the series (1 1 0), (2 1 0), (3 1 0). What do they all have in common and how do they differ?
  - c) Compare the (1 1 0) and the (1 -1 0) planes. What changes when one of the indices is replaced by its opposite (in this case k is replaced by k )?
  - d) Examine the (1 1 1) planes. How are they related to the  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  vectors? Generate the (2 2 2) and the (3 3 3) sets. What do they have in common with the (1 1 1) set? How do they differ?

Before proceeding to the next exercise, *uncheck* the **Show Miller Plane** box in the **Crystal Visualization** window.

## Exercise 2. Space groups and diffraction patterns.

In this exercise you will examine five different unit cells. Each is populated with the same "molecule". The data for each cell is already on the computer and can be simply loaded from the lab03/user# directory as done previously.

Unload the **emptycell** model by clicking on the button labeled with a "-" just above the list of Models. There will always be an empty model displayed. Don't worry about that.

1. Select **Load Model** from the **File** menu, and load the following models

**trixie.msi, molly.msi, oliver.msi, odo.msi and herman.msi**

The graphics window will only show one of these molecules. Just below the **File** menu button there is a pane that displays the names of the currently loaded models. There are three icons showing different ways of displaying the windows (a 2 x 2 pane, a main central window with five others about the edge and finally two overlaid windows). Select the icon with a main window and five about the edge. Below these icons are the names of the loaded models. Next to one of the models is a red marker. This indicates the model is currently displayed in the main window (and thus active). To the right of each of the model names is a check box, which turns turquoise when *clicked*. This tells the program which molecules are to be shown in the graphics window as a whole. *Click* to display all of the loaded models (*check* all the boxes to the right).

2. In the main graphics window you should now see the model selected with a red marker in the main window and the rest of the models in the surrounding mini-windows. The models are based on an arbitrary arrangement of three different "atoms", not a true molecule. Each model shows a single unit cell generated from those atoms by the symmetry elements in the cell.

If you rotate the molecule in the main window (RMB) you will notice that each of the other unit cells also rotates in unison.

Examine each unit cell in turn (make it the active one) and compare with the others. What are the differences between each of the five unit cells (*i.e.* number of "molecules", orientation of the molecules within the cell, shape of the cell)? Are there any similarities? What symmetry operations do you see in each case?

3. Make **molly** the active model. In the **Unit Cell/Cell Parameters** tab alter the  $\beta$  angle to be  $90^\circ$ . Compare this cell with the other two cells that have all  $90^\circ$  degree angles (**oliver** and **odo**) Are they the same? If so what is the same? If not, what is different? Restore the  $\beta$  angle to  $110^\circ$  before proceeding to the next step.

Now make **herman** the active model. Expand the unit cell, as previously done in the examination of the Miller planes, to a 2 x 2 x 1 cell. What symmetry can you see? Is this different from what you saw before?

4. Finally you will examine predicted X-ray diffraction patterns for two of these structures.

Set **molly** to be the active model. In the **Visualizer** window, click and hold the **Builders** button. This should open a list of different modules. Select the **ANALYTICAL** module.

Select the **Calculate Diffraction** option. A new window will pop-up. There are several check box options that can be changed. *Check* the **Single Crystal** box. *Click* on **Preferences** next to the **Single Crystal** box. In the new window, **Display S. Cr. Diffr.**, *uncheck* the **Label Reflections** box.

We will first examine the [0 1 0] layers. Enter these indices for U, V and W. Set **Layer Order** to 0. In the **Calculate Crystal Diffraction** window *click* on **CALCULATE**. The diffraction pattern will open in a separate window.

- a) The reflections displayed have indices (H 0 L). To display higher layers *i.e.* (H 1 L), (H 2 L) etc. use the **Layer Option** box. Examine the (H 0 L) layer noting angles. Are there any obvious  $90^\circ$  angles? What is the symmetry of the pattern? Repeat the exercise for the (H 1 L) and (H 2 L) layers. Answer the same questions.
- b) Examine the (0 K L) reflections by choosing 1, 0, 0 for U, V, W. Answer questions from (a). Examine the higher layers. Did the symmetry of the pattern change in going from the 0-th layer to 1-st layer? Describe the difference, if any.

- c) Finally you will examine the diffraction pattern generated from a different cell. Make **herman** the active model. Generate and examine the (H K 0) [ $u = 0, v = 0, w = 1$ ] diffraction pattern. What symmetry do you see? Generate the (H K 1) and (H K 2) patterns. Has the symmetry changed? How?
- d) Examine the (H 0 L) and (H 1 L) [ $u = 0, v = 1, w = 0$ ] diffraction patterns for **herman**. What symmetry do you see? To which previous patterns in this exercise are these patterns most similar?

### Exercise 3. Building the structure of benzene.

Although benzene normally crystallizes in the orthorhombic space group  $Pbca$ , under high pressure benzene adopts a higher density structure in the monoclinic space group  $P2_1/c$ . In this exercise you will build a molecule of benzene based on the atomic coordinates previously determined by X-ray crystallography.

0. Unload all the models you were just using.

Use the module selection box to return to **BUILDERS**.

1. The unit cell parameters for this structure are stored in the file **benzene.msi**. Load the unit cell the same way you loaded **emptycell.msi** in Exercise 1. You can examine the unit cell parameters by going to **Unit Cell** and choosing **Cell Parameters**. Are these parameters consistent with a monoclinic cell?
2. Now we are ready to input the *fractional* atomic coordinates listed below.

	X	Y	Z
C1	0.2556	0.0397	0.1213
C2	0.0604	0.2124	0.1119
C3	0.1951	-0.1726	0.0094
H1	0.4321	0.0672	0.2051
H2	0.1022	0.3590	0.1892
H3	0.3299	-0.2918	0.0159

From the **Crystal Building** menu select **Add Atom**. [*Important: The box to the right of coordinates must be changed from XYZ to ABC. This indicates that fractional coordinates are used.*] In the new **Add Atom** window enter the  $x, y$  and  $z$  coordinates for C1 separated by spaces. Enter **C** for **Element** and **C1** for **Name**. Once all the information for C1 has been entered, *click Add Atom*. Now you can enter the info for C2 and C3. When all three carbon atoms have been added, close the **Add Atom** window. In the **Crystal Building** window click **Unbuild Crystal**, then **Build Crystal**. You should now see hexagons representing benzene molecules (you can go back and add the hydrogen atoms if you wish; don't forget to **Unbuild Crystal** and then **Build Crystal** to connect the fragments).

- a) Only three carbon atoms were entered. Why is the entire benzene molecule displayed? What is the site symmetry of a benzene molecule?
- b) Examine the resulting unit cell. What symmetry elements can you identify?
- c) Generate the Miller planes as in Exercise 1. Do these planes correspond to any planes formed by the benzene molecules?

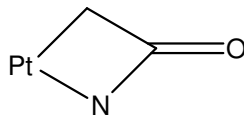
Now exit from **cerius2** before going to Exercise 4. In the **Visualizer** window pull down **File -> Exit**.

### Exercise 4. Using the Cambridge Structure Database

In Exercise 2 you built a molecule of benzene by entering the atomic coordinates for each atom. However, most molecules consist of dozens of atoms and building these would entail a tedious task of entering dozens or hundreds of numbers. Fortunately, the coordinates for published crystal structures can be retrieved from the **Cambridge Structural Database** and imported directly into **Cerius2** or another graphics program. The **Cambridge Structural Database** contains over 275,000 x-ray crystal structures and is a great place to start looking for experimental data when doing structural studies. Many different criteria can be used to search the database including full or partial structure, molecular formula, journal and author names or

even space group. In this exercise you will search for a structure in the database using a partial molecular structure. You will download the coordinates and examine the structure using **Cerius2**.

1. In a terminal window, type **ssh -X cambridge@chexcsd**. You will be given the password in class which you will input when prompted. Now type
2. **Conquest** is the graphical search builder for the Cambridge Structural Database. Type **Conquest** and the operational window will open up.
3. There are many criteria for CSD searching. In this exercise, you will use a molecular fragment.



Click on **Draw**. In the new window, *sketch* the 5 atom frame using all C atoms (default). [Sketching involves *clicking* and *dragging* with the left mouse button.] Place the N by *selecting* N from the bottom of the screen and then *clicking* on the appropriate atom in the sketch. Place the O in the same fashion. To place the Pt, *right click* on the C to be changed and select **More/Other Elements** to bring up the periodic table. *Select Pt* and then *click OK*. Now all that remains is to change the C-O bond from single to double. *Select double* from the **Bond** menu (near the bottom of screen). *Click* on the C-O bond. Now that the fragment is built, *click Store* (near the bottom right of screen). This set of criteria is Query 1. We could define multiple queries and combine them in a Boolean fashion but for this exercise, one query is sufficient.

Click on the **Search** button on the main **Build Queries Panel**. In the **Search Setup** menu, *click* on **Start Search**. The search results will be displayed in the **View Results** panel. The first result is **GUPYAR**. This name is the REFCODE, usually a 6 or 7 letter name that is a unique identifier in the database. The name has no meaning but is unique for a given structure. *Click* on the other REFCODE names to view the structures. You are interested in the structure containing a cyclooctadiene moiety. *Click* just to left of the REFCODE names of the unwanted structure. The checkmark should be replaced with an x mark. *Select Export Entries As* from under the **File** menu. **Select file type:** as **CIF: Crystallographic Information File**. Take note of the filename under which the data will be stored. It is probably *search1.cif*. Rename this to something unique and then *click* on the **Save** button. *Select Exit* from the **File** menu and then *click* on the final **Exit** button.

Type **exit** at the command line. Now copy the file you created over to the Graphics Lab machine. Type **sftp cambridge@chexcsd** you will be prompted for the password. Type **get mysearch.cif**. When the transfer is complete, type **bye**

4. Now we are ready to work with Cerius2 to study the nature of the structure. Type **cerius2** at the command line. Select **Load Model** from the **File** menu. Select **CIF** from the **File Format** menu (part of the **Load Model** dialog box). *Click* on the **mysearch1.cif** filename and then *click Load*.  
*Click* on > < icon to close the menu.