

Advanced Physical Chemistry
Using the Cambridge Structural Database to investigate symmetry

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As you already realize, crystals are symmetrical. There is a shorthand set of symbols to describe the symmetry elements found in crystals, called the Hermann-Mauguin symbols. The goal of the first assignment is to help you learn about the symmetry operations in crystals, and find out how they can be combined to form groups of operations called *space groups*. In the second assignment, you will see how these symmetry relationships play out in actual crystal structures you retrieve from the Cambridge Structural Database.

Books on reserve:

Glusker, *Crystal structure analysis for chemists and biologists*, QD945.G583 1994

Bernal, *Symmetry: A stereoscopic guide for chemists*, QD921.B45

Sands, *Introduction to crystallography*, QD905.S25

Reference book:

International tables of crystallography: Brief teaching edition of volume A,
Ref QD908 .I56 1993

Assignment 1:

Read about symmetry elements and symmetry operations in one of the books on reserve, and then look at some example space groups in the *International Tables*.

The most common space group for organic molecules is $P2_1/c$ (No. 14) so be sure to look at that one. Note the number of symmetry elements and the number of equivalent positions.

- Can you see the relationship between the equivalent positions (x,y,z notation) and the equivalent positions in the diagram of the unit cell? Note that $-x$ is the same as the symbol \bar{x} .
- Do the symmetry operations constitute a group?
- The equivalent positions in space group $P2_1/c$ are slightly different from the ones given in this handout on page 3. Why?

Learn the characteristics of the seven *crystal systems*.

Symmetry elements that include translation

Unit cell translation, the space group equivalent of the identity, always present corresponds to an equivalent position in a different (identical) unit cell

$$x+1, y+1, z+1$$

Screw axis combines rotation axis and translation,

symbol n_m ($n = 1, 2, 3, 4, 6$) plus subscript translation m/n ($m < n$)

2_1 (b axis) in monoclinic space groups is 2 (b axis) and translation $\frac{1}{2}$ along b

$$\begin{aligned} x, y, z \\ -x, y + \frac{1}{2}, -z \end{aligned}$$

Glide plane combines mirror and translation, symbol a , b , or c

c in monoclinic space groups is m (b axis) and translation $\frac{1}{2}$ along direction c

$$\begin{aligned} x, y, z \\ x, -y, \frac{1}{2}+z \end{aligned}$$

Assignment 2: Find a structure that you want to investigate for its symmetry and intermolecular interactions in the Cambridge Structural Database (CSD). For beginners, it's probably best to stick to the triclinic, monoclinic, or orthorhombic space groups. For this assignment, learn about:

- Unit cell size and shape
- Symmetry (practice transforming coordinates to symmetry-related positions)
- Packing diagram
- Intermolecular interactions such as ring stacking, ionic interactions, hydrogen bonding

Launch the ConQuest software. Under the Build Queries tab you see buttons that will allow you to search the database in various ways. If you store the query rather than searching with it right away, you can use the Combine Queries tab to employ logical operators in your search. Drag the boxes that represents the queries into "must have" to use the Boolean AND operator. Example: Author Glusker AND Element Co.

When you press the Search button, the database is searched according to your criteria, and "hits" appear in a column on the right hand side of the ConQuest screen. Each structure in the database has a unique **refcode**, an alphanumeric identifier such as CMBZAN10. Select each hit with the mouse to view a different structure.

There is quite a bit of information available in the database, as you can see by pressing the various tabs to the left of the ConQuest window. From the File menu choose Write PDF file to view/print.

When you are ready to display your structure, choose View Entries in Mercury in the File menu. Choose the refcode of the structure you want to display. Remember that you have a two-button mouse. The right mouse button gives you a menu.

Try pressing Help in Mercury. Note that there is a Tutorial on how to find nonbonded interactions.