

Inorganic Chemistry with Doc M.

Fall Semester, 2011

Day 5. Fast-track Symmetry and Point Groups (a quick and pragmatic intro).

Name(s):	Element:
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1. Identity. Everything has an identity symmetry element! The mystery is why I-identity is abbreviated E!
2. C_n is the proper rotation axis. Consider the rotation of a molecule. If you can rotate it 120° and get the same appearance to your molecule, the proper rotation is C_n where $n = 360/\text{amount of rotation}$. Build the following molecules using the gumdrops and toothpicks provided. Identify the rotation axes for each of these species.

Our work	Corrected answer (if necessary after discussion)
a. SO_3 (trigonal planar) <i>one C_3 (2 if counting cw and ccw) and three C_2</i>	
b. OH_2	
c. NH_3	
d. IF_7 (pentagonal bipyramid)	
e. XeF_4 (square planar)	
f. BrF_5 (square pyramid)	
g. HCl	
h. CO_2	

3. The principle rotation axis is the one with the highest n value and is always defined as the z-axis. In the example SO_3 , the principle rotation axis is C_3 . Identify the principle rotation axis for each of these.

Our work	Corrected answer (if necessary after discussion)
a. SO_3 C_3	
b. OH_2	
c. NH_3	
d. IF_7	
e. XeF_4	
f. BrF_5	
g. HCl	
h. CO_2	

4. Reflection planes

- σ_v This plane contains the principle rotation axis and there are usually n of them (e.g., SO_3 would have three.)
- σ_h This plane is perpendicular to the principle rotation axis and there are usually zero or one of them, but never more than one.

Using your models, complete the following tables for s_v and s_h .

Molecule:	σ_v	σ_h	σ_d
a. SO_3	yes	yes	no
b. OH_2			
c. NH_3			
d. IF_7			
e. XeF_4			
f. BrF_5			
g. HCl			
h. CO_2			

- σ_d This plane usually occurs between two σ_v planes. It is often not present. Assess the molecules above for σ_d planes.

5. Inversion center. This is an odd duck! Picture your molecule imploding through its center point and coming out completely inverted from whence it started. If you get the same thing back with no atoms seemingly having moved, the beast has an inversion center, i .

Our work	Corrected answer (if necessary after discussion)
a. SO_3	
b. OH_2	
c. NH_3	
d. IF_7	
e. XeF_4	
f. BrF_5	
g. HCl	
h. CO_2	

Part 2. Point groups.

In the real world, including the world of polyatomic molecules and ions, objects have one or more symmetry elements. They often occur in groups. For example, the rotation C_2 will always have a mirror plane of some sort. Interestingly, there are only a limited number of combinations of symmetry elements and these combinations are called **point groups** and I'm sure there is a reason why...

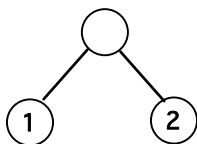
Point groups tend to be of three general types: those with very high symmetry, those with very low symmetry and those in between. A sphere and a circle are examples of very high symmetry and so are the Cartesian coordinate system (octahedron) and the tetrahedron. A clump of dirt or a crumpled up piece of paper are examples of things with very low symmetry. Most of the molecules we've been working with are in between.

Since this guide is a pragmatic approach designed to teach you as much as fast as possible with little regard for nuance and subtleties, here are some of the more common point groups and the symmetry elements they contain:

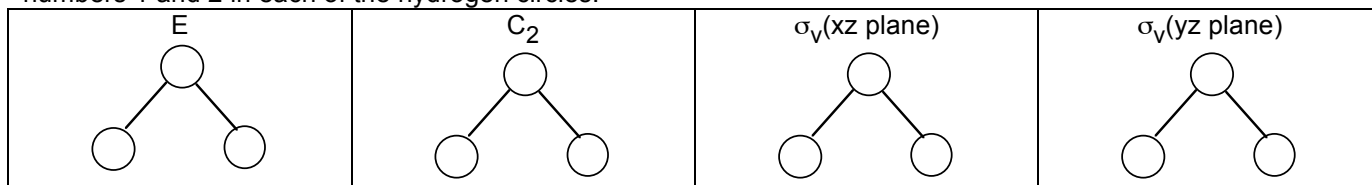
C_{nv} family point groups	Symmetry elements:
C_{2v}	E, C_2 , $\sigma_v(xz \text{ plane})$, $\sigma_v(yz \text{ plane})$
C_{3v}	E, two C_3 , three σ_v
C_{4v}	E, two C_4 , C_2 , two σ_v , two σ_d
C_{5v}	E, two C_5 , two C_5^2 , five σ_v
C_{6v}	
C_{7v}	

D_{nh} family point groups	Symmetry elements:
D_{2h}	E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, $\sigma_v(xy)$, $\sigma_v(xz)$, $\sigma_v(yz)$
D_{3h}	E, two C_3 , three C_2 , σ_h two S_3 , three σ_v
D_{4h}	E, two C_4 , $C_2(z\text{-axis})$, two C_2' , two C_2'' , i, two S_4 , σ_h , two σ_v , and two σ_d
D_{5h}	

Let's first focus on the C_{nv} family. Water is an example of a molecule with C_{2v} symmetry. Here is a picture of water with the two hydrogens numbered so we can refer to one or the other in our discussion. Sketch in the z-axis. For reference, this sheet of paper is the yz plane, so the x-axis is coming out towards us.

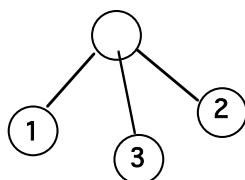


Now, let's see what happens when each of the C_{2v} symmetry *operations* is performed on this molecule. Write the numbers 1 and 2 in each of the hydrogen circles.

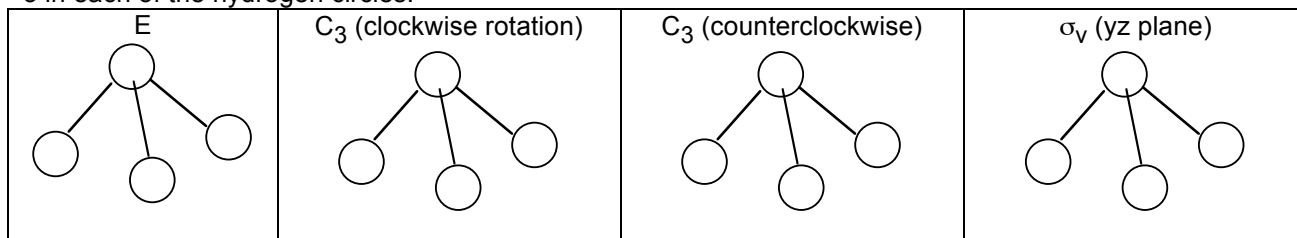


The main point here is that you can perform each of the symmetry operations and still maintain the same arrangement of atoms in space (if the atoms weren't "numbered," we wouldn't see any difference before and after an operation).

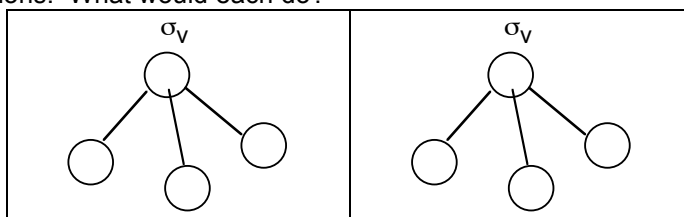
Let's now try a molecule with C_{3v} symmetry such as NH_3 . Again, the principle rotation axis, the C_3 axis, is the z-axis. Sketch in the z-axis. For reference, this sheet of paper is the yz plane, so Hydrogen #1 is in the plane, Hydrogen #2 is behind the plane and Hydrogen #3 is in front of the plane. Again, the x-axis is coming out towards us.



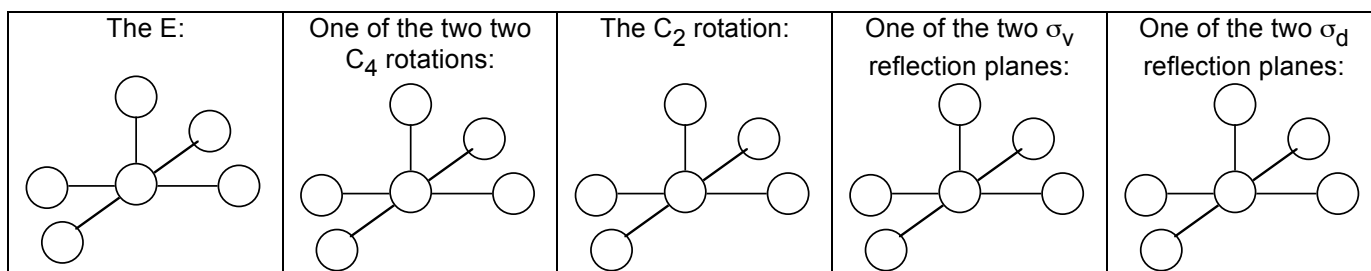
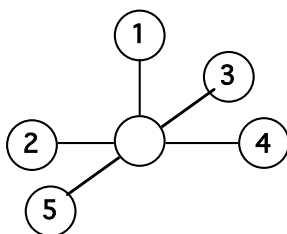
What happens when each of the C_{3v} symmetry operations is performed on ammonia. Write the numbers 1, 2 and 3 in each of the hydrogen circles.



There are two other reflections. What would each do?



The square pyramid is an example of C_{4v} symmetry. As per the table above, C_{4v} has E, two C_4 rotation axes, a C_2 rotation axis, two σ_v reflection planes, and two σ_d reflection planes.



Ok, you are probably wondering, where is the pragmatism promised in the beginning? Here it is: We can relate our ABE formulas to point groups. There are thirteen ABE structural groups all together and six of them are listed of the C_{nv} -type formulas. You will be able to fill in the rest of this table as you work through the rest of this worksheet (in other words, you can go on without filling in anything at the moment.)

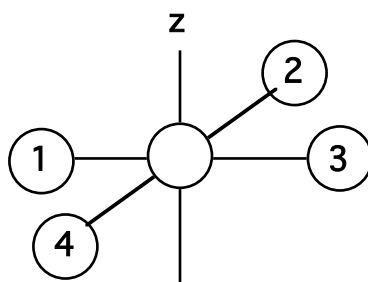
The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
2	AB_2	
3	AB_3	
3	AB_2E	C_{2v}
4	AB_4	
4	AB_3E	C_{3v}
4	AB_2E_2	C_{2v}
5	AB_5	
5	AB_4E	C_{2v}
5	AB_3E_2	C_{2v}
5	AB_2E_3	
6	AB_6	
6	AB_5E	C_{4v}
6	AB_4E_2	

Point groups eventually will make our lives easier! They are used to predict and understand IR and NMR spectra and are used to develop molecular orbital diagrams.

The D_{nh} groups. The C_{nv} point groups covers a lot of ground in terms of the common geometries and ABE formulas! A similarly important family of point groups is the D_{nh} group. The structures AB_3 , AB_5 , and AB_4E_2 are of this point group family. (Remember that simple molecules of the ABE type (one central element) represent only a small fraction of molecular geometries. For example, benzene is also an example of the D_{nh} group, specifically D_{6h} .)

Square planar molecules of formula AB_4E_2 all belong to the D_{4h} point group and therefore must have all of the symmetry components of the D_{4h} point group. These are: E, two C_4 , C_2 (z-axis), two C_2' (along x- and y-axes), two C_2'' (between the x- and y-axes), i, two S_4 (we'll discuss), σ_h , two s_v , and two σ_d . Apply these symmetry operations to the following square planar molecule:



<p>E</p>	<p>Do the clockwise C_4</p>	<p>C_2 (rotation around z-axis):</p>	<p>Do the C_2' rotation around the y-axis:</p>
<p>Do one of the two C_2'' (between the x- and y-axes),</p>	<p>i</p>	<p>Do one of the two S_4 (we'll discuss):</p>	<p>σ_h</p>
<p>Do either one of the two σ_v:</p>	<p>Do either one of the two σ_d</p>	<p>Doodle space</p>	<p>Leave blank: Official use only. Misuse may result in fines or imprisonment.</p> <p>(just kidding)</p>

The most striking difference between the C_{nv} and the D_{nh} point groups is the presence of the horizontal mirror plane, s_h , perpendicular to the z-axis. ABE structures that have identical tops and bottoms, that is σ_h mirror planes, belong to the D_{nh} point group. Add the three new D_{nh} point group designations to the table from the previous page:

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
3	AB_3	
5	AB_5	
6	AB_4E_2	

Structures with very high symmetry. Molecules and ions with many symmetry elements are easiest just to “spot.” There are four of these that we need to be concerned about:

$C_{\infty v}$	linear without σ_h	Example: HCl
$D_{\infty h}$	linear with σ_h	Example: CO ₂
T_d	tetrahedron	Example: CH ₄
O_h	octahedron	Example: SF ₆

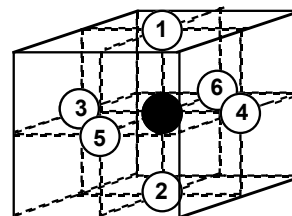
Now complete the rest of the table relating ABE formulas to point groups (here and on page 5):

The Relationship Between ABE Formulas and Point Groups

Structural groups	ABE formula	Point Group
2	AB ₂	
4	AB ₄	
5	AB ₂ E ₃	
6	AB ₆	

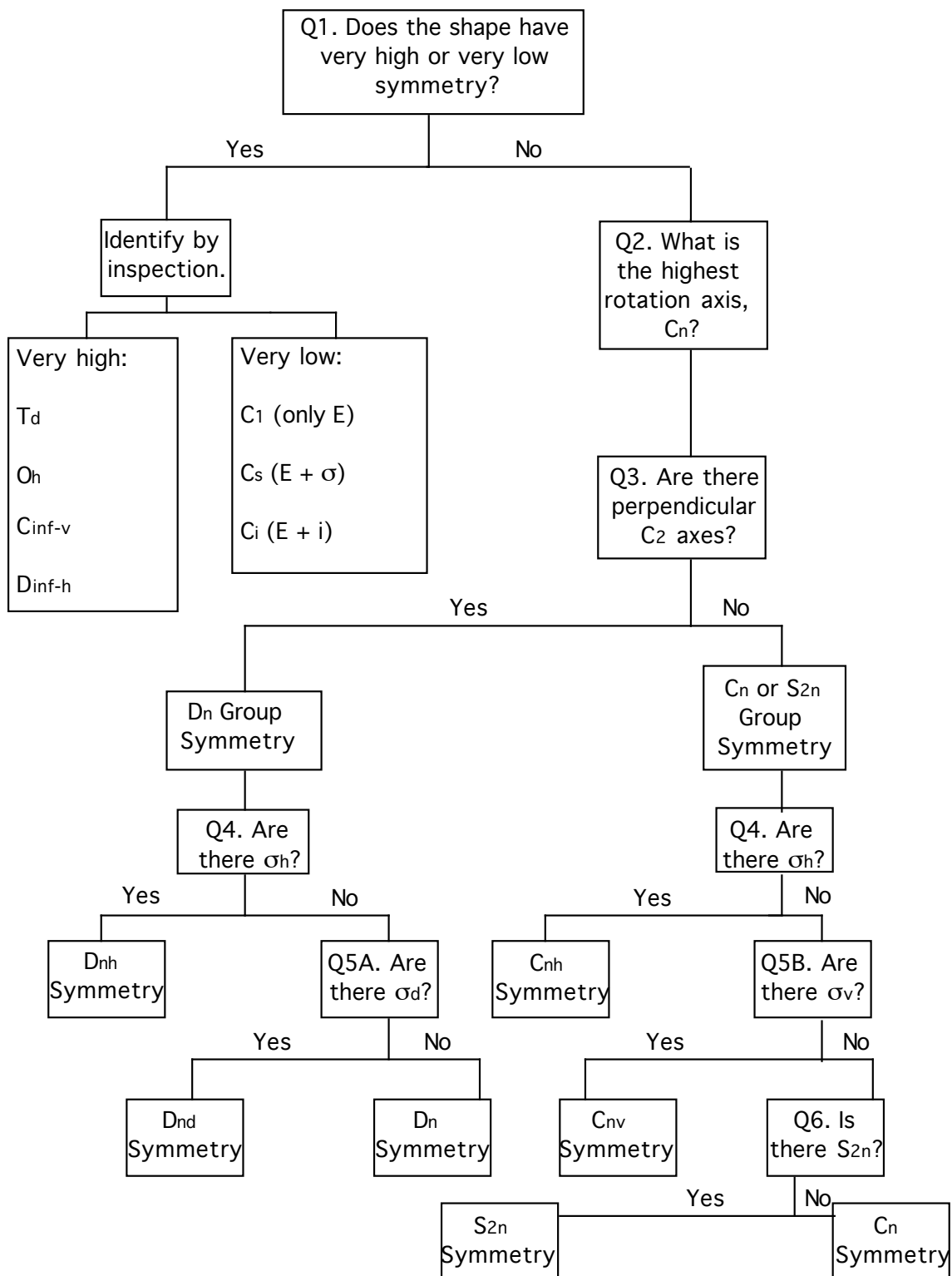
The octahedron. The point group O_h contains 41 symmetry elements (compare to C_{2v} which contained only 4 symmetry elements.) They are E, 8 C_3 , 6 C_2 , 6 C_4 , 3 $C_2 (=C_4^2)$, i, 6 S_4 , 3 σ_h , 6 σ_d . You can find these listed for all point groups as the column headings to the character tables found in Appendix C of our book.

As a “bonus,” try to find the various symmetry elements for the octahedron and (1) sketch the plane or axis being used along with the result. Apply each operation to the octahedral molecule shown at right.



<p>One of the 8 C_3</p>	<p>One of the 6 C_2</p>	<p>One of the 6 C_4</p>	<p>One of the 3 $C_2 (=C_4^2)$</p>
<p>i</p>	<p>One of the 6 S_4</p>	<p>One of the 3 σ_h</p>	<p>One of the 6 σ_d</p>

The following flow chart is useful when working with structures other than the straightforward ABE formulas.



Review for ACS Final Exam in Inorganic Chemistry

Symmetry and point groups

1. What is the symmetry point group for $\text{cis-PtBr}_2\text{Cl}_2^{-2}$? (Hint: square planar)
 - (a) D_{2h}
 - (b) C_{2v}
 - (c) C_{2h}
 - (d) D_{4h}
 - (e) C_1
2. Which symmetry element is not present in $\text{V}(\text{CN})_5(\text{Cl})^{-4}$? (Hint: octahedral)
 - (a) C_2
 - (b) C_4
 - (c) i
 - (d) σ_v
 - (e) σ_d
3. What is the symmetry point group for BrF_5 ?
 - (a) D_{4h}
 - (b) O_h
 - (c) D_{3h}
 - (d) C_{5v}
 - (e) C_{4v}
4. What is the symmetry point group for SF_5Cl ?
 - (a) D_{4h}
 - (b) C_{4v}
 - (c) C_{4h}
 - (d) D_{4h}
 - (e) O_h

Answers: B, C, E, B