

Theoretical Methods Laboratory (Second Year)

DEPARTMENT OF CHEMISTRY

Molecular Symmetry

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A template/guide to the write-up required and points for discussion are included at the end of the exercise (p.26). Look at the marking scheme carefully (p.27). Data sheets are included in this handout. You might find it convenient to enter data and make sketches and notes in the data sheets at points indicated in the text by

==> data sheet

Background reading: *Atkins and de Paula*, Physical Chemistry 7ed, Chapter 15 (Molecular Symmetry) and references cited therein. The following websites may also be useful: the first as a tutorial and the second for group theory tables.

<http://www.ch.ic.ac.uk/local/symmetry>

<http://www.chemistry.nmsu.edu/studntres/chem639/cgi-bin/group1.cgi>

Objectives

This 'experiment' consists of two exercises. Allow roughly equal time for each.

Exercise 1: Determine the symmetry operations that can be applied to several molecules, and hence the molecular point group.

Exercise 2: Determine the symmetry properties of some molecular vibrations and molecular orbitals. (This may not have been covered in lectures yet).

By the end of these exercises, you should be able to

- * Determine the point group of any molecule
- * Determine which irreducible representation of a point group labels the symmetry of a particular molecular vibration or molecular orbital

You will also have a better understanding of symmetry and some of its applications in chemistry.

Program Notes

The exercises run in the computer lab using Gaussview for Windows.
(Programs menu).

The files you need are available in the Mac-PC/symmlab folder.
(PC – Mac-PC icon on desktop)
(Macintosh – Connect to Server <afp://chnts1.ch.ic.ac.uk/Mac-PC>)

Copy the folders ex1 and ex2 to your network home directory (or somewhere else you can write to) first. The files contained in these directories should be opened from within Gaussview.

As part of the exercise, you will need to copy images from the Gaussview display. Two suggested ways of doing this:

- 1) Alt-Print Screen copies the current window to the clipboard. This can be pasted into e.g. PowerPoint or Word.
- 2) Gaussview can save graphics files in TIFF, JPEG or BMP format, which can be imported into another application. JPEG is recommended, as the files are compressed and smaller than TIFF or BMP.

Find a method that works for you before starting your write-up.

For exercise 1, you'll be opening Gaussian 03 input files (myfile.com) and viewing molecular structures. Some instructions and suggestions for using Gaussview are included in the text. There is also a built-in help menu.

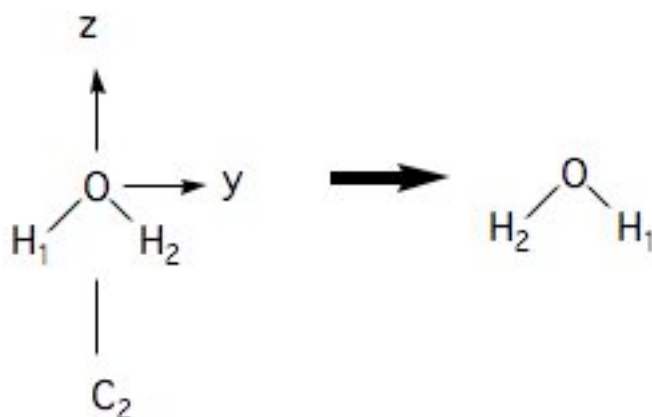
For exercise 2, you'll be opening Gaussian 03 formatted checkpoint files (myfile.fchk) and viewing molecular orbitals and vibrations.

Exercise 1: Point groups - symmetry elements and operations

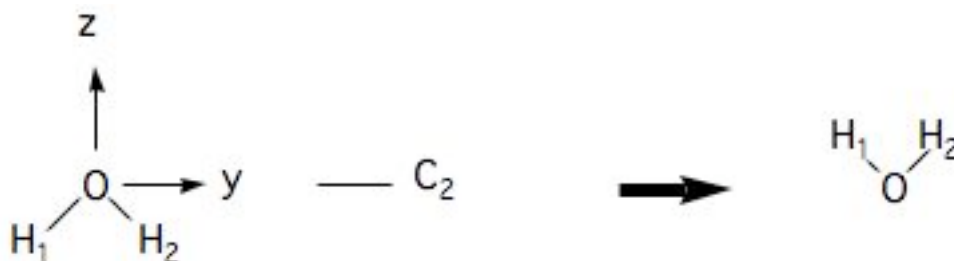
Introduction

A symmetry operation is defined as an operation which, when performed on a molecule, leaves the molecule in an indistinguishable state.

Thus a C_2 (180° rotation) about the z axis in H_2O leaves the molecule unchanged:



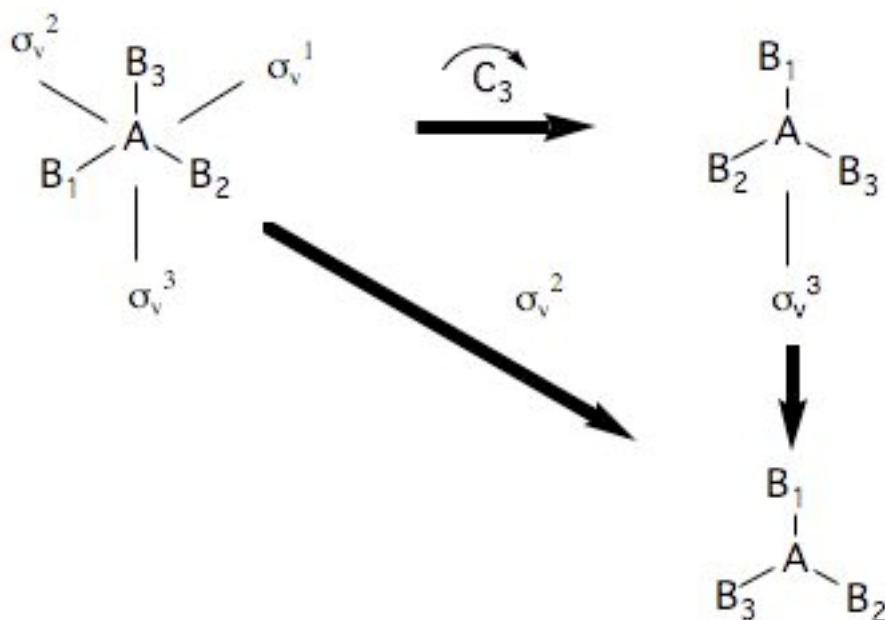
We have added labels to the H atoms so that one can *see* the result of the operation. A 180° rotation about the y axis is not a symmetry operation, however:



because the result of the operation is not superimposeable on the original. In finding symmetry operations one needs to develop some skill with 3-dimensional visualisation. In this exercise you will use the graphics display of **Gaussview** to manipulate molecular models and identify symmetry operations.

The complete set of symmetry operations of a molecule form a group.

What this means is that performing any two operations in succession is equivalent to performing a third operation, which is also a symmetry operation.



$$\sigma_v^2 = C_3 \cdot \sigma_v^3$$

(Notice the convention whereby the molecule moves but the symmetry elements are fixed in space). Because symmetry operations can be combined as shown above, in order to identify the group of all symmetry operations of a molecule, one need only identify certain *key* operations. These operations are called *generators*. Thus the group of a planar AB₃ molecule is D_{3h} and has the following types of symmetry operation.

$$D_{3h} = \{E \quad 2C_3 \quad 3C_2 \quad \sigma_h \quad 3S_3 \quad 3\sigma_v\}$$

where the symbol **3C₂** is used to denote the fact that there are 3 equivalent **C₂** rotation axes about each AB bond. A set of generators is

$$D_{3h} \text{ generators } \{C_3 \rightarrow S_3 \rightarrow C_2 \rightarrow \sigma_h\}$$

All the other symmetry operations are combinations of this sub-set. The process of finding the generators can be made systematic using a decision table or **flowchart** on the next page. The arrows above are intended to indicate the branching points in this flowchart.

(NB: the flowchart also indicates that there are relationships between point groups; they do not exist in isolation.)



EXERCISE 1

The objective is to identify the symmetry operations and assign the point group of following 6 molecules:

- 1 Chlorocubane (1_CHLOROCUB_updated.com)
- 2 all trans perhydrotriphenylene (2_PROPELLOR.com)
- 3 cyclo-octatetraene (3_CYCOCTTET_updated.com)
- 4 hexavinylbenzene (4_HEXVINBENZ_updated.com)
- 5 S₈ crown (5_S8-CROWN_updated.com)
- 6 dichlorodibromocyclohexane (6_BRCL_CYCHEX.com)

Procedure

a) By examining the molecule in various orientations on the screen, work through the flow chart and assign the *generators* and ultimately the point group for each molecule

==> **data sheet**

b) Consult the point group tables and identify the remaining symmetry elements in the group ==> **data sheet**

c) Make a note of all of the elements of the point group ==>**data sheet**. Save images of the computer screen with various orientations, and produce several labelled diagrams for each molecule that shows **each** symmetry operation of the group. (Several symmetry operations could be shown on the same diagram).

Performing symmetry operations on the computer screen: A demo with cyclohexane

You should first spend some time familiarising yourself with the Gaussview interface. The files you will use for this exercise are input files (extension .com) for the Gaussian 03 molecular structure program.

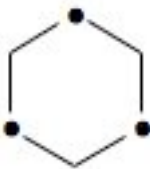
Select **File->Open**, and make sure the File Type is set to 'Gaussian Input Files *.com' and that you are in the ex1 directory (see p.2 for instructions on copying this). Open 0_CYCLOHEX.com.

- using the mouse, manipulate the cyclohexane so that you are looking at it from above.

(Mouse buttons:

- * left: rotates about axes in the plane of the screen
- * middle: translate
- * right: rotate perpendicular to the screen and scale)

By rotating the molecule from its starting position, you should see a hexagon



where the • indicate C atoms that are nearer to you. (Make small rotations around the other axes to convince yourself of this).

Work through the flowchart as described below.

- Look down the principal axis of rotation. Is it C_6 (i.e. $1/6$ of a turn)? No! This would take an **up** C atom (•) into a down C atom (no •). It is C_3 . Turn to the Flowchart. You have identified the decision in the “SELECT HIGHEST ORDER...” box.

To help with this, you can open more than one copy of the same structure (open 0_CYCLOHEX.com file again), and number the atoms (add labels using **View->Labels**). Doing this for the C_3 operation will show that the molecule can be moved, but end up in an indistinguishable state. Clicking within a window may accidentally add a CH_4 group to the molecule you've opened: undo this with **Edit->Undo**.

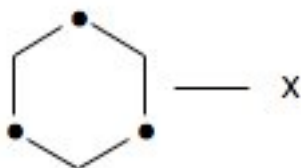
- The next decision involves identifying an S_{2n} , S_n or $i = S_2$ operation. In this case we have identified $n=3$ (from the C_3). Do we have an $S_{2n}=S_6$? Yes! Remember that S_6 is a compound operation $\sigma_h \cdot C_6$ (rotation about an axis, followed by reflection in a plane perpendicular to this axis) as illustrated below.



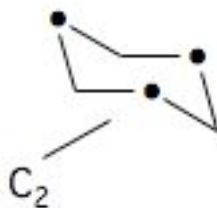
The C_6 rotates $1/6$ of a turn, but this is not a symmetry operation. (Try this on the screen by rotating about the axis you are looking down to convince yourself) The σ_h is a reflection at right angles to this C_6 that brings atoms that are away from you towards you and vice versa. You can always recognise an S_{2n} from the following figure (i.e. two staggered C_3 triangles are interchanged)



- The next decision involves identifying the existence of a C_2 axis that is at 90° to the principal axis C_3 .



To see this more clearly rotate the molecule so that you are looking at it from the side



Then rotate about the C_2 axis. There are two indistinguishable states.

- The last decision involves the identification of σ_h . Clearly since the molecule is not planar, this is not a symmetry operation, so the group is D_{nd} where $n=3$, thus D_{3d} .
- From the point group tables (follow second [www](#) link on p.1 and select point D_{3d} group), the additional symmetry elements are E (identity), i (inversion) and $3\sigma_d$ (diagonal reflection planes; written s_d if you follow the [www](#) link above).

DATA SHEET

Exercise 1: Point groups - symmetry elements and operations

demo: cyclohexane

a) Flowchart point group assignment

proper axis $C_3 \rightarrow$ improper axis yes = $S_6 \rightarrow 3 C_2 \rightarrow \sigma_h$ no \rightarrow = D_{3d}

b) Additional symmetry elements

$i \ 3\sigma_d$

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

$D_{3d} = \{E \ 2C_3 \ 3C_2 \ i \ 2S_6 \ 3\sigma_d\}$

1) Chlorocubane

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

2) all trans perhydrotriphenylene

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagram printed from computer screen)

3) cyclo-octatetraene

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

4) hexavinylbenzene

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

5) S₈ Crown

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

6) dibromodichlorocyclohexane

a) Flowchart point group assignment

b) Additional symmetry elements

c) Symmetry Elements (to be shown on several diagrams printed from computer screen)

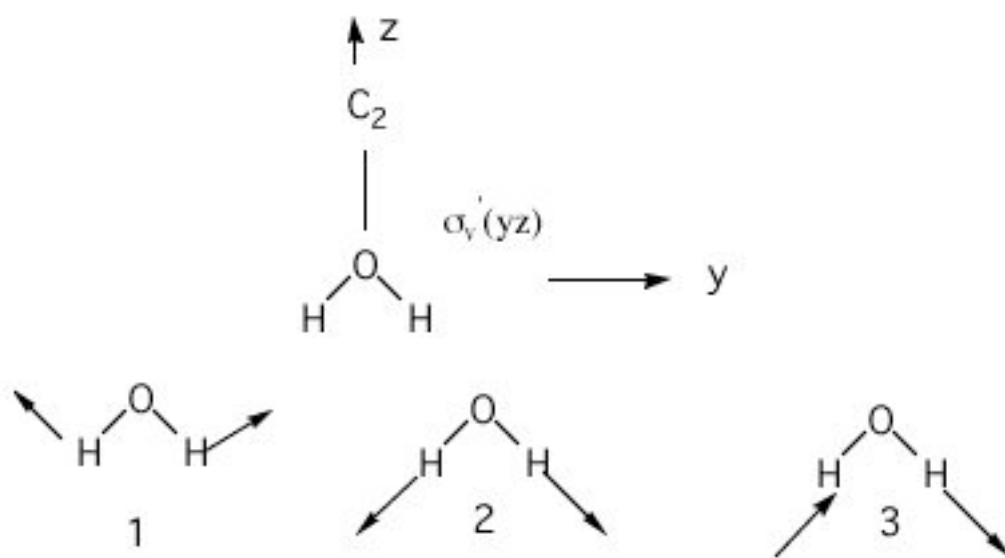
Exercise 2: Symmetry properties of molecular vibrations and molecular orbitals.

To determine symmetry properties (irreps) of some molecular vibrations and Molecular Orbitals

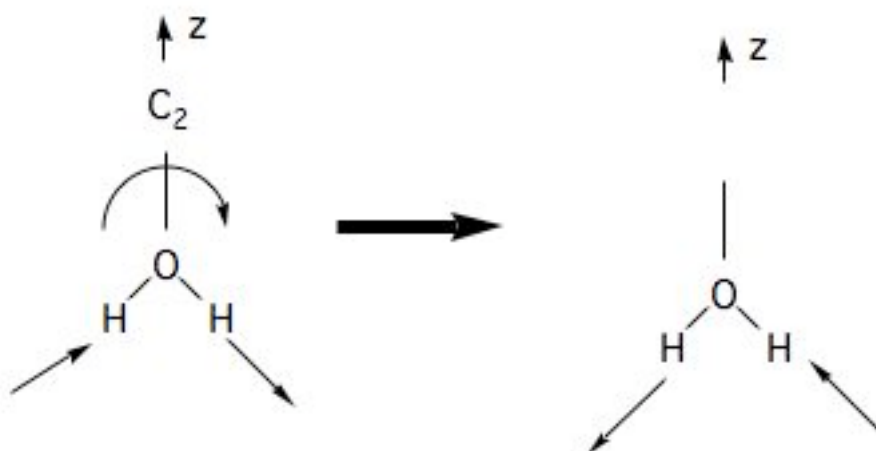
Introduction

In the spectroscopy of a molecule that has symmetry, one observes transitions between states with well-defined symmetry properties. For example, in vibrational spectroscopy, in the case of a molecule with an inversion centre i , one sees transitions in the IR only for vibrations that are anti-symmetric under inversion, while those vibrations that are symmetric under inversion are seen in the Raman spectrum. Thus spectroscopy can often give information about the symmetry of a molecular system. In order to interpret spectra of inorganic systems, arguments about the symmetry of the MOs (in the case of UV spectroscopy) or the symmetry of the vibrations (in the case of IR spectroscopy) are often used. The purpose of this exercise is to examine the symmetries of some molecular vibrations and MOs for some simple systems.

What do we mean by the symmetry of a vibration? A simple example illustrates the main ideas. Three possible internal vibrations of H_2O (numbered 1 to 3) are sketched below together with the symmetry operations in point group C_{2v} .



It should be obvious that if one rotates vibration **1** around the C_2 (z) axis that it is superimposeable. But on performing the same operation on vibration **3**, the vibration changes its sign (arrows point in the opposite direction).



Thus vibrations **1** and **2** are *symmetric* under C_2 but vibration **3** is *anti-symmetric*. We can classify the behaviour of each of these vibrations as *symmetric* (**1**) or *anti-symmetric* (**-1**) and collect the results as shown in the table below

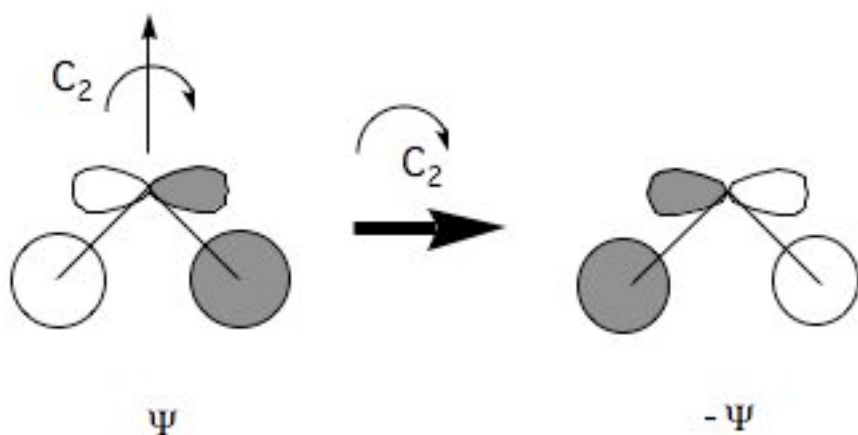
C_{2v}	E	C_2	$\sigma_v (xz)$	$\sigma_v' (yz)$
vib 1	1	1	1	1
vib 2	1	1	1	1
vib 3	1	-1	-1	1

Vibrations or molecular orbitals that have such well-defined symmetry properties under the operations of a group are said to belong to an *irreducible representation* (or irrep for short). As you can see, vibrations **1** and **2** belong to one irrep, but **3** belongs to a different one because it has a different symmetry under C_2 and $\sigma_v (xz)$. The set of $\{1 / -1\}$ for each irrep is called the *character* of that irrep. Each group has only a small number of possible irrep (i.e. only certain symmetries are possible). In C_{2v} there are only 4 possible irrep or symmetries that are collected in character tables of the form shown below.

C_{2v}	E	C_2	$\sigma_v (xz)$	$\sigma_v' (yz)$
A₁	1	1	1	1
A₂	1	1	-1	-1
B₁	1	-1	1	-1
B₂	1	-1	-1	1

In the first column are *labels* for the irrep. Thus **1** and **2** are **A₁** and **3** is **B₂**

Similar considerations apply to molecular orbital symmetries. One of the bonding MOs in H_2O is a mixture of an O p_y and an antisymmetric combination of 2 H 1s orbitals as shown below



If it is transformed under a C_2 rotation it changes sign as shown above. You should be able to verify that it has symmetry B_2

C_{2v}	E	C_2	$\sigma_v (xz)$	$\sigma_v' (yz)$
B_2	1	-1	-1	1

EXERCISE 2

1) Vibrations and MO symmetries of H₂O (Demonstration)

i) Symmetry of B₂ vibration in H₂O

From the ex2 directory,

- **open** the file **h2ovibmo_updated.fchk** from the **File->Open** pull-down menu. (Change File type to 'Gaussian Formatted Checkpoint Files *.fchk' from exercise 1)

- select **Vibrations** from the **Results** menu. You will see the frequencies of the vibrations of the molecule (in cm⁻¹). The lowest energy vibration is selected by default. You can choose to show displacement vectors, start an animation and adjust the displacement. You should see that is the same motion shown as vibration **1** above.

(Be aware that bonds may hide some of the displacement vectors)

You may also find it useful to turn on **View->Cartesian Axes**.

- display the **4391** cm⁻¹ vibration. Sketch the form of the vibration (by drawing arrows to show the nature of the nuclear motions. Determine the *character* (1 or -1) of the vibration under the symmetry operations, and complete the following table, which is reproduced in the data sheet. ==> **data sheet**

freq	C _{2v}	E	C ₂	σ _v (xz)	σ _v ' (yz)
4391	B ₂				

Close the Display Vibrations window when you are finished.

ii) Symmetry of homo-2 in H₂O

- Select **Edit->MOs**. Select orbital 3 from the MO list (highlights it yellow). Click the button **Visualise** (not Calculation), then **Update**.

You should be able to see that this orbital has the same symmetry as the sketch given above and that it has the symmetry properties given below.

C _{2v}	E	C ₂	σ _v (xz)	σ _v ' (yz)
B ₂	1	-1	-1	1

Make a sketch of this MO that demonstrates that it is antisymmetric with respect to reflection in the xz plane ==>**data sheet**

Having calculated the surface for this orbital, you can alternatively display it in the main Gaussview window for the molecule, from the **Results->Surfaces** menu. For MO=3, select **Surface Actions->Show Surface**. You can also add xyz axes using **View->Cartesian Axes**. Having displayed the surface this way, you can also select **View->Display Format->Surface**, and change **Solid** to **Mesh**.

iii) Symmetry of lumo, lumo+1, homo and homo-1 in H₂O

Determine the symmetries of the remaining orbitals using the procedure described above (**Edit->MOs**), look up the irrep label in the group theory / character tables, and thus complete the table in the ==>**data sheet**

2) B₂Br₂ Vibrations

In general, a molecule has $3N-6$ internal vibrations where N is the number of atoms. Thus there are 6 vibrations in B₂Br₂. The molecule has C_{2v} symmetry. The objective is to determine the symmetry of these 6 vibrations.

- **open** the file **bfbr2ns_updated.fchk** and animate the display of each vibration in turn. Determine the symmetry and make a sketch of each ==>**data sheet**

Draw in-plane vibrations with arrows, and indicate out of plane motion with a + or - for each atom.

3) BCl₃ Vibrations

BCl₃ must also have 6 internal vibrations but has higher symmetry (D_{3h}). If you examine the character tables for D_{3h} you will see that there are 2 dimensional irreps labelled E' and E". These representations are associated with 2 fold degeneracy, which becomes possible for point groups that have a 3 fold rotation axis or higher (explained in more detail below). In this case, one must have E type representations and consequently degeneracy.

- **open** the file **bcl3.fchk** animate the display of each vibration in turn. Determine the symmetry and make a sketch of each ==>**data sheet**

The non-degenerate vibrations are those with frequency 536 and 600 cm⁻¹. You should analyse these in full first.

The remaining vibrations are in 2 degenerate pairs (313,313) and (1085,1085). For both vibrations in a pair, you should compute the character for

D _{3h}	E		3C ₂	σ _h		3σ _v
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and then add up the result, comparing with the character table. This will distinguish between E' and E'' irreducible representations, and allow you to complete the rest of the table. (NB: make sure you use the same C_2 axis and σ_v reflection plane for both degenerate vibrations).

For vibrations associated with E symmetry:

- i) For each component of the degenerate pair, reflections, inversion and C_2 are associated with characters of +1 or -1, but the total character of the E representation is the **sum** of the characters associated with each of the degenerate pair of vibrations. The total must always be zero for C_2 and σ_v . Consequently we can resolve the degenerate vibrations into vibrations that are symmetric and anti-symmetric components.
- ii) The character under S_n or C_n etc is never + or -1. Under these operations the degenerate pair are simply transformed among themselves. The character under the E (identity) operation is always 2.
- iii) The character under σ_h determines whether the degenerate pair of vibrations is E' or E'' , and hence the rest of the table for BCl_3 can be completed ==>**data sheet**

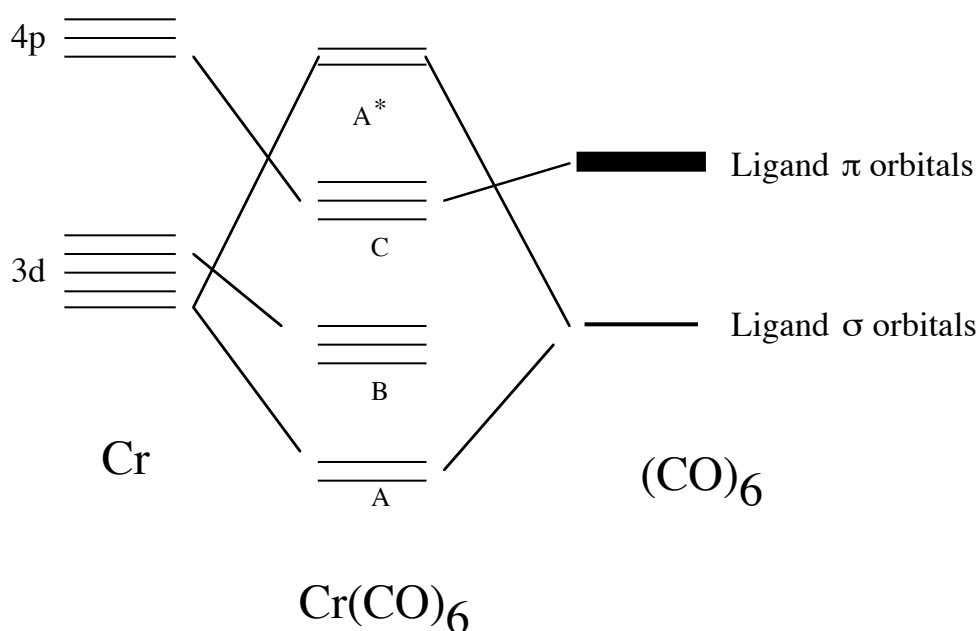
Correlate the vibrations of $BFBr_2$ with those of BCl_3 . (i.e. attempt to find the vibration in BCl_3 that most resembles the corresponding vibration in $BFBr_2$) ==>**data sheet**

One might expect that the vibrations of $BFBr_2$ and BCl_3 are very similar. You should discover that you can match up a pair of degenerate BCl_3 vibrations with a very similar pair of non-degenerate vibrations in $BFBr_2$. This is a general feature: C_{2v} is a *subgroup* of D_{3h} , the degenerate representations of D_{3h} become non-degenerate when considered as representations of C_{2v} .

4) Symmetry properties of the bonding orbitals in $\text{Cr}(\text{CO})_6$

The highest occupied and lowest unoccupied sets of MOs in transition metal complexes have very predictable forms and occur in *doubly* and *triply degenerate* sets, because of the high point group symmetry (O_h). In this exercise we look at the symmetry of the orbitals that result from the interaction of the Cr p and d shell orbitals with the CO ligand σ and π orbitals. In each example studied, the objective is to determine the symmetry of the orbitals and to relate this to the bonding interactions involved (e.g. which σ vs π orbitals of the ligand match the central atom symmetries).

The Cr atom in $\text{Cr}(\text{CO})_6$ is usually considered to have 6 d electrons in 3 *triply degenerate*, doubly occupied d orbitals that are essentially non-bonding: **shell B** in the correlation diagram below. The remaining 2 d orbitals interact with the ligand σ orbitals to form bonding and anti-bonding *doubly degenerate* sets **A** and **A*** in the diagram below. The non-bonding ligand π orbitals interact to form another *triply degenerate* set **C**, which interacts only very weakly with the Cr 4p orbitals. The order of the set C and **A*** depends upon the complex considered and there are many other σ^* orbitals that intervene energetically between the B-C and C-A* that we will not be concerned with.



Because these *frontier* orbitals are degenerate they only have simple symmetry properties under simple symmetry operations such as reflections, inversions and C_2 operations as we have seen in the previous exercise. The classification of the central atom orbital into the irrep of O_h can be obtained from group tables. In the correlation diagram above, only orbitals that have the *same* symmetry can interact. Thus if one has determined the symmetry of the Cr orbitals (from group theory / character tables) then the symmetry of the ligand orbitals is determined. It remains only to examine nature of the bonding.

i) classification of central atom d and p orbitals

- consult the character tables: lookup p_x , d_{xy} etc (right hand columns), find the irreducible representations these orbitals transform as, and complete the table given in the **==> data sheet**

ii) Symmetries of frontier orbital sets A B C A*

- **open** the file **crco.fchk** and display the MOs of each orbital set listed in the data sheet in turn. Complete the table (using the procedure below) in the **==> data sheet**

For each MO set you are asked to identify the central atom type (i.e. d_{xy} etc) and the nature of the ligand bond (eg σ CO or π CO). The overall symmetry of the MO can then be deduced from the table completed in i). Experiment with the Isovalue (cutoff) when visualising orbitals: it may be easier to see the ligand interactions with higher values (smaller spatial extent) than the default 0.02).

DATA SHEET:

Exercise 2: Symmetry properties of molecular vibrations and molecular orbitals.

1) Vibrations and MO symmetries of H₂O (Demonstration)

i) Symmetry properties of B₂ vibration.

freq	C _{2v}	E	C ₂	σ _v (xz)	σ _v ' (yz)
4391	B ₂				

ii) Symmetry properties of B₂ MO.

iii) Symmetry of lumo, lumo+1, homo and homo-1 in H₂O

MO	C _{2v}	E	C ₂	σ _v (xz)	σ _v ' (yz)
mo 7					
mo 6					
mo 5					
mo 4					

2) BFB₂ Vibrations

freq	C _{2v}	E	C ₂	σ _v (xz)	σ _v ' (yz)
195					
368					
504					
574					
876					
1382					

3) BCl₃ Vibrations

freq	D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₃	3σ _v
536							
600							
313	E	*****	*****			*****	
313	E	*****	*****			*****	
Sum							
1085	E	*****	*****			*****	
1085	E	*****	*****			*****	
Sum							

4) Symmetry properties of the bonding orbitals in $\text{Cr}(\text{CO})_6$

i) Classification of central atom orbitals

Orbital	O_h irrep
$p_x p_y p_z$	
$d_{z^2} d_{x^2-y^2}$	
$d_{xy} d_{xz} d_{yz}$	

ii) Symmetries of frontier orbital sets A B C A*

SET A

	Cr orbital irrep	Ligand orbital σ/π description
mo 41		
mo 42		
symmetry of shell A		

SET B

	Cr orbital irrep	Ligand orbital σ/π description
mo 43		
mo 44		
mo 45		
symmetry of shell B		

SET C

	Cr orbital irrep	Ligand orbital σ/π description
mo 58		
mo 59		
mo 60		
symmetry of shell B		

SET A*

	Cr orbital irrep	Ligand orbital σ/π description
mo 62		
mo 63		
symmetry of shell A*		

Molecular Symmetry

Suggested guide/template for write up 10-15 pages

You should start by reading the discussions in e.g. Atkins and the handout itself.

Marks are given for correct results, but also for demonstrating that you understand how the results are obtained, and what they mean. A few carefully constructed diagrams with clear explanations are more likely to demonstrate this. Marks will be lost for unthinking copy/paste.

Introduction: Exercises 1 and 2

Exercise 1:

Theory

Briefly discuss the concepts of symmetry elements and symmetry operations, groups of symmetry operations (point groups) in your own words.

Results and Discussion

For the six molecules being tested, give the point group, flowchart assignment, and additional symmetry elements (from the data sheet). All symmetry elements should be illustrated for each molecule.

Comment on the symmetry elements that are present in both cyclohexane (demo) and chlorocubane, and those that are only present in one or other of the two molecules.

Exercise 2:

Theory

Briefly discuss the concept of an irreducible representation of a point group.

Results and Discussion

Tabulate and summarise the results you collected in completing the data sheet for each of the four examples.

What is a degenerate irreducible representation, and what symmetry element(s) must be present for these to occur? Discuss this, referring to the results you obtained for BFBr_2 and BCl_3 .

For CrCO_6 , discuss the relationship between the correlation diagram on page 19 of the handout, the orbitals you obtained (data sheet / diagrams) and their bonding characteristics. E.g. the T_{2g} orbitals are nonbonding and located mainly on the central metal atom.

Conclusions

2nd Year Lab 2005
Mark Scheme for Computer Experiments.

Molecular Symmetry

Imperial College Department of Chemistry

Please note reports should NOT exceed 15 pages in length.

Student Name:

Marker:

Presentation

- Legibility and Structure (is the report well laid out?) /10
- Figures and Tables (are these well presented, labelled and clear?) /10

Grammar

- Spelling (deduct marks for persistent errors)
- Grammatical construction (does it read well?)
- Proof reading (has the report been properly proof read?) /10

Content

- Description of Aims and Theory /5
- (Have correct results been obtained) /30
- Understanding of the theory involved (has the student shown a good overall grasp of theory being used?) /5
- Discussion of each exercise 2 x 15 /30

Bonus Points

- Independent thought in interpretation. /5
- Additional experiments / improvements to expt. /5

TOTAL MARK /100