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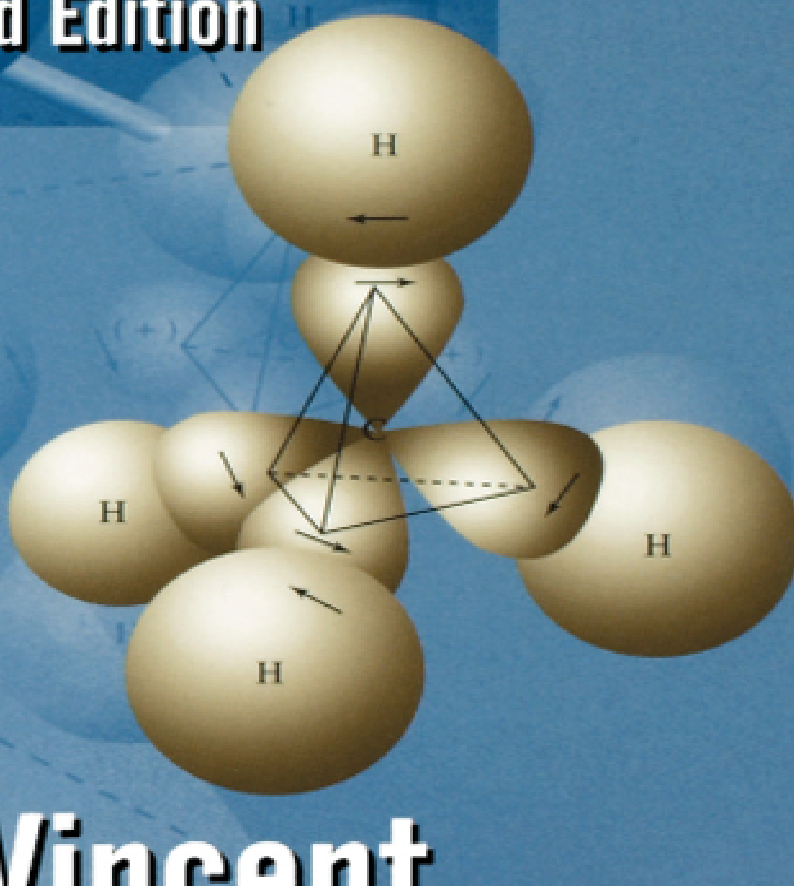
MOLECULAR SYMMETRY AND GROUP THEORY

Second Edition



Alan Vincent

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Molecular Symmetry and Group Theory

A Programmed Introduction to Chemical Applications

SECOND EDITION

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Preface to the Second Edition

The first edition of this book was well received by both students and teachers. The second edition, therefore, has required only minor changes to the first seven chapters. In these I have put more emphasis on the idea of the basis of a reducible representation and have clarified a few small ambiguities which reviewers have pointed out. The diagrams have also been completely re-drawn. The major addition in this edition is a completely new chapter on linear combinations. This not only introduces the projection operator method as the rigorous approach to finding the form of vibrations, wave functions, etc., but goes on to develop a simplified approach to the subject making direct use of the character table. Again the emphasis is on the application of the techniques to real chemical problems rather than on the mathematics of the method. I hope that this will give readers an enthusiasm for symmetry methods and encourage them to learn more via the excellent advanced texts cited in the bibliography.

Finally I would like to thank the (often anonymous) reviewers whose comments have been helpful in the process of revision and all the staff at John Wiley & Sons for their patience as I failed to meet various deadlines.

Alan Vincent
Kingston University
2000

How to use the Programmes

Each programme starts with a list of learning objectives, and a summary of the knowledge you will need before starting. You should study these sections carefully and make good any deficiencies in your previous knowledge. You may find it helpful at this stage to look at the revision notes at the end of the programme which give a summary of the material covered. The test, also at the end, will show you the sort of problems you should be able to tackle after working through the main text (but don't at this stage look at the answers!).

The body of each programme consists of information presented in small numbered sections termed *frames.* Each frame ends with a problem or question and then a line. You should cover the page with a sheet of paper or card and pull it down until you come to the line at the end of the frame. Read the frame and write down your answer to the question. This is most important - your learning will be much greater if you commit yourself actively by writing your answer down. You can check immediately whether or not your answer is right because each frame starts with the correct answer to the previous frame's question.

If you work through the whole programme in this way you will be learning at your own pace and checking on your progress as you go. If you are working at about the right pace you should get most of the questions right, but if you get one wrong you should read the frame again, look at the question, its answer, and any explanation offered, and try to understand how the answer was obtained. When you are satisfied about the answer go on to the next frame.

Learning a subject (as opposed to just reading a book about it) can be a long job. Don't get discouraged if you find the programmes taking a long time. Some students find this subject easy and work through each programme in about an hour or even less. Others have been known to take up to four hours for some programmes. Provided the programme objectives are achieved the time spent is relatively unimportant.

After completing each programme try the test at the end and only proceed to the next programme if your test score is up to the standard indicated.

Each programme finishes with a page of revision notes which should be helpful either to summarise the programme before or after use, or to serve as revision material later.

I hope you find the programmes enjoyable and useful.

Programme 1

Symmetry Elements and Operations

Objectives

After completing this programme, you should be able to:

1. Recognise symmetry elements in a molecule.
2. List the symmetry operations generated by each element.
3. Combine together two operations to find the equivalent single operation.

All three objectives are tested at the end of the programme.

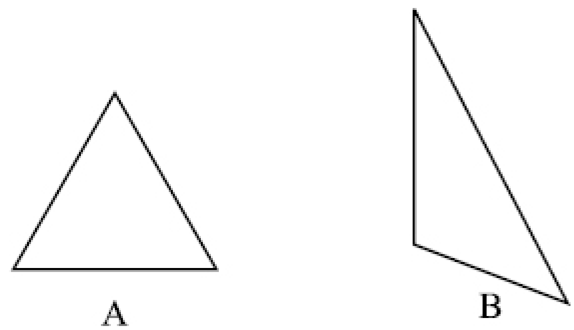
Assumed Knowledge

Some knowledge of the shapes of simple molecules is assumed.

Symmetry Elements and Operations

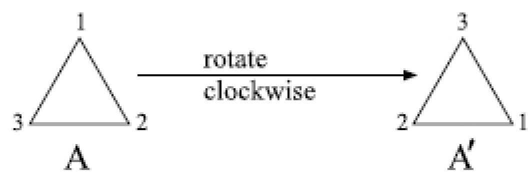
1.1 The idea of symmetry is a familiar one, we speak of a shape as being “symmetrical”, “unsymmetrical” or even “more symmetrical than some other shape”. For scientific purposes, however, we need to specify ideas of symmetry in a more quantitative way.

Which of the following shapes would you call the more symmetrical?



1.2 If you said A, it shows that our minds are at least working along similar lines!

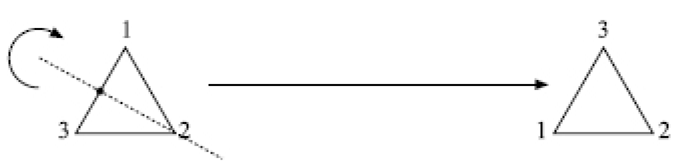
We can put the idea of symmetry on a more quantitative basis. If we rotate a piece of cardboard shaped like A by one third of a turn, the result looks the same as the starting point:



Since A and A′ are *indistinguishable* (not identical) we say that the rotation is a symmetry operation of the shape.

Can you think of another operation you could perform on a triangle of cardboard which is also a symmetry operation? (Not the anticlockwise rotation!)

1.3 Rotate by half a turn about an axis through a vertex i.e. turn it over



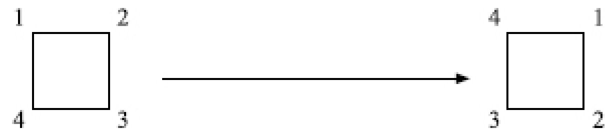
How many operations of this type are possible?

1.4 Three, one through each vertex.

We have now specified the first of our symmetry operations, called a PROPER ROTATION, and given the symbol C. The symbol is given a subscript to indicate the

ORDER of the rotation. One third of a turn is called C_3, one half a turn C_2, etc.

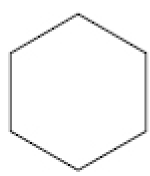
What is the symbol for the operation:



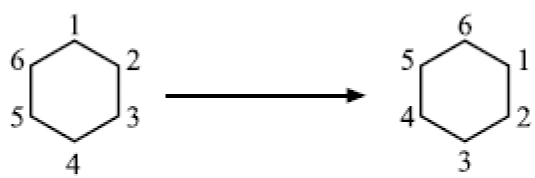
1.5 C_4. It is rotation by $\frac{1}{4}$ of a turn.

A symmetry *operation* is the operation of actually doing something to a shape so that the result is indistinguishable from the initial state. Even if we do not do anything, however, the shape still possesses an abstract geometrical property which we term a symmetry *element.* The element is a geometrical property which is said to generate the operation. The element has the same symbol as the operation.

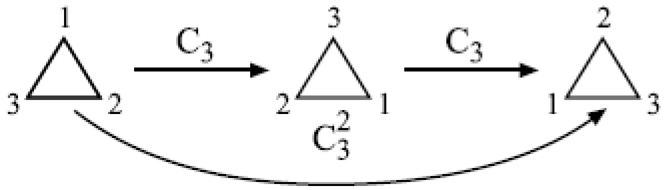
What obvious symmetry element is possessed by a regular six-sided shape:



1.6 C_6, a six-fold rotation axis, because we can rotate it by $\frac{1}{6}$ of a turn

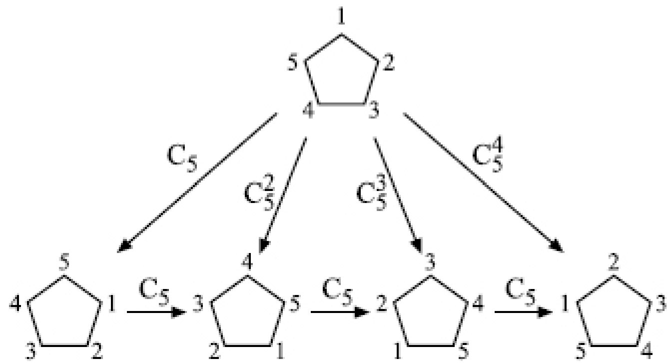


One element of symmetry may generate more than one operation e.g. a C_3 axis generates two operations called C_3 and C_3^2:



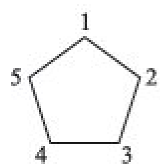
What operations are generated by a C_5 axis?

1.7 C_5, C_5^2, C_5^3, C_5^4



What happens if we go one stage further i.e. C_5^5?

1.8 We get back to where we started i.e.



The shape is now more than indistinguishable, it is IDENTICAL with the starting point. We say that C_5^5, or indeed any $C_n^n = E$, where E is the IDENTITY OPERATION, or the operation of doing nothing. Clearly this operation can be performed on anything because everything looks the same after doing nothing to it! If this sounds a bit trivial I apologise, but it is necessary to include the identity in the description of a molecule's symmetry in order to be able to apply the theory of Groups.

We have now seen two symmetry elements, the identity, E, and a proper rotation axis C_n. Can you think of a symmetry element which is possessed by all *planar* shapes?

1.9 A plane of symmetry.

This is given the symbol σ (sigma). The element generates only one operation, that of reflection in the plane.

Why only one operation? Why can't we do it twice – what is σ^2?

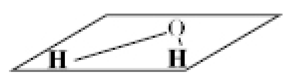
1.10 σ^2 = E, the identity, because reflection in a plane, followed by reflection back again, returns all points to the position from which they started, i.e. to the *identical* position.

Many molecules have one or more planes of symmetry. A flat molecule will always have a plane in the molecular plane e.g. H_2O, but this molecule also has one other plane.

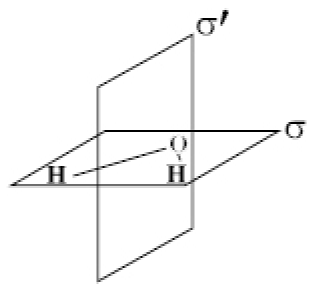
Can you see where it is?

AT THIS STAGE SOME READERS MAY NEED TO MAKE USE OF A KIT OF MOLECULAR MODELS OR SOME SORT OF 3-DIMENSIONAL AID. IN THE ABSENCE OF A PROPER KIT, MATCHSTICKS AND PLASTICINE ARE QUITE GOOD, AND A FEW LINES PENCILLED ON A BLOCK OF WOOD HAVE BEEN USED.

1.10a You were trying to find a second plane of symmetry in the water molecule:

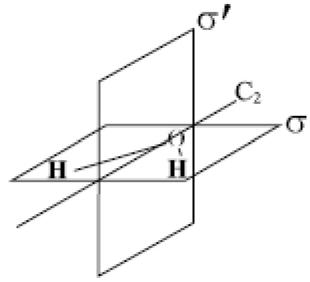


1.11 σ is the plane of the molecule, σ' is at right angles to it and reflects one H atom to the other.



The water molecule can also be brought to an indistinguishable configuration by a simple rotation. Can you see where the proper rotation axis is, and what its order is?

1.12 C_2, a twofold rotation axis, or rotation by half a turn.



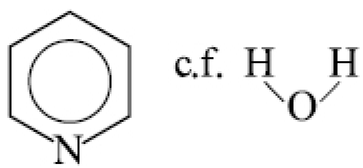
A C_2 axis passing through space is the hardest of all symmetry elements to see. It will be much easier to visualise if you use a model of the molecule.

This completes the description of the symmetry of water. It actually has FOUR elements of symmetry – one of which is possessed by all molecules irrespective of shape. Can you list all four symmetry elements of the water molecule?

1.13 E C_2 σ σ' Don't forget E!

Each of these elements generates only one operation, so the four symbols also describe the four operations.

Pyridine is another flat molecule like water. List its symmetry elements.

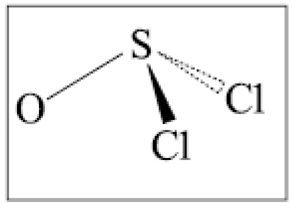


1.14 E C_2 σ σ' i.e. the same as water.

Many molecules have this set of symmetry elements, so it is convenient to classify them all under one name, the set of symmetry operations is called the C_{2v} point group, but more about this nomenclature later.

There is a simple restriction on planes of symmetry which is rather obvious but can sometimes be helpful in finding planes. A plane must either pass through an atom, or else that type of atom must occur in pairs, symmetrically either side of the plane. Take the molecule $SOCl_2$, which has a plane, and apply this consideration. Where must the plane be?

1.15 Through the atoms S and O because there is only one of each:

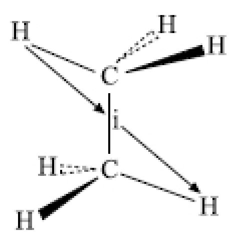


The molecule NH_3 possesses planes. Where must they lie?

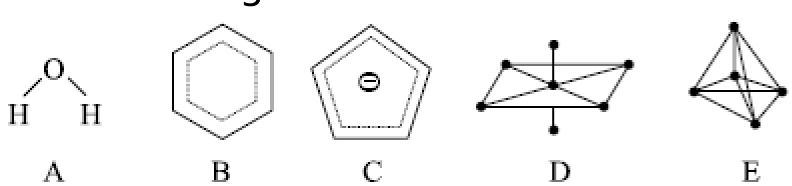
1.16 Through the nitrogen (only one N), and through at least one hydrogen (because there is an odd number of hydrogens). Look at a model and convince yourself that this is the case.

A further element of symmetry is the INVERSION CENTRE, i. This generates the operation of inversion through the centre. Draw a line from any point to the centre of the molecule, and produce it an equal distance the other side. If it comes to an equivalent point, the operation of inversion is a symmetry operation, e.g. ethane in the staggered conformation:

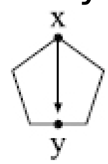
N.B. The operation of inversion cannot be physically carried out on a model.



Which of the following have inversion centres



1.17 Only B and D e.g., for C, the operation i would take point x to point y which is certainly not equivalent:

An inversion centre may be: 

a. In space in the centre of a molecule (ethane, benzene); or

b. At a single atom in the centre of the molecule (D above)

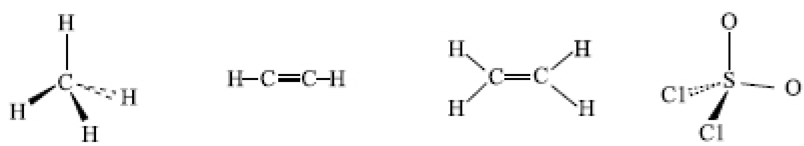
If it is in space, all atoms must be present in even numbers, spaced either side of the centre. If it is at an atom, then that type of atom *only* must be present in an odd number. Hence a molecule AB_3 cannot have an inversion centre but a molecule AB_4 might possibly have one.

Use this consideration to decide which of the following MIGHT POSSIBLY have a centre of inversion.

NH_3 CH_4 C_2H_2 C_2H_4 $SOCl_2$ SO_2C1_2

1.18 CH_4, C_2H_2, C_2H_4, SO_2C1_2 fulfil the rules, i.e. have no atoms present in odd numbers, or have only one such atom.

Which of these actually have inversion centres?



1.19 Only C_2H_2 and C_2H_4. Both have an inversion centre midway between the two carbon atoms.

What is the operation i^2?

1.20 i^2 = E, for the same reason that σ^2 = E (Frame 1.10).

We now have the operations E, σ, C_n, i. Only one more is necessary in order to specify molecular symmetry completely. That is called an IMPROPER ROTATION and is given the symbol S, again with a subscript showing the order of the axis. The element is sometimes called a