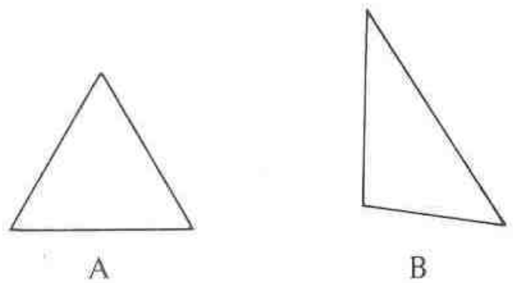
Symmetry Elements and Operations

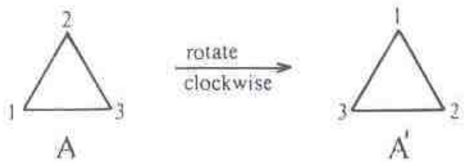
1.1 The idea of symmetry is a familiar one, we speak of a shape as being "symmetrical", "unsymmetrical" or even "more symmetrical than some other shape". For scientific purposes, however, we need to specify ideas of symmetry in a more quantitative way.

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:

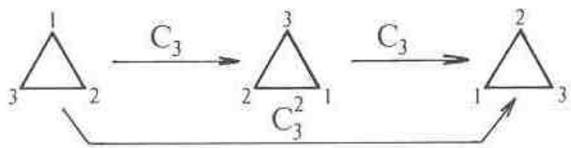
1.5 C_4. It is rotation by 1/4 of a turn.

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 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:

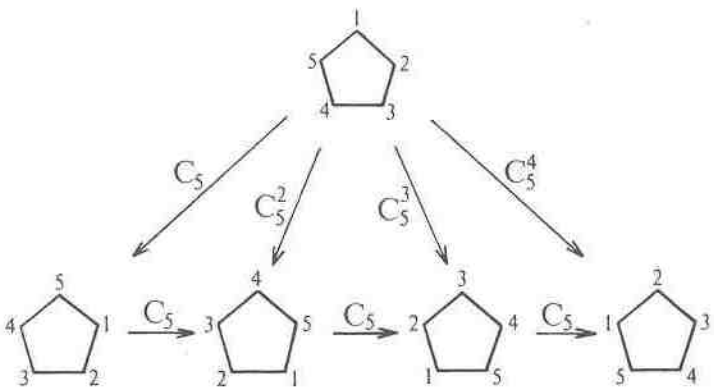
1.6 C_6, a six-fold rotation axis, because we can rotate it by 1/6 of a turn

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:



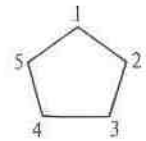
What operations are generated by a C_5 axis ?

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 $\sigma^2 = E$, 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?

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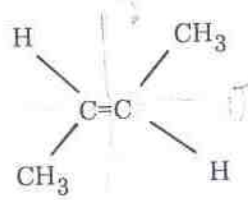
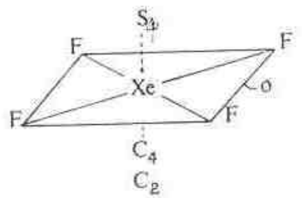
2. Set up the multiplication table for the *operations* of the molecule *trans* but-2-ene. Apply the top operation then the side operation:



	E	C_2	σ	i
E				
C_2				
σ				
i				

3. In this question you have to state the single symmetry operation of XeF_4 which has the same effect as applying a given operation several times. The diagram below shows the location of the symmetry elements concerned.



What operation has the same effect as:

a. S_4^2

b. S_4^3

c. S_4^4

d. C_4^2

e. C_4^3

f. C_4^4

g. σ^2

h. i^2

Answers

Give yourself one mark for each underlined answer you get right. (The others are so easy, they are not worth a mark!)

1. A. E $\underline{E}$ $\underline{C_2}$ $\underline{\sigma}$ $\underline{\sigma'}$

B. E $\underline{C_4}$ $\underline{C_2}$ $\underline{2\sigma}$ $\underline{2\sigma'}$

C. E $\underline{C_2}$ $\underline{C_2}$ $\underline{C_2}$ $\underline{i}$ $\underline{\sigma}$ $\underline{\sigma'}$ $\underline{\sigma''}$

D. E $\underline{C_5}$ $\underline{5C_2}$ $\underline{\sigma}$ $\underline{5\sigma'}$ $\underline{S_5}$

Total = 20

2.

	E	C_2	σ	i
E	E	C_2	σ	i
C_2	C_2	$\underline{E}$	$\underline{i}$	$\underline{\sigma}$
σ	σ	$\underline{i}$	$\underline{E}$	$\underline{C_2}$
i	i	$\underline{\sigma}$	$\underline{C_2}$	$\underline{E}$

Total = 9

3. a. $S_4^2 = \underline{C_2}$

b. $S_4^3 = \underline{S_4^3}$

c. $S_4^4 = \underline{E}$

d. $C_4^2 = \underline{C_2}$

e. $C_4^3 = \underline{C_4^3}$

f. $C_4^4 = \underline{E}$

g. $\sigma^2 = \underline{E}$

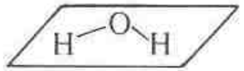
h. $i^2 = \underline{E}$

Total = 8

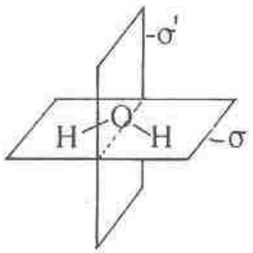
Grand Total = 37

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:



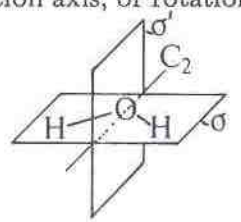
1.11



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.

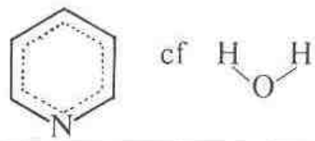


This completes the description of the symmetry of water. It actually has FOUR elements of symmetry - one of which is possessed by all molecules irrespective of shape. Can you list all four symmetry elements of the water molecule?

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.

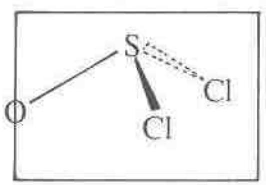


1.14 E C_2 σ σ ′ i.e. the same as water.

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:

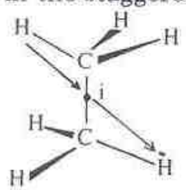


The molecule NH_3 possesses planes. Where must they lie?

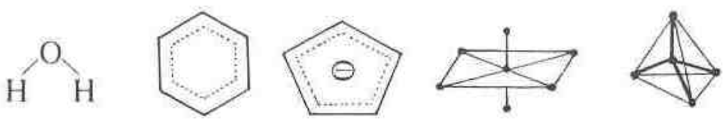
1.16 Through the nitrogen (only one N), and through at least one hydrogen (because there is an odd number of hydrogens). Look at a model and convince yourself that this is the case.

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.

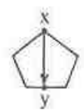


Which of the following have inversion centres



A B C D E

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:

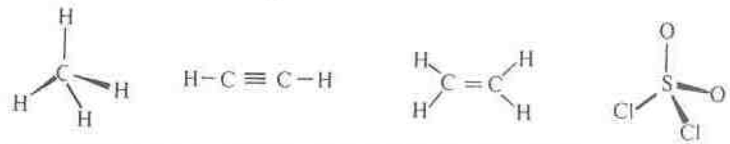
a. In space in the centre of a molecule (ethane, benzene) or
b. At a single atom in the centre of the molecule (D above).

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_2Cl_2

1.18 CH_4, C_2H_2, C_2H_4, SO_2Cl_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?



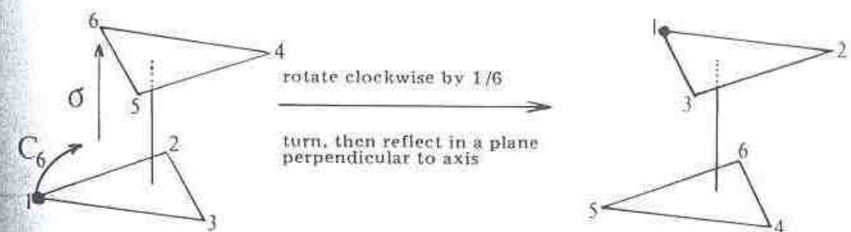
1.19 Only C_2H_2 and C_2H_4. Both have an inversion centre midway between the two carbon atoms.

What is the operation i^2?

1.20 $i^2 = E$, for the same reason that $\sigma^2 = E$ (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 rotation-reflection axis, and this describes the operation very well.

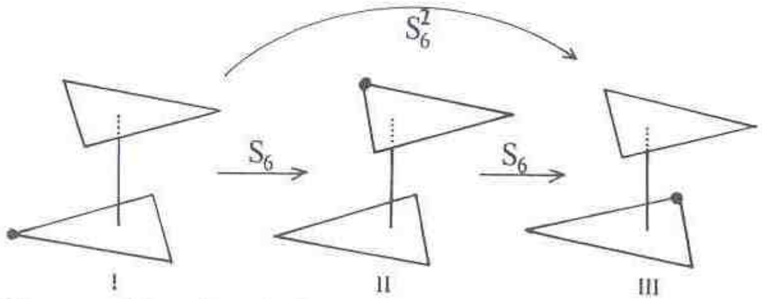
The S operation is rotation by $1/_n$ of a turn, followed by reflection in a plane *perpendicular to the axis*, e.g. ethane in the staggered conformation has an S_6 axis because it is brought to an indistinguishable arrangement by a rotation of 1/6 of a turn, followed by reflection:



N.B. Neither C_6 nor σ are present on their own.

In this example the effect of the symmetry operation has been shown by labelling one corner of the drawing. Draw the position of the label after the S_6 operation is applied

1.21



Now consider what single symmetry operation will take this molecule from state I directly to state III i.e. what single operation is the same as S_6^2?

1.22 $S_6^2 = C_3$, rotation by one third of a turn, because the molecule has been rotated by 2/6 of a turn ($= C_3$) and reflected twice ($\sigma^2 = E$).

What happens to the marker if S_6 is applied once more, i.e. what single operation has the same effect as S_6^3 (Use a model or the diagram above).

1.23 $S_6^3 = i$. In general $S_n^{n/2} = i$ if n is even and n/2 is odd. The operation $S_n^{n/2}$ is then not counted by convention.

If S_n (n even) is present, and $S_{n/2}$ is odd, i is present but the converse is not necessarily true.

Now apply S_6 once more, so that it has been applied four times in all.

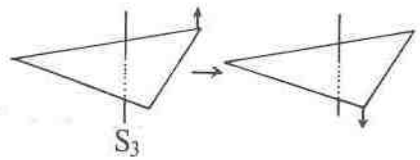
What other operation gives the same result as S_6^4?

1.24 $S_6^4 = C_3^2$ for the same reason that $S_6^2 = C_3$ (Frame 1.22) i.e. we have now rotated by 1/6 of a turn 4 times ($= C_3^2$), and reflected 4 times ($= E$)

S_6^5 is a unique operation, and $S_6^6 = E$. This is again true for any S_n of even n.

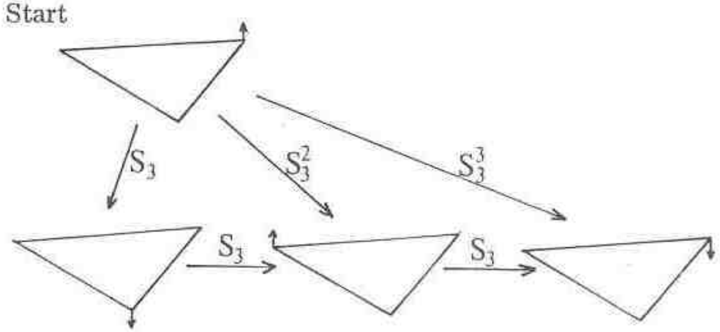
Let us now look at S_n of odd n because the case is rather different from even n. It may at first seem rather a trivial operation, because both C_n and a perpendicular plane must both be present, but it is necessary to include it to apply Group Theory to symmetry.

Use as the model a flat equilateral triangle with one vertex "labelled"; This label is only to help us to follow the effect of the operations, for example the application of S_3 moves the label as shown:



Write down the result of applying S_3 clockwise once, twice and then three times.

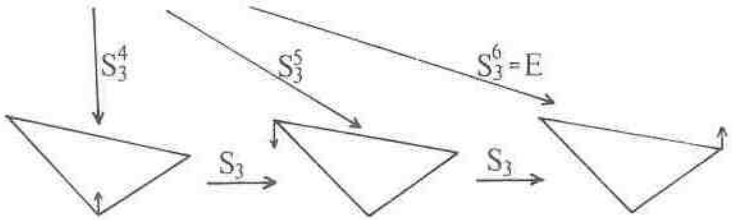
1.25 Start



In contrast to S_6 and C_3, applying the operation n times, where n is the order of the axis does not bring us back to the identity.

Keep going, then, when do we get E?

1.26



This result is quite general, for n odd $S_n^{2n} = E$, because we have rotated through two whole circles, and reflected an even number of times.

The equilateral triangle also has E, C_3, and σ among its elements of symmetry. Many of the operations we have generated by using the S_3 element of symmetry could have been generated by using other elements e.g., $S_3^2 = C_3^2$. Write these equivalents underneath the symbol S_3^n where appropriate

$S_3 \quad S_3^2 \quad S_3^3 \quad S_3^4 \quad S_3^5 \quad S_3^6$

e.g. C_3^2

1.27

$S_3 \quad S_3^2 \quad S_3^3 \quad S_3^4 \quad S_3^5 \quad S_3^6$

$C_3^2 \quad \sigma \quad C_3 \quad \quad E$

By convention, only S_3 and S_3^5 are counted as distinct operations generated by the S_3 symmetry element.

Do a similar analysis for the symmetry element C_6 (proper rotation axis) of benzene, which also has C_3 and C_2 axes colinear with the C_6. Clearly $C_6^2 = C_3$ since rotation by two sixths of a turn is the same as rotation by one third of a turn. Write the operations which have the same effect as C_6 C_6^2 C_6^3 C_6^4 C_6^5 and C_6^6.

1.28

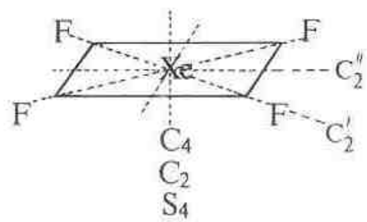
$C_6 \quad C_6^2 \quad C_6^3 \quad C_6^4 \quad C_6^5 \quad C_6^6$

$C_3 \quad C_2 \quad C_3^2 \quad \quad E$

Again, by convention, only the operations C_6 and C_6^5 are counted, the others are taken to be generated by C_3 and C_2 axes colinear with C_6.

We have just been looking at the operations generated by a particular symmetry element, let us now turn to the identification of symmetry elements in a molecule. You must first be quite sure you appreciate the difference between a symmetry *element* and the symmetry *operation(s)* generated by the element. If you are not confident of this point, have another look at frames 1.5 to 1.13.

Some molecules have a great many symmetry elements, some of which are not immediately obvious e.g. Xe F_4:

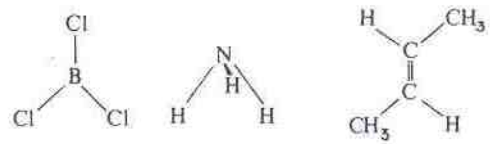


also E, i
σ_h (molecular plane)
2σ vertically through C_2'
2σ′ vertically through C_2''

Hence the complete list of symmetry elements is:

$E \quad C_4 \quad C_2 \quad S_4 \quad i \quad 2C_2' \quad 2C_2'' \quad \sigma_h \quad 2\sigma \quad 2\sigma'$

List the symmetry elements of the following molecules:



(assume CH_3 groups spherical)

If there is a set of, say, three equivalent planes, write them as 3σ, but if there are three non equivalent planes, write σ σ′ σ″. Similarly for other elements.

1.29 BCl_3 : E C_3 S_3 $3C_2$ 3σ σ (a somewhat similar c to XeF_4)

NH_3: E C_3 3σ

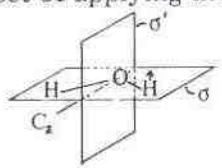
Butene: E C_2 σ i

We will now look at what happens if two symmetry operations are combined, or performed one after the other. The result is always the same as doing one symmetry operation alone, so we can write an equation such as:

$\sigma C_2 = \sigma'$

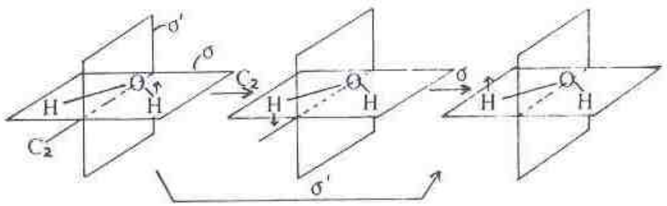
This equation means that the operation C_2 *followed by* the operation σ gives the same result as the operation σ'. Note that the order in which the operations are performed is from right to left. I apologise for the introduction of back to front methods, but this is the convention universally used in the mathematics of operators, and the reason for it will become evident when we begin to use matrices to represent symmetry operations.

Confirm that this relationship is in fact true for the water molecule. It may help to put a small label on your model to show the effect of applying the operations:

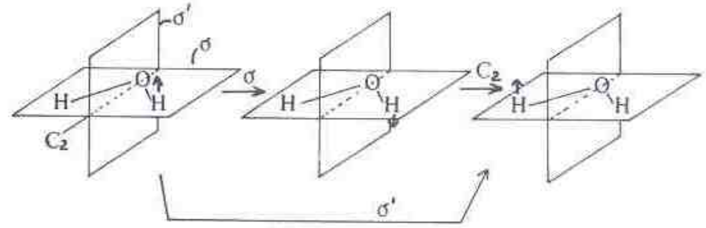


Draw the position of the arrow after applying C_2, and then after applying σ to the result. Hence confirm that $\sigma C_2 = \sigma'$.

1.30



1.31



In this case the two operations COMMUTE i.e., $\sigma C_2 = C_2 \sigma$, but this is not always true.

Use this diagram with an arrow to set up a complete multiplication table for the symmetry **OPERATIONS** of the water molecule, putting the product of the top operation, then the side operation, in the spaces:

	E	C_2	σ	σ'
E				
C_2				
σ				
σ'				

1.32

	E	C_2	σ	σ'
E	E	C_2	σ	σ'
C_2	C_2	E	σ'	σ
σ	σ	σ'	E	C_2

You should now be able to:

A. Recognise symmetry elements in a molecule

B. List the operations generated by each element

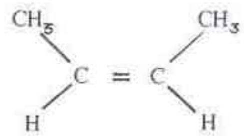
C. Combine together two operations to find the equivalent single operation.

I'm afraid the next page is a short test to see how well you have learned about elements and operations. After you have done it, mark it yourself, and it will give you some indication of how well you have understood this work.

Symmetry Elements and Operations Test

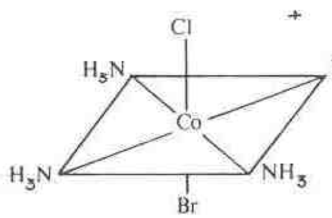
1. List the symmetry elements of the molecules.

A



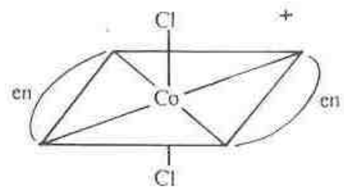
(assume CH_3 spherical)

B

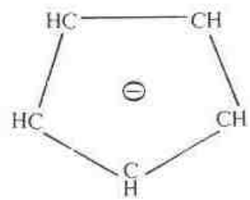


(assume NH_3 spherical)

C



D



To be able to proceed confidently to the next programme you should have obtained at least:

Question 1	(Objective 1)	15/20	(Frames 1.1 - 1.20)
Question 2	(Objective 2)	7/9	(Frames 1.28 - 1.32)
Question 3	(Objective 3)	4/8	(Frames 1.6 - 1.10, 1.19 - 1.2

If you have not obtained these scores you would be well advised to return to the frames shown, although a low score on question 3 is less serious than the other two.

Symmetry Elements and Operations Revision notes

The symmetry of a molecule can be described by listing all the symmetry elements of the molecule. A molecule possesses a symmetry element if the application of the operation generated by the element leaves the molecule in an *indistinguishable* state. There are five different elements necessary to completely specify the symmetry of all possible molecules

E	the identity
C_n	a proper rotation axis of order n
σ	a plane of symmetry
i	an inversion centre
S_n	an improper (or rotation-reflection) axis of order n.

Each of the elements E, σ , i only generates one operation, but C_n and S_n can generate a number of operations because the effect of applying the operation a number of times can count as separate operations e.g., the C_3 element generates operations C_3 and C_3^2. Some such multiple applications of an operation have the same effect as a single application of a different operation. In these cases only the single case is counted, e.g., $C_4^2 = C_2$, and only C_2 is counted.

If two operations are performed successively on a molecule, the result is always the same as the application of only one different operation. It is therefore possible to set up a multiplication table for the symmetry operations of a molecule to show how the operations combine together. When writing an equation to represent the successive application of symmetry elements it is necessary to remember that $\sigma\ \sigma'\ C_4$ means C_4 followed by σ', followed by σ .