

Combining Symmetry Operations (Multiplication)

- ☞ Multiplication of symmetry operations is the successive performance of two or more operations to achieve an orientation that could be reached by a single operation.
- ☞ The order in which successive different symmetry operations are performed can affect the result.
- ☞ Multiplication of symmetry operations is *not* in general commutative, although certain combinations may be.
- ☞ In writing multiplications of symmetry operation we use a "right-to-left" notation:

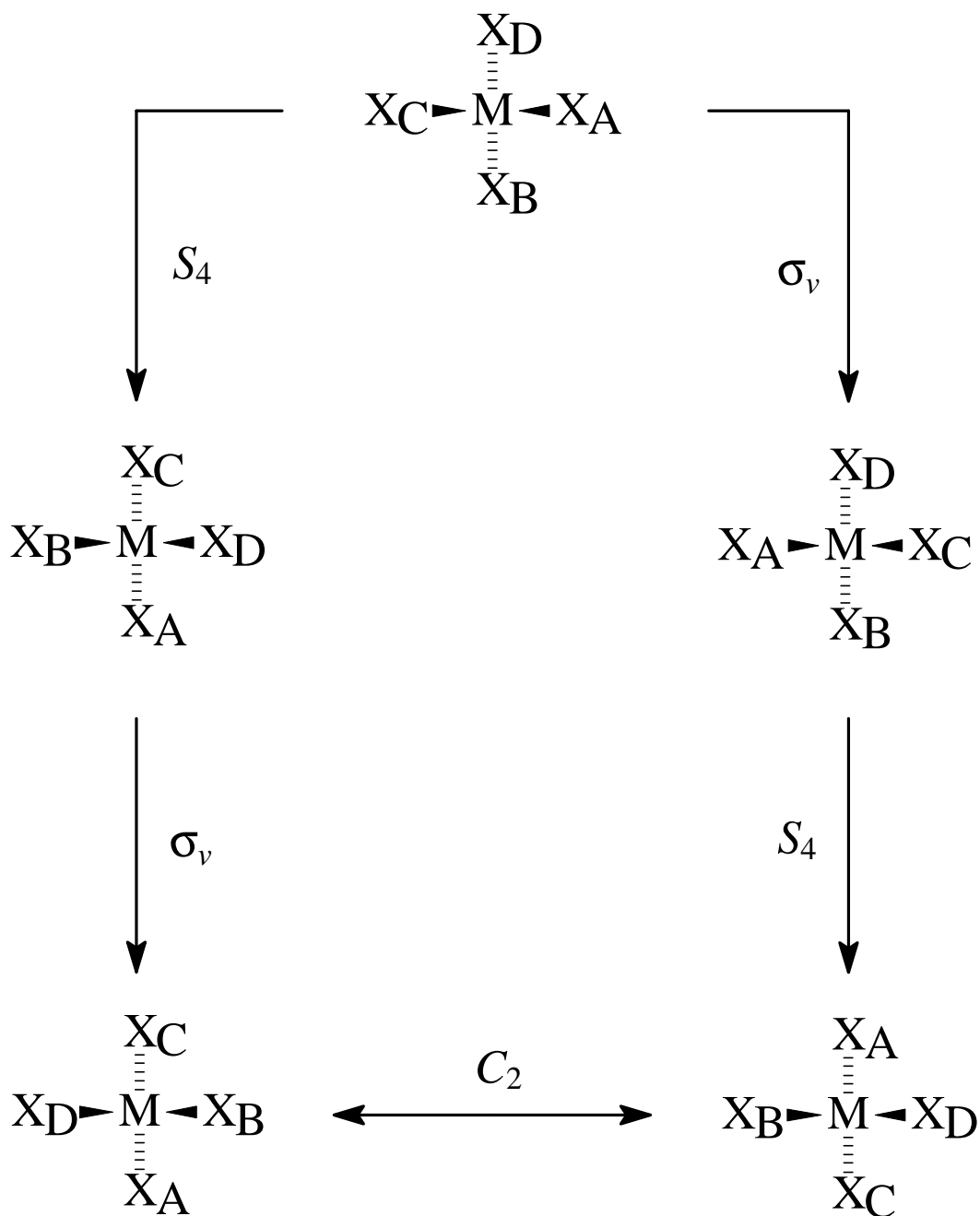
$BA = X$ "Doing A then B has the same result as the operation X ."

- ✓ We cannot assume that reversing the order will have the same result.
- ✓ It may be that either $BA \neq AB$ or $BA = AB$.

- ☞ Multiplication is associative:

$$C(BA) = (CB)A$$

Fig. 1.12 The order of performing S_4 and σ_v , shown here for a tetrahedral MX_4 molecule, affects the result. The final positions in each case are not the same, but they are related to each other by C_2 .



Multiplication Tables

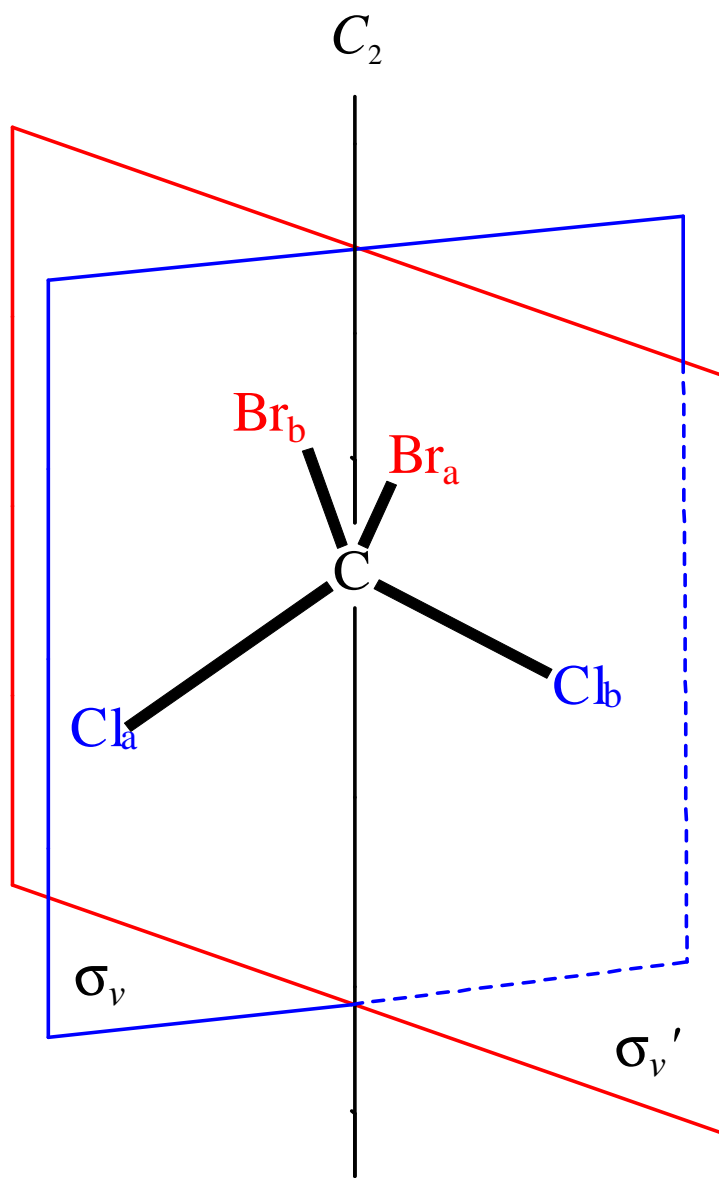
- ☞ All possible binary combinations of symmetry operations can be summarized in a multiplication table.

	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>
<i>E</i>	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>
<i>A</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>E</i>
<i>B</i>	<i>B</i>	<i>C</i>	<i>E</i>	<i>A</i>
<i>C</i>	<i>C</i>	<i>E</i>	<i>A</i>	<i>B</i>

- ✓ Combination order is "top" then "side"; e.g.,

	<i>E</i>	<i>A</i>	<i>B</i>	<i>C</i>
<i>E</i>	<i>EE = E</i>	<i>EA = A</i>	<i>EB = B</i>	<i>EC = C</i>
<i>A</i>	<i>AE = A</i>	<i>AA = B</i>	<i>AB = C</i>	<i>AC = E</i>
<i>B</i>	<i>BE = B</i>	<i>BA = C</i>	<i>BB = E</i>	<i>BC = A</i>
<i>C</i>	<i>CE = C</i>	<i>CA = E</i>	<i>CB = A</i>	<i>CC = B</i>

Fig. 1.13 Symmetry elements of CBr_2Cl_2 .



Matrix Notation of the Effects of the Operations

$$[E] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix}$$

$$[C_2] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_b \\ \text{Br}_a \\ \text{Cl}_b \\ \text{Cl}_a \end{bmatrix}$$

$$[\sigma_v] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_b \\ \text{Br}_a \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix}$$

$$[\sigma'_v] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_b \\ \text{Cl}_a \end{bmatrix}$$

Multiplication Table for the Operations of CBr_2Cl_2

	E	C_2	σ_v	σ_v'
E				
C_2				
σ_v				
σ_v'				

Step 1: Combinations with identity.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2			
σ_v	σ_v			
σ_v'	σ_v'			

Step 2: Binary self-combinations.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E		
σ_v	σ_v		E	
σ_v'	σ_v'			E

Multiplication Table for the Operations of CBr_2Cl_2

Step 3: Mixed binary combinations.

$$C_2\sigma_v = ?$$

$$[\sigma_v] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_b \\ \text{Br}_a \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix}$$

$$[C_2] \times \begin{bmatrix} \text{Br}_b \\ \text{Br}_a \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_b \\ \text{Cl}_a \end{bmatrix}$$

This result is the same as that achieved by σ_v' alone:

$$[\sigma_v'] \times \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_a \\ \text{Cl}_b \end{bmatrix} = \begin{bmatrix} \text{Br}_a \\ \text{Br}_b \\ \text{Cl}_b \\ \text{Cl}_a \end{bmatrix}$$

$$\pencil C_2\sigma_v = \sigma_v'$$

Complete Multiplication Table

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

General Results:

- ✓ The first row of results duplicates the list of operations in the header row.
- ✓ The first column of results duplicates the list of operations in the label column.
- ✓ Every row shows every operation once and only once.
- ✓ Every column shows every operation once and only once.
- ✓ The order of resultant operations in every row is different from any other row.
- ✓ The order of resultant operations in every column is different from any other column.