PG SEMISTR II, UNIT III, SYMMETRY ELEMENTS

BY

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Group Representations

The set of four matrices that describe all of the possible symmetry operations in the C_{2v} point group that can act on a point with coordinates *x, y, z* is called the total representation of the C_{2v} group.

$$\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix} \quad \begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} \quad \begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix} \quad \begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$$

$$\mathbf{E} \qquad\qquad \mathbf{C_2} \qquad\qquad \sigma_{\mathbf{xz}} \qquad\qquad \sigma_{\mathbf{yz}}$$

Note that each of these matrices is block diagonalized, i.e., the total matrix can be broken up into blocks of smaller matrices that have no off-diagonal elements between blocks.

These block diagonalized matrices can be broken down, or reduced into simpler one-dimensional representations of the 3-dimensional matrix.

If we consider symmetry operations on a point that only has an *x* coordinate (e.g., *x*, 0, 0), then only the first row of our total representation is required:

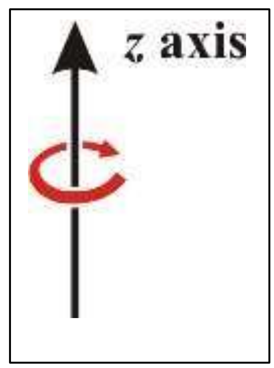
C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_1	1	–1	1	–1	*x*

We can do a similar breakdown of the y and z coordinates to setup a table:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_1	1	–1	1	–1	*x*
Γ_2	1	–1	–1	1	*y*
Γ_3	1	1	1	1	*z*

These three 1-dimensional representations are as simple as we can get and are called irreducible representations.

There is one additional irreducible representation in the C_{2v} point group. Consider a rotation R_z :



The identity operation and the C_2 rotation operations leave the direction of the rotation R_z unchanged. The mirror planes, however, reverse the direction of the rotation (clockwise to counter-clockwise), so the irreducible representation can be written as:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
Γ_4	1	1	–1	–1	R_z

4 Classes of symmetry operations =

4 Irreducible representations!!

Now lets consider a case where we have a 2-dimensional irreducible representation. Consider the matrices for C_{3v}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} \cos 120^\circ & -\sin 120^\circ & 0 \\ \sin 120^\circ & \cos 120^\circ & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

E $\qquad$ **C_3** $\qquad$ **σ_v**

In this case the matrices block diagonalize to give two reduced matrices. One that is 1-dimensional for the *z* coordinate, and the other that is 2-dimensional relating the *x* and *y* coordinates.

Multidimensional matrices are represented by their characters (trace), which is the sum of the diagonal elements.

Since cos(120º) = –0.50, we can write out the irreducible representations for the 1- (*z*) and 2-dimensional "degenerate" *x* and *y* representations:

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	*z*
Γ_2	2	–1	0	*x,y*

As with the C_{2v} example, we have another irreducible representation (3 symmetry classes = 3 irreducible representations) based on the R_z rotation axis. This generates the full group representation table:

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	z
Γ_2	2	–1	0	x,y
Γ_3	1	1	–1	R_z