CHAPTER 4
GROUP THEORY AND VIBRATIONAL SPECTROSCOPY

Before going to study the application of group theory in the field of molecular spectroscopy, we have to show how to obtain a representation of the point group of any molecule using a set of 3N vectors (three Cartesian coordinate vectors on each of the N atoms; N is the number of atoms) and how to reduce this into its irreducible components. The general symbol for any representation is Γ and Γ_{3N} indicates that 3N vectors are used as bases. To obtain the value of Γ_{3N} one of the two following method is used.

1-The Use of Transformation Matrix

This is illustrated for the SO_2 molecule as an example as follows:

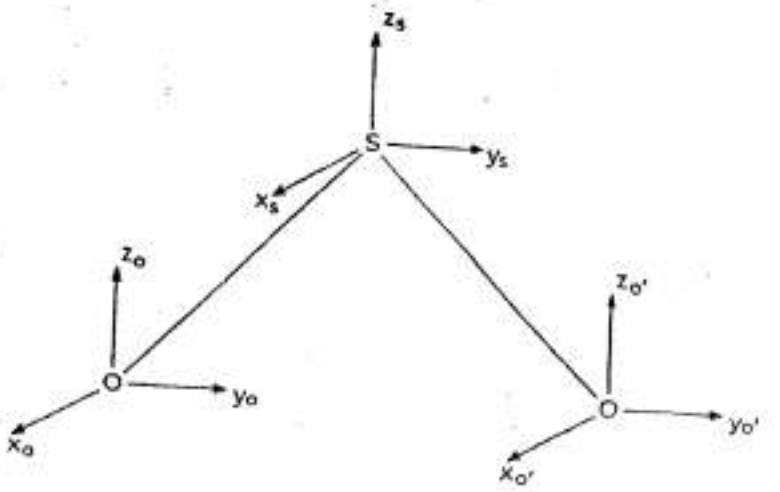


Fig.1. Cartesian coordinate system for SO_2 (C_{2v})

To construct the representation generated by the nine vectors, we must find their transformation matrix under the symmetry operations of the C_{2v} point group. For example the operation $\sigma(xz)$ gives the following transformations:

$x_o \rightarrow x_{o'}$, $y_o \rightarrow y_{o'}$, $z_o \rightarrow z_{o'}$, $x_{o'} \rightarrow x_o$, $y_{o'} \rightarrow y_o$, $z_{o'} \rightarrow z_o$, $x_s \rightarrow x_s$, $y_s \rightarrow y_s$ and $z_s \rightarrow z_s$

the 9x9 matrix for this transformation is

$$\sigma(xz)\begin{bmatrix} x_O \\ y_O \\ z_O \\ x_O' \\ y_O' \\ z_O' \\ x_S \\ y_S \\ z_S \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_O \\ y_O \\ z_O \\ x_O' \\ y_O' \\ z_O' \\ x_S \\ y_S \\ z_S \end{bmatrix}$$

We need only the character of this matrix (X) and in this case $X(\sigma_{xz}) = 1$. Similar matrices are obtained from the other symmetry operations.

$$E: \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$C_2: \begin{bmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\sigma(yz): \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

Now the characters of the transformation matrices are written down the C_{2v} table as follows:

C_{2v}	E	C_2	σ(xz)	σ(yz)
A_1	+1	+1	+1	+1
A_2	+1	+1	-1	-1
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	-1
Γ_{3N}	9	-1	1	3

We can now use the equation listed in rule (3) in the last chapter to reduce Γ_{3N} for SO_2 molecule into its irreducible components

$a_{A1} = ¼[(1x9x1) + (1x-1x1) + (1x1x1) + (1x3x1)] = 12/4 = 3$

$a_{A2} = ¼[(1x9x1) + (1x-1x1) + (1x1x-1) + (1x3x-1)] = 4/4 = 1$

$a_{B1} = ¼[(1x9x1) + (1x-1x-1) + (1x1x1) + (1x3x-1)] = 8/4 = 2$

$a_{B2} = ¼[(1x9x1) + (1x-1x-1) + (1x1x-1) + (1x3x1)] = 12/4 = 3$

therefore we can say that $\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$

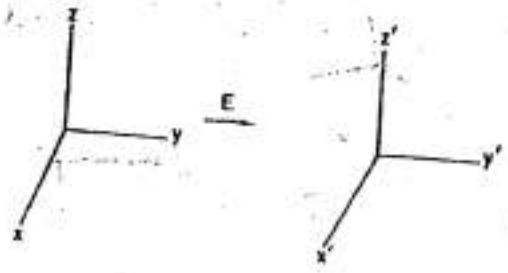
In this the number of irreducible representations equals the number of basis vectors i.e. nine.

3- The Method of Unshifted Atom

The method of transformation matrix becomes more difficult in case of molecules more complicated than SO_2. To present a simple method for calculation of Γ_{3N} we must take into account one of the rule of matrix multiplication: *if any atom and its associated vectors are shifted to a different position in space by any symmetry operation, then these vectors contribute zero to X(R).* In general, therefore, *only the vectors on unshifted atoms can contribute to the character of a given symmetry operation in* Γ_{3N}.

Then firstly we must count the number of unshifted atoms for every symmetry operation and calculate the contribution to X(R) for every unshifted atom. This proceed as follows:

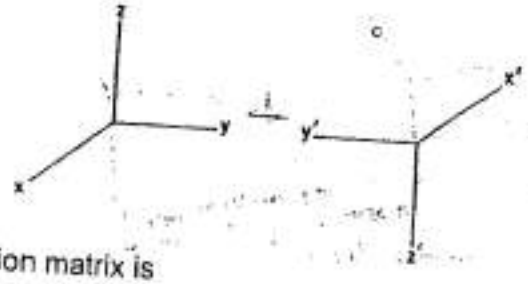
(i) *The identity* (E): in this case all three vectors remain unchanged for each un shifted atom (x'=x, y'=y and z'=z)



The transformation matrix therefore include the diagonal elements

$$\begin{matrix} +1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & +1 \end{matrix}$$ then X(E)/unshifted atom = +3

(ii) *Inversion* (i): in this case we have (x'=-x, y'=-y and z'=-z), thus:



and the transformation matrix is

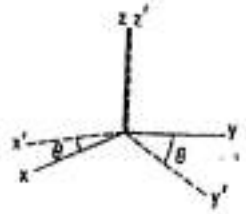
$$\begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$$ then X(E)/unshifted atom = -3

(iii) *Reflection in symmetry plane* (σ): the effect of any σ on an unshifted atom is represented by the following figure (x'=x, y'=-y and z'=z)

The transformation matrix therefore is

$$\begin{matrix} +1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{matrix}$$ then X(E)/unshifted atom = +1

iv- *Proper Rotation* (c_n^1) : rotation by (360/n)° about the z axis as an example is represented by



The diagonal elements of the transformation matrix are given by the components of x' along the x direction and y' along the y direction i.e. cos (360/n)° in each case, while z' = z. The transformation matrix in this case is:

$$\begin{matrix} +\cos(630/n)^\circ & 0 & 0 \\ 0 & +\cos(630/n)^\circ & 0 \\ 0 & 0 & 1 \end{matrix}$$ then $X(C_n^1) = 1+2\cos(630/n)^\circ$

v- *Improper Rotation* (S_n^1): this is exactly like C_n^1 except that z'=-z, so $X(S_n^1)$/unshifted atom is $-1+2+\cos(630/n)^\circ$.

Table 1 lists the above mentioned contributions per unshifted atoms

R	X(R)	R	X(R)
E	+3	C_3^1, C_3^2	0
i	-3	C_4^1, C_4^3	+1
σ	+1	C_6^1, C_6^5	+2
C_2	-1	S_3^1, S_3^5	-2

Now to calculate Γ_{3N} for SO_2 molecule using the method of unshifted atoms, the number of atoms lift unshifted by any symmetry operation is determined then multiplied by the factors listed in table 1 (do it your self).

Example (1): *Calculate Γ_{3N} then give its irreducible components for $POCl_3$ molecule*