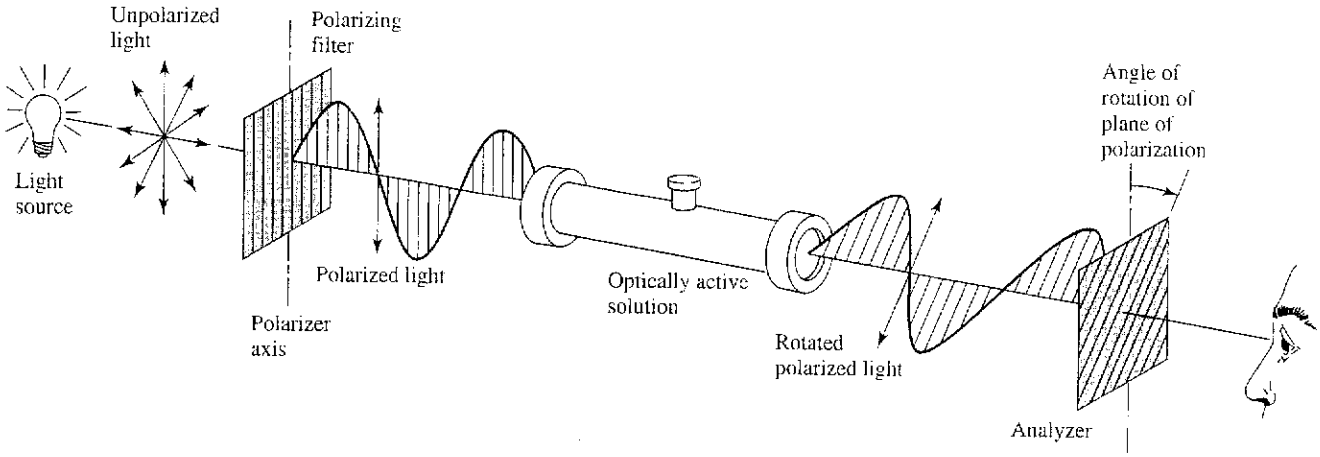


FIGURE 4-19 Rotation of Plane-Polarized Light.

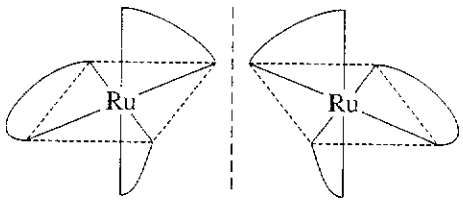


FIGURE 4-20 Chiral Isomers of $[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$.

D_3 symmetry (Figure 4-20). Mirror images of this molecule look much like left- and right-handed three-bladed propellers. Further examples will be discussed in Chapter 9.

4-4-2 MOLECULAR VIBRATIONS

Symmetry can be helpful in determining the modes of vibration of molecules. Vibrational modes of water and the stretching modes of CO in carbonyl complexes are examples that can be treated quite simply, as described in the following pages. Other molecules can be studied using the same methods.

Water (C_{2v} symmetry)

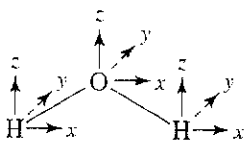


FIGURE 4-21 A Set of Axes for the Water Molecule.

Because the study of vibrations is the study of motion of the individual atoms in a molecule, we must first attach a set of x, y, and z coordinates to each atom. For convenience, we assign the z axes parallel to the C_2 axis of the molecule, the x axes in the plane of the molecule, and the y axes perpendicular to the plane (Figure 4-21). Each atom can move in all three directions, so a total of nine transformations (motion of each atom in the x, y, and z directions) must be considered. For N atoms in a molecule, there are $3N$ total motions, known as **degrees of freedom**. Degrees of freedom for different geometries are summarized in Table 4-9. Because water has three atoms, there must be nine different motions.

We will use transformation matrices to determine the symmetry of all nine motions and then assign them to translation, rotation, and vibration. Fortunately, it is only necessary to determine the characters of the transformation matrices, not the individual matrix elements.

In this case, the initial axes make a column matrix with nine elements, and each transformation matrix is 9×9. A nonzero entry appears along the diagonal of the matrix only for an atom that does not change position. If the atom changes position during the symmetry operation, a 0 is entered. If the atom remains in its original location and

TABLE 4-9
Degrees of Freedom

Number of Atoms	*Total Degrees of Freedom*	*Translational Modes*	*Rotational Modes*	*Vibrational Modes*
N (linear)	$3N$	3	2	$3N - 5$
3 (HCN)	9	3	2	4
N (nonlinear)	$3N$	3	3	$3N - 6$
3 (H_2O)	9	3	3	3

the vector direction is unchanged, a 1 is entered. If the atom remains but the vector direction is reversed, a -1 is entered. (Because all the operations change vector directions by 0° or 180° in the C_{2v} point group, these are the only possibilities.) When all nine vectors are summed, the character of the reducible representation Γ is obtained. The full 9×9 matrix for C_2 is shown as an example; note that only the diagonal entries are used in finding the character.

$$
\begin{matrix} \\ \mathrm{O} \\ \\ \\ \mathrm{H}_a \\ \\ \\ \mathrm{H}_b \\ \\ \end{matrix}
\begin{Bmatrix} x' \\ y' \\ z' \\ x' \\ y' \\ z' \\ x' \\ y' \\ z' \end{Bmatrix}
=
\left[\begin{array}{ccccccccc}
-1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hdashline
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\hdashline
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0
\end{array}\right]
\begin{Bmatrix} x \\ y \\ z \\ x \\ y \\ z \\ x \\ y \\ z \end{Bmatrix}
\begin{matrix} \\ \mathrm{O} \\ \\ \\ \mathrm{H}_a \\ \\ \\ \mathrm{H}_b \\ \\ \end{matrix}
$$

The H_a and H_b entries are not on the principal diagonal because H_a and H_b exchange with each other in a C_2 rotation, and $x'(H_a) = -x(H_b)$, $y'(H_a) = -y(H_b)$, and $z'(H_a) = z(H_b)$. Only the oxygen atom contributes to the character for this operation, for a total of -1.

The other entries for Γ can also be found without writing out the matrices, as follows:

E: All nine vectors are unchanged in the identity operation, so the character is 9.

C_2: The hydrogen atoms change position in a C_2 rotation, so all their vectors have zero contribution to the character. The oxygen atom vectors in the x and y directions are reversed, each contributing -1, and in the z direction they remain the same, contributing 1, for a total of -1. [The sum of the principal diagonal $= \chi(C_2) = (-1) + (-1) + (1) = -1$.]

$\sigma_v(xz)$: Reflection in the plane of the molecule changes the direction of all the y vectors and leaves the x and z vectors unchanged, for a total of $3 - 3 + 3 = 3$.

$\sigma_v'(yz)$: Finally, reflection perpendicular to the plane of the molecule changes the position of the hydrogens so their contribution is zero; the x vector on the oxygen changes direction and the y and z vectors are unchanged, for a total of 1.

Because all nine direction vectors are included in this representation, it represents all the motions of the molecule, three translations, three rotations, and (by difference) three vibrations. The characters of the reducible representation Γ are shown as the last row below the irreducible representations in the C_{2v} character table.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz
Γ	9	−1	3	1		

Reducing representations to irreducible representations

The next step is to separate this representation into its component irreducible representations. This requires another property of groups. The number of times that any irreducible representation appears in a reducible representation is equal to the sum of the products of the characters of the reducible and irreducible representations taken one operation at a time, divided by the order of the group. This may be expressed in equation form, with the sum taken over all symmetry operations of the group.[4]

$$\begin{pmatrix}\text{Number of irreducible}\\ \text{representations of}\\ \text{a given type}\end{pmatrix} = \frac{1}{\text{order}} \sum_R \left[\begin{pmatrix}\text{number}\\ \text{of operations}\\ \text{in the class}\end{pmatrix} \times \begin{pmatrix}\text{character of}\\ \text{reducible}\\ \text{representation}\end{pmatrix} \times \begin{pmatrix}\text{character of}\\ \text{irreducible}\\ \text{representation}\end{pmatrix} \right]$$

In the water example, the order of C_{2v} is 4, with one operation in each class $(E, C_2, \sigma_v, \sigma_v')$. The results are then

$$n_{A_1} = \frac{1}{4}[(9)(1) + (-1)(1) + (3)(1) + (1)(1)] = 3$$

$$n_{A_2} = \frac{1}{4}[(9)(1) + (-1)(1) - (3)(-1) + (1)(-1)] = 1$$

$$n_{B_1} = \frac{1}{4}[(9)(1) + (-1)(-1) + (3)(1) + (1)(-1)] = 3$$

$$n_{B_2} = \frac{1}{4}[(9)(1) + (-1)(-1) - (3)(-1) + (1)(1)] = 2$$

The reducible representation for all motions of the water molecule is therefore reduced to $3A_1 + A_2 + 3B_1 + 2B_2$.

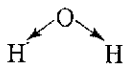
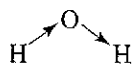
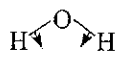
Examination of the columns on the far right in the character table shows that translation along the x, y, and z directions is $A_1 + B_1 + B_2$ (translation is motion along the x, y, and z directions, so it transforms in the same way as the three axes) and that rotation in the three directions (R_x, R_y, R_z) is $A_2 + B_1 + B_2$. Subtracting these from the total above leaves $2A_1 + B_1$, the three vibrational modes, as shown in Table 4-10. The number of vibrational modes equals $3N - 6$, as described earlier. Two of the modes are totally symmetric (A_1) and do not change the symmetry of the molecule, but one is antisymmetric to C_2 rotation and to reflection perpendicular to the plane of the molecule (B_1). These modes are illustrated as symmetric stretch, symmetric bend, and antisymmetric stretch in Table 4-11.

[4]This procedure should yield an integer for the number of irreducible representations of each type; obtaining a fraction in this step indicates a calculation error.

TABLE 4-10
Symmetry of Molecular Motions of Water

All Motions	*Translation* (x, y, z)	*Rotation* (R_x, R_y, R_z)	*Vibration (Remaining Modes)*
$3A_1$	A_1		$2A_1$
A_2		A_2	
$3B_1$	B_1	B_1	B_1
$2B_2$	B_2	B_2	

TABLE 4-11
The Vibrational Modes of Water

A_1		Symmetric stretch: change in dipole moment; more distance between positive hydrogens and negative oxygen *IR active*
B_1		Antisymmetric stretch: change in dipole moment; change in distances between positive hydrogens and negative oxygen *IR active*
A_1		Symmetric bend: change in dipole moment; angle between H—O vectors changes *IR active*

A molecular vibration is infrared active (has an infrared absorption) only if it results in a change in the dipole moment of the molecule. The three vibrations of water can be analyzed this way to determine their infrared behavior. In fact, the oxygen atom also moves. Its motion is opposite that of the hydrogens and is very small, because its mass is so much larger than that of the hydrogen atoms. The center of mass of the molecule does not move in vibrations.

Group theory can give us the same information (and can account for the more complicated cases as well; in fact, group theory in principle can account for *all* vibrational modes of a molecule). In group theory terms, a vibrational mode is active in the infrared *if it corresponds to an irreducible representation that has the same symmetry (or transforms) as the Cartesian coordinates x, y, or z*, because a vibrational motion that shifts the center of charge of the molecule in any of the x, y, or z directions results in a change in dipole moment. Otherwise, the vibrational mode is not infrared active.

EXAMPLES

Reduce the following representations to their irreducible representations in the point group indicated (refer to the character tables in Appendix C):

C_{2h}	E	C_2	i	σ_h
Γ	4	0	2	2

Solution:

$$n_{A_g} = \frac{1}{4}[(4)(1) + (0)(1) + (2)(1) + (2)(1)] = 2$$

$$n_{B_g} = \frac{1}{4}[(4)(1) + (0)(-1) + (2)(1) + (2)(-1)] = 1$$

$$n_{A_u} = \frac{1}{4}[(4)(1) + (0)(1) + (2)(-1) + (2)(-1)] = 0$$

$$n_{B_u} = \frac{1}{4}[(4)(1) + (0)(-1) + (2)(-1) + (2)(1)] = 1$$