

Chapter 9. The Symmetry of Rovibronic Wave Functions

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chap. 10 and 11, and Bunker and Jensen (1998), Chap. 12.*

9.1 Introduction

We found out in the previous chapter that the complete internal wave function Φ_{int} consists of the product of rovibronic Φ_{rve}^0 and nuclear spin $\Phi_{\text{ns},t}$ wave functions

$$\Phi_{\text{int}} = \Phi_{\text{rve}}^0 \Phi_{\text{ns},t}. \quad (9.1)$$

We also showed that the irreducible representations generated by Φ_{int} and $\Phi_{\text{ns},t}$ are readily determined through their transformation properties under the elements of the MS group of the molecule under consideration and applying the Pauli principle. This in turn allowed us to evaluate which rovibronic representations are realizable. But since we know that, to a good level of approximation, the rovibronic wave function is the product of the electronic, vibrational, and rotational wave functions, then we must determine the symmetry of these three functions before we can proceed any further.

9.2 The Classification of the Electronic Wave Function

As we saw in Chapter 2, the electronic wave function $\Phi_{\text{elec},n}$ is built up by (in what follows we will drop the ‘,n’ subscript and simply denote the electronic wave function with Φ_{elec})

- a. Establishing a set of molecular orbitals (MO) consisting of linear combinations of atomic orbitals.
- b. Multiplying each MO with each of the two possible one-electron spin functions, and calculating a Slater determinant (see equation (2.32)) to get a suitable electronic function.

This process can be refined or expanded, but it will be sufficient for our purposes. We therefore concentrate on determining the symmetry of the wave functions resulting from this process. It should be clear that the Slater determinant produces a function that is the sum of products of MOs. Each MO consists of the multiplication of an orbital component by a spin function (α or β , using the usual convention; see equation (8.8)). If there are n electrons involved in the problem, then there will also be n different MOs, as well as $n!$ different realizable products of MOs and terms in the sum resulting from the Slater determinant. Furthermore, the $n!$ MO products only differ in the details of how each electron is assigned within a given MO. That is, they only differ in the labeling of the electrons. Because a MO has a well-defined character, under the elements of the MS group of the molecule, that does not depend on its associated electron label, then we are led to the important fact that *all the MO products that make up the Slater determinant have the same symmetry in the MS group of the molecule. Therefore, determining the*

symmetry of one product of MOs is equivalent to determining that of the electronic wave function itself.

Let us consider the water molecule as an example of how we can use this to our advantage. There are ten electrons involved in the H_2O molecule with the following available AOs in the ground state (the protons are labeled 1 and 2)

$$\begin{aligned} \text{H}_1 &: 1s(\text{H}_1) \\ \text{H}_2 &: 1s(\text{H}_2) \\ \text{O} &: 1s(\text{O}), 2s(\text{O}), 2p_x(\text{O}), 2p_y(\text{O}), 2p_z(\text{O}). \end{aligned} \quad (9.2)$$

Using MS group of water is $C_{2v}(M)$ (see Table 9-1), we now investigate the transformation properties of the AOs under the elements of the group, evaluate their character, and assemble the functions of similar symmetry to make bonding and anti-bonding MOs.

Table 9-1 – The character table for $C_{2v}(M)$, the MS group for water.

$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$
R_{rot} :	R^0	R_0^π	$R_{\pi/2}^\pi$	R_z^π
A_1 :	1	1	1	$:T_x$
A_2 :	1	1	-1	$:\hat{J}_x$
B_1 :	1	-1	-1	$:T_y, \hat{J}_z$
B_2 :	1	-1	1	$:T_z, \hat{J}_y$

To correctly assess the transformation properties of the AOs we must remember that *i*) permutations affect the nuclei only, *ii*) the inversion and permutation-inversion operators affect the electrons also by inverting the sign of their coordinates in the space-fixed coordinate system, but *iii*) the transformation of the AOs are relative to the molecule-fixed axes x , y , and z . As an example, the effect of the $C_{2v}(M)$ elements on the $2p_z(\text{O})$ AO is shown in Figure 9-1. Using these properties we can write the following table.

Table 9-2 – The transformation of the AOs of water under the $C_{2v}(M)$ group.

$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$
$1s(\text{H}_1)$:	$1s(\text{H}_1)$	$1s(\text{H}_2)$	$1s(\text{H}_1)$	$1s(\text{H}_2)$
$1s(\text{H}_2)$:	$1s(\text{H}_2)$	$1s(\text{H}_1)$	$1s(\text{H}_2)$	$1s(\text{H}_1)$
$1s(\text{O})$:	$1s(\text{O})$	$1s(\text{O})$	$1s(\text{O})$	$1s(\text{O})$
$2s(\text{O})$:	$2s(\text{O})$	$2s(\text{O})$	$2s(\text{O})$	$2s(\text{O})$
$2p_x(\text{O})$:	$2p_x(\text{O})$	$2p_x(\text{O})$	$2p_x(\text{O})$	$2p_x(\text{O})$
$2p_y(\text{O})$:	$2p_y(\text{O})$	$-2p_y(\text{O})$	$-2p_y(\text{O})$	$2p_y(\text{O})$
$2p_z(\text{O})$:	$2p_z(\text{O})$	$-2p_z(\text{O})$	$2p_z(\text{O})$	$-2p_z(\text{O})$

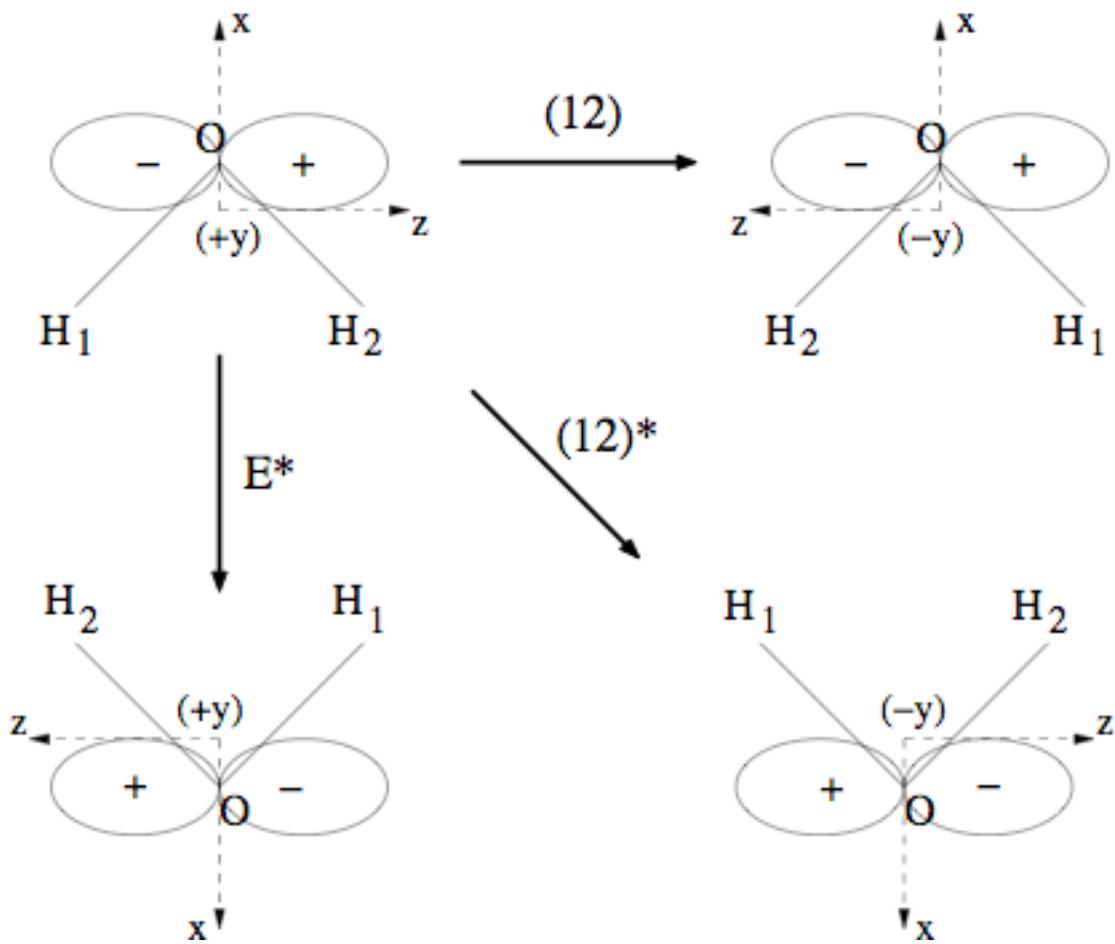


Figure 9-1 – The effect of the $C_{2v}(M)$ elements on the $2p_z(O)$ AO. This AO is represented by the two ellipses. Take note that the molecule-fixed axes are shown, and that they are tied to the nuclei.

Obviously, because of their spherical symmetry the $1s(O)$ and $2s(O)$ AOs are invariant under any symmetry operation, while the $1s(H_1)$ and $1s(H_2)$ AOs can transform into one another. Using the results of Table 9-2 we can now easily calculate the character Γ of the AOs, when taken as a whole, to be

$$\chi^\Gamma[E] = 7, \quad \chi^\Gamma[(12)] = 1, \quad \chi^\Gamma[E^*] = 5, \quad \chi^\Gamma[(12)^*] = 3. \quad (9.3)$$

Following our usual procedure, we now use equation (6.60)

$$a_i = \frac{1}{h} \sum_R \chi^\Gamma[R] \chi^{\Gamma_i}[R]^*, \quad (9.4)$$

to decompose this character into

$$\begin{aligned}
a_{A_1} &= \frac{1}{4}(7+1+5+3) = 4 \\
a_{A_2} &= \frac{1}{4}(7+1-5-3) = 0 \\
a_{B_1} &= \frac{1}{4}(7-1-5+3) = 1 \\
a_{B_2} &= \frac{1}{4}(7-1+5-3) = 2,
\end{aligned} \tag{9.5}$$

or alternatively

$$\Gamma = 4A_1 \oplus B_1 \oplus 2B_2. \tag{9.6}$$

We continue our analysis with the projection operators (i.e., equation (7.22)) to obtain the symmetry-adapted functions (which are not normalized here)

$$\begin{aligned}
A_1 &: 1s(O), 2s(O), 2p_x(O), [1s(H_1) + 1s(H_2)] \\
B_1 &: 2p_y(O) \\
B_2 &: 2p_z(O), [1s(H_1) - 1s(H_2)].
\end{aligned} \tag{9.7}$$

Bonding and anti-bonding MOs are defined from these orbitals as follows

$$\begin{aligned}
(1a_1) &= 1s(O) \\
(2a_1) &= 2s(O) + [1s(H_1) + 1s(H_2)] \\
(2a_1)^* &= 2s(O) - [1s(H_1) + 1s(H_2)] \\
(3a_1) &= 2p_x(O) + [1s(H_1) + 1s(H_2)] \\
(3a_1)^* &= 2p_x(O) - [1s(H_1) + 1s(H_2)] \\
(1b_1) &= 2p_y(O) \\
(1b_2) &= 2p_z(O) + [1s(H_1) - 1s(H_2)] \\
(1b_2)^* &= 2p_z(O) - [1s(H_1) - 1s(H_2)].
\end{aligned} \tag{9.8}$$

Remember that in order for two orbitals to combine their energies have to be sufficiently close (see Chapter 2); this is the reason why we do not combine $1s(O)$ with $[1s(H_1) + 1s(H_2)]$, for example. Because electrons can occupy any of two spin states, each MO listed in equation (9.8) contains in general zero, one, or two electrons. To find the electronic ground state we now merely need to rank these MOs with increasing

energy and fill them accordingly with the ten available electrons. In this case we have for the ground state \tilde{X} ¹

$$\tilde{X} : (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2. \quad (9.9)$$

We are now in a position to evaluate the representation generated by the orbital component of the electronic ground state of H₂O with (we have not dealt with the spins yet; see below)

$$\begin{aligned}\Gamma^{\tilde{X}} &= (A_1 \otimes A_1) \otimes (A_1 \otimes A_1) \otimes (B_2 \otimes B_2) \otimes (A_1 \otimes A_1) \otimes (B_1 \otimes B_1) \\ &= A_1 \otimes A_1 \otimes A_1 \otimes A_1 \otimes A_1 = A_1.\end{aligned}\quad (9.10)$$

For the first excited electronic state \tilde{A} , the last electron lying in the most energetic orbital state ($(1b_1)$ in this case) of the ground state will be promoted to the orbital with the next available energy level. For water, the next AO that can be added to those listed in equation (9.2) is a 3s(O). Just like the 1s(O) and 2s(O) AOs, it is invariant under the elements of the MS group and will form a new totally symmetric MO, which we call $(4a_1)$. The first excited electronic state is therefore

$$\tilde{A} : (1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^1 (4a_1)^1, \quad (9.11)$$

and

$$\Gamma^{\tilde{A}} = (A_1 \otimes A_1) \otimes (A_1 \otimes A_1) \otimes (B_2 \otimes B_2) \otimes (A_1 \otimes A_1) \otimes B_1 \otimes A_1 = B_1. \quad (9.12)$$

This symmetry state must be combined (i.e., multiplied) with the corresponding representation generated by the electronic spin function. How this is done depends on the amount spin-orbit interactions present for a given molecule. We consider the two limiting cases in what follows.

9.2.1 Hund's Case b) for Electronic Spin Functions

This is the simplest case. It happens when the amount of electronic spin-orbit coupling (i.e., the magnetic coupling of the electron spin with the electronic and nuclear orbital motions) is negligible. In situations where this condition applies, it is adequate to quantize the individual spin operators along the space-fixed axes (as opposed to the

¹ **Note:** Although it is reasonable to assume that the $(1a_1)$ MO (i.e., 1s(O)) should have the lowest energy or that a given bonding MO lies lower in energy than its corresponding anti-bonding MO, the ranking of MO energies is not generally straightforward. This should really be accomplished with a careful analysis, taking into account the overlap existing between the different hydrogen and oxygen AOs composing the MOs. But this is beyond the scope of our analysis.

molecule-fixed axes), and use the corresponding wave functions in the evaluation of the Slater determinant (in a manner similar as was done for nuclear spins in the previous chapter). This is the so-called **Hund's case b**). Since the space-fixed spin functions (i.e., α and β) are unaffected by the symmetry operators of the MS group (since they are related to the space-fixed, and not the molecule-fixed, axes), then the Hund's case b) spin basis functions will be totally symmetric. That is, *the symmetry and classification of the electronic wave function Φ_{elec} is determined without considering the electronic spin*. One merely adds the **multiplicity** $2S+1$ to the electronic symmetry species to specify the spin state, where S is the quantum number associated to the total electronic spin. For example, for water on the ground state \tilde{X} we have $S=0$, as two electrons occupy each MO, and we write

$$\Gamma^{\tilde{X}} = {}^{2S+1}A_1 = {}^1A_1. \quad (9.13)$$

For the first excited state \tilde{A} the electronic spin can be $S=0$ or $S=1$ depending on the spin state of the two unpaired ($1b_1$) and ($4a_1$) electrons. We therefore write

$$\Gamma^{\tilde{A}} = {}^1B_1 \oplus {}^3B_1. \quad (9.14)$$

9.2.2 Hund's Case a) for Electronic Spin Functions

When the electronic spin-orbit coupling is strong the electrons will be tied to the molecule-fixed axes. The spins of the electrons are thus quantized along this set of axes, and we especially have

$$\hat{s}_z = \lambda_{z\xi}\hat{s}_\xi + \lambda_{z\eta}\hat{s}_\eta + \lambda_{z\zeta}\hat{s}_\zeta, \quad (9.15)$$

for the z -component of the spin expressed, now as a function of the Euler matrix (see equation (3.1)) and the space-fixed spin components. This two-dimensional spin matrix associated to \hat{s}_z is expressed for the basis formed by the space-fixed α and β states. It must therefore be diagonalized to the molecule-fixed system, and the new corresponding eigenfunctions will acquire a dependence on the Euler angles in the process. These are the spin functions that will be used to calculate the Slater determinant. Because of this dependence on the Euler angles, the spin functions will not be invariant under the elements of the MS group and, contrary to the Hund's case b), *the symmetry and classification of the electronic wave function Φ_{elec} cannot be determined without considering the electronic spin*.

The question of how the symmetry of the electronic spin function is determined is quite involved and we will be covered in Chapter 13. We will only mention that the products of spin eigenfunctions are associated with the total spin operators \hat{S}^2 and \hat{S}_z and transform as the irreducible representations $D^{(S)}$ of the full rotation group K (see Chapter 5). This group, like the MS group, is also a symmetry group of the Hamiltonian and the character of its irreducible representations can be evaluated by taking the trace of equations (4.88)

of Chapter 4 (i.e., with $J \rightarrow S$ and a trace on m and k in $D_{mk}^{(J)}$). The character of the products of spin functions is therefore completely determined by S , and their species in the MS group are determined by correlating the full rotation group to the equivalent rotation group of the MS group. The resulting MS group irreducible representations for the products of the spin functions are multiplied with that resulting from the products of the orbital component of the MOs to get the representations generated by the electronic wave function Φ_{elec} .

9.3 The Transformation Properties of the Rovibrational Coordinates

Since the vibrational wave functions depend on the Euler angles and the normal coordinates, we must first understand how these coordinates transform under the symmetry elements of the MS group.

9.3.1 The Transformation Properties of the Euler Angles and the Rovibronic Angular Momentum

We know that the permutation and permutation-inversion operators that make up the different MS groups can interchange the positions of nuclei and, since the molecule-fixed axes x , y , and z are tied to the molecule, alter the Euler angles. It was shown in Section 6.3.1 that any permutation and permutation-inversion transformation R results from the product of three different operators with

$$R = R_{\text{ve}} R_{\text{rot}} R_{\text{ns}} \quad (9.16)$$

where R_{ve} is an operator belonging to the molecular point group and R_{ns} is a nuclear spin permutation operator; both of these leave the orientation of the molecule-fixed axes unchanged. On the other hand, the operation R_{rot} consists of a rotation of the molecule-fixed axes and is therefore responsible for the change in the Euler angles. By a judicious choice of the a , b , and c labels this operator will take one of the following forms

$$R_{\text{rot}} = \begin{cases} R_\alpha^\pi \\ R_z^\beta, \end{cases} \quad (9.17)$$

where the R_α^π is a rotation by π radians about an axis that makes an angle α with the x -axis in the xy -plane and R_z^β is a rotation by β radians about the z -axis. The effect of this last rotation is easily calculated and is written in Table 9-3. The effect of R_α^π , however, deserves a closer study, which follows.

The rotation by π radians about an axis that makes an angle α with the x -axis in the xy -plane resulting on a transformed set of axes x'' , y'' , and $z'' (= -z)$ is shown in Figure 9-2. As can be seen from this figure, components along the new axes are expressed as functions of the components along the original axes with

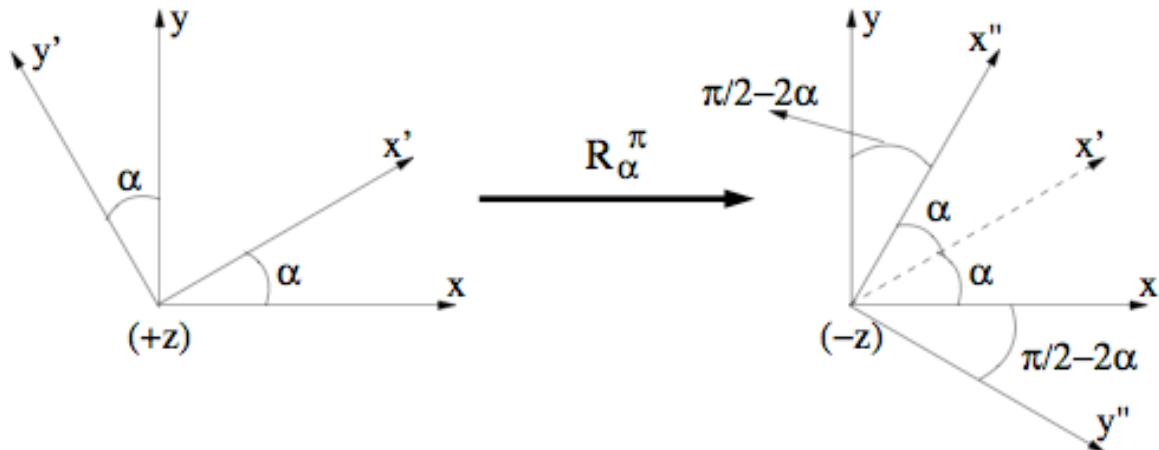


Figure 9-2 – The effect of R_α^π on the molecule-fixed axes.

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{bmatrix} \cos(2\alpha) & \sin(2\alpha) & 0 \\ \sin(2\alpha) & -\cos(2\alpha) & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (9.18)$$

since $\cos(\pi/2 - 2\alpha) = \sin(2\alpha)$. We can further relate the new coordinates to the space-fixed coordinate with the Euler matrix

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{bmatrix} \cos(2\alpha) & \sin(2\alpha) & 0 \\ \sin(2\alpha) & -\cos(2\alpha) & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \lambda_{x\xi} & \lambda_{x\eta} & \lambda_{x\zeta} \\ \lambda_{y\xi} & \lambda_{y\eta} & \lambda_{y\zeta} \\ \lambda_{z\xi} & \lambda_{z\eta} & \lambda_{z\zeta} \end{bmatrix} \begin{pmatrix} \xi \\ \eta \\ \zeta \end{pmatrix}, \quad (9.19)$$

with

$$\begin{aligned} \lambda_{x\xi} &= \cos(\theta)\cos(\phi)\cos(\chi) - \sin(\phi)\sin(\chi) \\ \lambda_{y\xi} &= -\cos(\theta)\cos(\phi)\sin(\chi) - \sin(\phi)\cos(\chi) \\ \lambda_{z\xi} &= \sin(\theta)\cos(\phi) \\ \lambda_{x\eta} &= \cos(\theta)\sin(\phi)\cos(\chi) + \cos(\phi)\sin(\chi) \\ \lambda_{y\eta} &= -\cos(\theta)\sin(\phi)\sin(\chi) + \cos(\phi)\cos(\chi) \\ \lambda_{z\eta} &= \sin(\theta)\sin(\phi) \\ \lambda_{x\zeta} &= -\sin(\theta)\cos(\chi) \\ \lambda_{y\zeta} &= \sin(\theta)\sin(\chi) \\ \lambda_{z\zeta} &= \cos(\theta), \end{aligned} \quad (9.20)$$

from the material covered at the beginning of Chapter 3.

Table 9-3 – The Transformation properties of the Euler angles, the rovibronic angular momentum, and rotational eigenvectors.

	R_α^π	R_z^β
ϕ	$\phi + \pi$	ϕ
θ	$\pi - \theta$	θ
χ	$2\pi - 2\alpha - \chi$	$\chi + \beta$
J_x	$J_x \cos(2\alpha) + J_y \sin(2\alpha)$	$J_x \cos(\beta) + J_y \sin(\beta)$
J_y	$J_x \sin(2\alpha) - J_y \cos(2\alpha)$	$-J_x \sin(\beta) + J_y \cos(\beta)$
J_z	$-J_z$	J_z
$ J, k, m\rangle$	$(-1)^J e^{-2ik\alpha} J, -k, m\rangle$	$e^{ik\beta} J, k, m\rangle$

But we can also express equation (9.19) with only one transformed Euler matrix as

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{bmatrix} \lambda_{x\xi}'' & \lambda_{x\eta}'' & \lambda_{x\xi}'' \\ \lambda_{y\xi}'' & \lambda_{y\eta}'' & \lambda_{y\xi}'' \\ \lambda_{z\xi}'' & \lambda_{z\eta}'' & \lambda_{z\xi}'' \end{bmatrix} \begin{pmatrix} \xi \\ \eta \\ \zeta \end{pmatrix}, \quad (9.21)$$

where the matrix elements have the same form as those defined in equations (9.20), but with a dependency on the transformed Euler angles ϕ'' , θ'' , and χ'' . Equating the last row of the matrix resulting from equation (9.19) to that of the matrix from equation (9.21) we have

$$\begin{aligned} \sin(\theta'') \cos(\phi'') &= -\sin(\theta) \cos(\phi) \\ \sin(\theta'') \sin(\phi'') &= -\sin(\theta) \sin(\phi) \\ \cos(\theta'') &= -\cos(\theta), \end{aligned} \quad (9.22)$$

which implies that

$$\phi'' = \phi \text{ or } \pi + \phi, \quad \text{and} \quad \theta'' = \pi \pm \theta. \quad (9.23)$$

From the top two elements of the last column of the same two matrices we also find that

$$\begin{aligned} -\cos(2\alpha) \sin(\theta) \cos(\chi) + \sin(2\alpha) \sin(\theta) \sin(\chi) &= -\sin(\theta) \cos(2\alpha + \chi) \\ &= -\sin(\theta'') \cos(\chi'') \\ -\sin(2\alpha) \sin(\theta) \cos(\chi) - \cos(2\alpha) \sin(\theta) \sin(\chi) &= -\sin(\theta) \sin(2\alpha + \chi) \\ &= \sin(\theta'') \sin(\chi''), \end{aligned} \quad (9.24)$$

and by taking their ratio

$$\chi'' = 2\pi - 2\alpha - \chi, \quad (9.25)$$

since this Euler angle is defined such that $0 \leq \chi'' \leq 2\pi$. Inserting this result in the first of equations (9.24) implies that $\sin(\theta) = \sin(\theta'')$, or from the second of equations (9.23)

$$\theta'' = \pi - \theta \text{ and } \phi'' = \phi + \pi. \quad (9.26)$$

The ambiguity in ϕ'' is resolved by inserting equation (9.26) in the first or second of equations (9.22). Finally, since the components of the angular momentum \hat{J}_α operator will transform according to equation (9.18), then the transformation properties listed in Table 9-3 are accounted for (except for the eigenvectors to be derived later).

Referring to Figure 9-1 for the water molecule, we can easily assess that the rotation associated to the symmetry operators of the $C_{2v}(M)$ group are

$$\begin{aligned} E &\leftrightarrow R^0 \\ (12) &\leftrightarrow R_0^\pi \\ E^* &\leftrightarrow R_{\pi/2}^\pi \\ (12)^* &\leftrightarrow R_z^\pi, \end{aligned} \quad (9.27)$$

where R^0 is the identity, and therefore

$$\begin{aligned} E(\phi, \theta, \chi) &= R^0(\phi, \theta, \chi) = (\phi, \theta, \chi) \\ (12)(\phi, \theta, \chi) &= R_0^\pi(\phi, \theta, \chi) = (\phi + \pi, \pi - \theta, 2\pi - \chi) \\ E^*(\phi, \theta, \chi) &= R_{\pi/2}^\pi(\phi, \theta, \chi) = (\phi + \pi, \pi - \theta, \pi - \chi) \\ (12)^*(\phi, \theta, \chi) &= R_z^\pi(\phi, \theta, \chi) = (\phi, \theta, \chi + \pi). \end{aligned} \quad (9.28)$$

The transformations of the molecule-fixed components of the angular momentum operator are also seen to be

$$\begin{aligned} E(\hat{J}_x, \hat{J}_y, \hat{J}_z) &= R^0(\hat{J}_x, \hat{J}_y, \hat{J}_z) = (\hat{J}_x, \hat{J}_y, \hat{J}_z) \\ (12)(\hat{J}_x, \hat{J}_y, \hat{J}_z) &= R_0^\pi(\hat{J}_x, \hat{J}_y, \hat{J}_z) = (\hat{J}_x, -\hat{J}_y, -\hat{J}_z) \\ E^*(\hat{J}_x, \hat{J}_y, \hat{J}_z) &= R_{\pi/2}^\pi(\hat{J}_x, \hat{J}_y, \hat{J}_z) = (-\hat{J}_x, \hat{J}_y, -\hat{J}_z) \\ (12)^*(\hat{J}_x, \hat{J}_y, \hat{J}_z) &= R_z^\pi(\hat{J}_x, \hat{J}_y, \hat{J}_z) = (-\hat{J}_x, -\hat{J}_y, \hat{J}_z). \end{aligned} \quad (9.29)$$

Comparison with the character table for $C_{2v}(M)$ (i.e., Table 9-1) shows that \hat{J}_x , \hat{J}_y , and \hat{J}_z transform as A_2 , B_2 , and B_1 , respectively. The set of rotations associated to the elements of the MS group, stated in equations (9.27) for water, form the so-called

molecular rotation group, and the mapping between the two sets of element is usually included in the character table, as well as the transformation properties of the molecule-fixed angular momentum components (as in Table 9-1).

9.3.2 The Transformation Properties of the Normal Coordinates

When establishing the mathematical relationship between the $3N$ Cartesian displacement coordinates $\Delta\alpha_i$ of the nuclei (for a molecule containing N nuclei) and the $3N - 6$ normal coordinates Q_i we needed to introduce six “zero frequency” coordinates (three translational and three rotational) T_x, T_y, T_z, R_x, R_y , and R_z to supplement the normal coordinates in order to obtain a simple orthogonal matrix transformation between the two sets of coordinates. More precisely, referring to equation (3.46) of Chapter 3 we can write

$$\Delta\alpha_i = \sum_{j=1}^{3N} m_i^{-1/2} l_{\alpha i,j} Q_j, \quad (9.30)$$

where $l_{\alpha i,j}$ is the aforementioned $3N \times 3N$ orthogonal matrix, and

$$(Q_{3N-5}, Q_{3N-4}, Q_{3N-3}, Q_{3N-2}, Q_{3N-1}, Q_{3N}) = (T_x, T_y, T_z, R_x, R_y, R_z). \quad (9.31)$$

Assuming that under the elements R of the MS group the $3N$ augmented normal coordinates transform according to a set of matrices $D^\Gamma[R]$ that generate the reducible representation Γ such that

$$RQ_j = \sum_{j=1}^{3N} D^\Gamma[R]_{jk} Q_k, \quad (9.32)$$

then the Cartesian coordinates will transform as follows (with $l'_{\alpha i,j} = m_i^{-1/2} l_{\alpha i,j}$)

$$\begin{aligned} R\Delta\alpha_i &= \sum_{j=1}^{3N} l'_{\alpha i,j} RQ_j \\ &= \sum_{j=1}^{3N} l'_{\alpha i,j} \sum_{k=1}^{3N} D^\Gamma[R]_{jk} Q_k \\ &= \sum_{j,k=1}^{3N} l'_{\alpha i,j} D^\Gamma[R]_{jk} \sum_{m=1}^{3N} l'^{-1}_{k,\alpha m} \Delta\alpha_m \\ &= \sum_{j,k,m=1}^{3N} l'_{\alpha i,j} D^\Gamma[R]_{jk} l'^{-1}_{k,\alpha m} \Delta\alpha_m \\ &= \sum_{m=1}^{3N} (l' D^\Gamma[R] l'^{-1})_{im} \Delta\alpha_m, \end{aligned} \quad (9.33)$$

where equation (9.30) and its inverse were used, as well as equation (9.32). However, we can also write for the transformation of the Cartesian coordinates under R that

$$R\Delta\alpha_i = \sum_{m=1}^{3N} \bar{D}^\Gamma [R]_{im} \Delta\alpha_m, \quad (9.34)$$

with the result that

$$\bar{D}^\Gamma [R] = l'D^\Gamma [R]l'^{-1}. \quad (9.35)$$

That is, the two sets of matrix representations are related through a similarity transformation. It follows from this that *the Cartesian displacement coordinates and the augmented normal coordinates generate the same reducible representation of the MS group*. This result implies that *we can determine the representation of the $3N - 6$ normal coordinates by calculating the representation of the $3N$ Cartesian displacements and subtracting the representation generated by the T_x, T_y, T_z, R_x, R_y , and R_z coordinates from them*.

As we will soon see, the representation generated by the $\Delta\alpha_i$'s is easily determined, but we need to find out how T_x, T_y, T_z, R_x, R_y , and R_z transform under the elements of the MS group before we can go any further.

9.3.2.1 The Transformation Properties of R_α and T_α ²

Before we go on to determine the transformation properties of T_α and R_α under the elements of the MS group, we now review some fundamental properties of orthogonal matrices.

An orthogonal matrix M is one for which its inverse matrix equals its transpose M^T

$$MM^T = \hat{1}, \quad (9.36)$$

where $\hat{1}$ is the unit matrix. Alternatively we can write

$$M_{ij}M_{jk}^T = M_{ij}M_{kj} = \delta_{ik}. \quad (9.37)$$

In general, the inverse of a matrix is defined as the transpose of the matrix' cofactors divided by its determinant. For example, if C_{ij} is a cofactor, then (the reader should verify this)

$$C_{im} = \frac{1}{2} \epsilon_{ijk} \epsilon_{mnp} M_{jn} M_{kp}, \quad (9.38)$$

² In this section, summation on a repeated index is implied unless otherwise specified.

then we have

$$M_{mi}^{-1} = \frac{C_{mi}^T}{\|M\|}. \quad (9.39)$$

For an orthogonal matrix

$$M_{mi}^{-1} = \frac{C_{mi}^T}{\|M\|} = M_{im}, \quad (9.40)$$

of from equation (9.38)

$$\|M\| M_{im} = C_{im} = \frac{1}{2} \varepsilon_{ijk} \varepsilon_{mnp} M_{jn} M_{kp}. \quad (9.41)$$

If the matrix is orthonormal, then $\|M\| = 1$ and

$$M_{im} = \frac{1}{2} \varepsilon_{ijk} \varepsilon_{mnp} M_{jn} M_{kp}. \quad (9.42)$$

Finally, we can also establish that

$$\begin{aligned} \varepsilon_{mrs} M_{im} &= \frac{1}{2} \varepsilon_{mrs} \varepsilon_{ijk} \varepsilon_{mnp} M_{jn} M_{kp} = \frac{1}{2} (\delta_{rn} \delta_{sp} - \delta_{rp} \delta_{sn}) \varepsilon_{ijk} M_{jn} M_{kp} \\ &= \frac{1}{2} \varepsilon_{ijk} (M_{jr} M_{ks} - M_{js} M_{kr}), \end{aligned} \quad (9.43)$$

and finally

$$\varepsilon_{mrs} M_{im} = \varepsilon_{ijk} M_{jr} M_{ks}. \quad (9.44)$$

It is readily verified that the matrices R_α^π and R_z^β are orthonormal. Let us now consider one more time the transformation of the molecule-fixed components of the total orbital angular momentum operator \hat{J}_α , where $\alpha = x, y$, or z , under the action of an operator R of the MS group, which can be written as (see Section 6.3.1)

$$R = R_{ve} R_{rot} R_{ns}. \quad (9.45)$$

It should be clear that only R_{ve} and R_{rot} could modify \hat{J}_α , since R_{ns} only affects nuclear spins. As far as the total orbital angular momentum is concerned the effect of R_{ve} will consist of exchanging the labels of identical particles, while that of R_{rot} will bring a

rotation R_α^π or R_z^β to the molecule-fixed axes. However, since the total orbital angular momentum is made of the sum of contributions from the individual particles, then the operator R_{ve} will be of no consequence to \hat{J}_α . We therefore write

$$\begin{aligned} R\hat{J}_\alpha &= R_{ve}R_{\text{rot}} \left(\sum_i \hat{J}_{\alpha_i} \right) = \sum_j R_{\text{rot}} \hat{J}_{\alpha_j} = \sum_j \hat{J}'_{\alpha_j} = \sum_j M_{\alpha\beta} \hat{J}_{\beta_j} \\ &= M_{\alpha\beta} \hat{J}_\beta, \end{aligned} \quad (9.46)$$

where $M_{\alpha\beta}$ is an element of the matrix corresponding to R_{rot} (i.e., R_α^π or R_z^β depending on the case) for the given operator considered. This transformation of the angular momentum can also be asserted as follows. Let us assume that the angular momentum in the transformed coordinate system can be written as

$$\begin{aligned} \hat{J}'_\alpha &= \sum_i m_i \epsilon_{\alpha\beta\gamma} \Delta\beta'_i \hat{P}'_{\gamma_i} = \sum_i m_i \epsilon_{\alpha\beta\gamma} (M_{\beta\mu} \Delta\mu_i) (M_{\gamma\nu} \hat{P}_{\nu_i}) \\ &= \sum_i m_i (\epsilon_{\alpha\beta\gamma} M_{\beta\mu} M_{\gamma\nu}) \Delta\mu_i \hat{P}_{\nu_i}, \end{aligned} \quad (9.47)$$

which, using equation (9.44), transforms to

$$\begin{aligned} \hat{J}'_\alpha &= \sum_i m_i (\epsilon_{\eta\mu\nu} M_{\alpha\eta}) \Delta\mu_i \hat{P}_{\nu_i} \\ &= M_{\alpha\eta} \sum_i m_i \epsilon_{\eta\mu\nu} \Delta\mu_i \hat{P}_{\nu_i} \\ &= M_{\alpha\eta} \hat{J}_\eta. \end{aligned} \quad (9.48)$$

This is exactly the same result as was obtained in equation (9.46). (Incidentally, this shows that the fact that the cross product of two transformed vectors equals the transformation of the cross product of the original vectors is due to the orthonormal nature of the transformation matrix.)

Let us now consider the transformation of R_α . From equation (3.37) of Chapter 3 we write

$$R_\alpha = (\mu_{\alpha\alpha}^e)^{1/2} \sum_i m_i \epsilon_{\alpha\beta\gamma} \Delta\beta_i^e \Delta\gamma_i, \quad (9.49)$$

where there is no implied summation on α . It should be clear that under R_{rot} the part included in the summation on i transforms the same way as \hat{J}_α (i.e., they are both cross products), so we write

$$R_{\text{rot}} R_\alpha = \sum_\beta \left(\frac{\mu_{\alpha\alpha}^e}{\mu_{\beta\beta}^e} \right)^{1/2} M_{\alpha\beta} R_\beta. \quad (9.50)$$

For a spherical top R_α will transform exactly as \hat{J}_α since $\mu_{\alpha\alpha}^e = \mu_{\beta\beta}^e$ for any α and β . This is also true for a symmetrical top since the two principal axes with the same value of $\mu_{\alpha\alpha}^e$ can be chosen to be the x - and y -axes while the matrices associated to R_α^π and R_z^β only couple these two axes (i.e., $M_{\alpha z} = M_{z\alpha} = 0$ for $\alpha = x$ and y ; see Table 9-3). This result will hold even for an asymmetric top because in this case we can only have rotations by 0 or π radians, which leads diagonal rotation matrices (i.e., $M_{\alpha\beta} \propto \delta_{\alpha\beta}$).

We therefore find that *the coordinates R_α transform in the same manner as the molecule-fixed components of the total orbital angular momentum \hat{J}_α under any operator of the MS group.*

For the transformation of T_α we have to discern between permutation and permutation-inversion operators. The reason for this lies in the way the coordinate displacements in the space-fixed coordinate system (i.e., $\Delta\xi, \Delta\eta$, and $\Delta\zeta$) relate to molecule-fixed displacements (i.e., $\Delta x, \Delta y$, and Δz). Indeed we see from equation (9.21) that if $\lambda''_{\alpha\beta}$ is an element of the transformed Euler matrix for a permutation operator P , then the corresponding element for the permutation-inversion operator $P^* = E^*P$ must be $-\lambda''_{\alpha\beta}$ since the inversion brings the following transformation

$$\begin{aligned} \Delta\xi &\rightarrow -\Delta\xi \\ \Delta\eta &\rightarrow -\Delta\eta \\ \Delta\zeta &\rightarrow -\Delta\zeta. \end{aligned} \quad (9.51)$$

From equation (3.36) of Chapter 3 we have

$$T_\alpha = M_N^{-1/2} \sum_i m_i \Delta\alpha_i, \quad (9.52)$$

and therefore

$$\begin{aligned} R_{\text{rot}} T_\alpha &= M_N^{-1/2} \sum_i m_i \Delta\alpha'_i = M_N^{-1/2} \sum_i m_i (M_{\alpha\beta} \Delta\beta_i) \\ &= M_{\alpha\beta} T_\beta. \end{aligned} \quad (9.53)$$

So if R_{rot} and R_{rot}^* are the rotations associated to P and P^* , respectively, then

$$\begin{aligned} R_{\text{rot}} T_\alpha &= M_{\alpha\beta} T_\beta \\ R_{\text{rot}}^* T_\alpha &= -M_{\alpha\beta} T_\beta. \end{aligned} \quad (9.54)$$

Now, because \hat{J}_α (and R_α) contains two vectors, which both transform in the same manner (see equation (9.47)), then it is unaffected by this sign change when going from P to P^* , this is not so for T_α . We therefore conclude that *the operators T_α transform similarly to \hat{J}_α and R_α under any permutation operator, but transform with opposite sign to \hat{J}_α and R_α under permutation-inversion operators.*

9.3.2.2 The Transformation Properties of the Cartesian Displacement and Normal Coordinates

To determine the representation Γ_{Car} generated by the Cartesian displacements coordinates we will investigate how they transform under the elements of the MS group, and then decompose this representation into the realized irreducible representations. For example, for the water molecule we must consider the E , (12) , E^* , and $(12)^*$ operators and their effect on $\Delta\alpha_i$, for $\alpha = x, y$, and z and $i = 1, 2$, and 3. The effect of (12) is shown in **Figure 9-3**. It is easy to see that

$$(12)(\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \Delta x_3, \Delta y_3, \Delta z_3) \\ = (\Delta x_2, -\Delta y_2, -\Delta z_2, \Delta x_1, -\Delta y_1, -\Delta z_1, \Delta x_3, -\Delta y_3, -\Delta z_3), \quad (9.55)$$

since the protons exchange labels and the y and z axes are reversed. Going through the same process for all the symmetry operators will yield the results listed in Table 9-4 (Figure 9-1 will help in the process), along with the transformation of T_α and R_α (from Table 9-1. The character generated by the transformations is also included at the bottom of Table 9-4). It will be appreciated that only the coordinates of nuclei that are not permuted under the action of an operator contribute to the character. For example, only the oxygen nucleus needs to be considered in the cases of (12) and $(12)^*$. So the character associated with Cartesian displacement coordinates of the water nuclei is

$$\chi^{\Gamma_{\text{Car}}}[E] = 9, \quad \chi^{\Gamma_{\text{Car}}}[(12)] = -1, \quad \chi^{\Gamma_{\text{Car}}}[E^*] = 3, \quad \chi^{\Gamma_{\text{Car}}}[(12)^*] = 1. \quad (9.56)$$

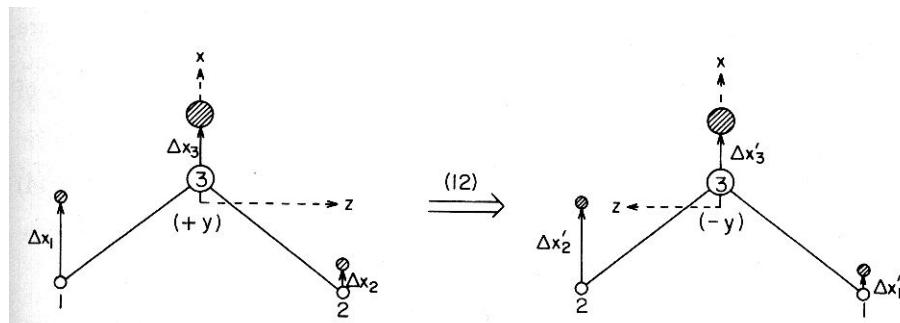


Figure 9-3 – The effect of the (12) operator on the Cartesian displacement coordinates for the water molecule.

Table 9-4 – The transformation of the Cartesian displacement coordinates of water, as well as that of T_α and R_α , under the effect of the symmetry elements of the $C_{2v}(M)$ group.

E	(12)	E^*	$(12)^*$	E	(12)	E^*	$(12)^*$	
Δx_1	Δx_2	Δx_1	Δx_2	T_x	T_x	T_x	T_x	$: A_1$
Δx_2	Δx_1	Δx_2	Δx_1	T_y	$-T_y$	$-T_y$	T_y	$: B_1$
Δx_3	Δx_3	Δx_3	Δx_3	T_z	$-T_z$	T_z	$-T_z$	$: B_2$
Δy_1	$-\Delta y_2$	$-\Delta y_1$	Δy_2	R_x	R_x	$-R_x$	$-R_x$	$: A_2$
Δy_2	$-\Delta y_1$	$-\Delta y_2$	Δy_1	R_y	$-R_y$	R_y	$-R_y$	$: B_2$
Δy_3	$-\Delta y_3$	$-\Delta y_3$	Δy_3	R_z	$-R_z$	$-R_z$	R_z	$: B_1$
Δz_1	$-\Delta z_2$	Δz_1	$-\Delta z_2$					
Δz_2	$-\Delta z_1$	Δz_2	$-\Delta z_1$					
Δz_3	$-\Delta z_3$	Δz_3	$-\Delta z_3$					
$\Gamma_{\text{Car}} :$		9	-1	3	1			

Using, as usual, equation (6.60) we find

$$\Gamma_{\text{Car}} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2. \quad (9.57)$$

We also know that

$$\begin{aligned} \Gamma(T_\alpha) &= A_1 \oplus B_1 \oplus B_2 \\ \Gamma(R_\alpha) &= A_2 \oplus B_2 \oplus B_1, \end{aligned} \quad (9.58)$$

and therefore

$$\Gamma(Q_1, Q_2, Q_3) = \Gamma_{\text{Car}} - [\Gamma(R_\alpha) \oplus \Gamma(T_\alpha)] = 2A_1 \oplus B_2. \quad (9.59)$$

Water has $3N - 6 = 3$ vibrational degrees of freedom. There will therefore be two one-dimensional normal coordinates Q_1 and Q_2 of symmetry A_1 and another Q_3 of symmetry B_2 . The three corresponding normal modes of vibration are shown in Figure 9-4.

9.4 The Classification of the Rovibrational Wave Function

Now that we have established the transformation properties of the Euler angles and the normal coordinates, we are ready to use these results to determine the symmetry classification of the rovibrational wave. As this wave function is expressible as a product of a rotational wave function (a function of the Euler angles) and a vibrational wave function (a function of the normal coordinates), we treat both cases independently.

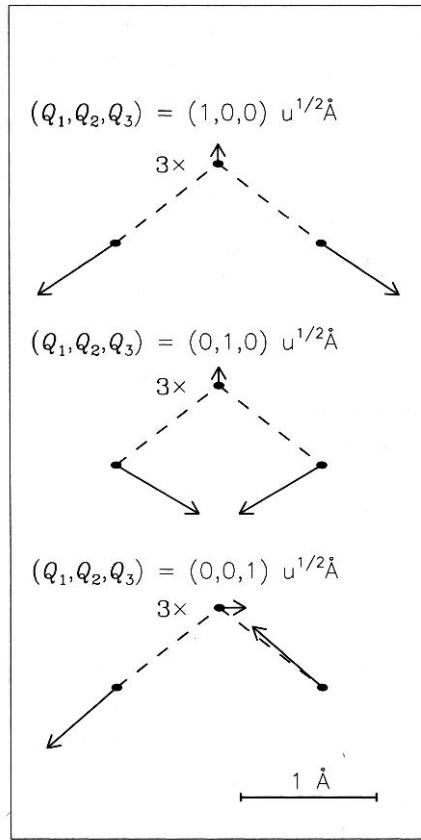


Figure 9-4 – The three normal modes of vibration corresponding to the Q_1 , Q_2 , and Q_3 normal coordinates of the water molecule.

9.4.1 The Classification of Rotational Wave Functions

We know from Chapter 4 that the eigenvectors associated with rotational wave functions of a symmetric top molecule are

$$|\Phi_{\text{rot}}\rangle = |J, K, m\rangle, \quad (9.60)$$

with $K = |k|$. Moreover, these kets can be built up from the fundamental $|J, 0, 0\rangle$ ket using the ladder operators \hat{J}_m^\pm and \hat{J}_s^\pm with

$$|J, \pm k, \pm m\rangle = N_\pm (\hat{J}_m^\mp)^k (\hat{J}_s^\pm)^m |J, 0, 0\rangle, \quad (9.61)$$

where N_\pm is some positive normalization constant. For asymmetric top molecules, the eigenvectors are not simply given by equation (9.60) but by linear combinations of the $|J, K, m\rangle$ kets. It therefore follows that we will be able to determine the symmetry of the wave function for these two types of molecules by investigating the effect of the R_α^π and R_z^β rotations associated to the MS group operators on the ladder operators and the

$|J,0,0\rangle$ ket. An investigation of the classification of spherical top wave functions requires a discussion of the full rotation group and the so-called correlation tables (in a manner somewhat similar to what is needed for a treatment of the Hund's case a)) and will not be given here. For simplicity, we also limit ourselves to when J is an integer. Let us then look at the effect of the aforementioned rotations on the molecule-fixed ladder operator

$$\begin{aligned} R_z^\beta \hat{J}_m^\pm &= \left\{ [\hat{J}_x \cos(\beta) + \hat{J}_y \sin(\beta)] \pm i [\hat{J}_y \cos(\beta) - \hat{J}_x \sin(\beta)] \right\} R_z^\beta \\ &= [\cos(\beta) \hat{J}_m^\pm \mp i \sin(\beta) \hat{J}_m^\pm] R_z^\beta \\ &= e^{\mp i\beta} \hat{J}_m^\pm R_z^\beta, \end{aligned} \quad (9.62)$$

and

$$\begin{aligned} R_\alpha^\pi \hat{J}_m^\pm &= \left\{ [\hat{J}_x \cos(2\alpha) + \hat{J}_y \sin(2\alpha)] \pm i [-\hat{J}_y \cos(2\alpha) + \hat{J}_x \sin(2\alpha)] \right\} R_\alpha^\pi \\ &= e^{\pm i2\alpha} \hat{J}_m^\mp R_\alpha^\pi. \end{aligned} \quad (9.63)$$

It should be obvious that the space-fixed ladder \hat{J}_s^\pm operator is unaffected by these rotations, since the axes on which this angular momentum is projected onto are by definition unchanging. We therefore have

$$\begin{aligned} R_z^\beta \hat{J}_s^\pm &= \hat{J}_s^\pm R_z^\beta \\ R_\alpha^\pi \hat{J}_s^\pm &= \hat{J}_s^\pm R_\alpha^\pi. \end{aligned} \quad (9.64)$$

Turning our attention to the wave function associated to the $|J,0,0\rangle$ ket, we find using Table 9-3 and equations (4.80), (4.83), (4.84), and (4.86) that

$$\begin{aligned} R_z^\beta |J,0,0\rangle &= |J,0,0\rangle \\ R_\alpha^\pi |J,0,0\rangle &= (-1)^J |J,0,0\rangle, \end{aligned} \quad (9.65)$$

since for the second equation $\cos(\pi - \theta) = -\cos(\theta)$ and the Legendre polynomials transforms as $P_J[-\cos(\theta)] = (-1)^J P_J[\cos(\theta)]$. It can therefore readily be shown from equations (9.61) to (9.65) that

$$\begin{aligned} R_z^\beta |J,k,m\rangle &= e^{ik\beta} |J,k,m\rangle \\ R_\alpha^\pi |J,k,m\rangle &= (-1)^J e^{-2ik\alpha} |J,-k,m\rangle. \end{aligned} \quad (9.66)$$

These transformations were included at the bottom of Table 9-3 for easy reference. We now apply these results to two specific examples.

9.4.1.1 Symmetric Top Case - H_3^+

The character table of the $D_{3h}(\text{M})$ group for the H_3^+ ion is given in Table 9-5. The rotation associated with each symmetry operator is listed in the same table and can be determined through a study of Figure 9-5; only one operator per class suffices for this.

Table 9-5 – The character table of the $D_{3h}(\text{M})$ group for the H_3^+ ion.

$D_{3h}(\text{M})$:	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$	
	1	2	3	1	2	3	
R_{rot} :	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^\pi$	R_z^π	$R_z^{5\pi/3}$	R_0^π	
A'_1 :	1	1	1	1	1	1	
A''_1 :	1	1	1	-1	-1	-1	$:\Gamma(\mu_A)$
A'_2 :	1	1	-1	1	1	-1	$:\hat{J}_z$
A''_2 :	1	1	-1	-1	-1	1	$:\hat{T}_z$
E' :	2	-1	0	2	-1	0	$:(T_x, T_y)$
E'' :	2	-1	0	-2	1	0	$:(\hat{J}_x, \hat{J}_y)$

We now use equations (9.66) to find the transformation of the $|J,k,m\rangle$ eigenvectors under the element of the MS group through the effect of their associated rotations.

When $K = 0$, we have

$$\begin{aligned}
 E|J,0,m\rangle &= R^0|J,0,m\rangle = |J,0,m\rangle \\
 (123)|J,0,m\rangle &= R_z^{2\pi/3}|J,0,m\rangle = |J,0,m\rangle \\
 (23)|J,0,m\rangle &= R_{\pi/2}^\pi|J,0,m\rangle = (-1)^J|J,0,m\rangle \\
 E^*|J,0,m\rangle &= R_z^\pi|J,0,m\rangle = |J,0,m\rangle \\
 (123)^*|J,0,m\rangle &= R_z^{5\pi/3}|J,0,m\rangle = |J,0,m\rangle \\
 (23)^*|J,0,m\rangle &= R_0^\pi|J,0,m\rangle = (-1)^J|J,0,m\rangle.
 \end{aligned} \tag{9.67}$$

When $K > 0$, because of the last of equations (9.66) we have to consider the two eigenvectors $|J,\pm K, m\rangle$ together; they will span a two-dimensional representation. For example, we can calculate

$$\begin{aligned}
 E|J,\pm K,m\rangle &= R^0|J,\pm K,m\rangle = |J,\pm K,m\rangle \\
 (123)|J,\pm K,m\rangle &= R_z^{2\pi/3}|J,\pm K,m\rangle = e^{\pm i 2K\pi/3}|J,\pm K,m\rangle \\
 (23)|J,\pm K,m\rangle &= R_{\pi/2}^\pi|J,\pm K,m\rangle = (-1)^J e^{\mp i K\pi}|J,\mp K,m\rangle \\
 &= (-1)^{J+K}|J,\mp K,m\rangle,
 \end{aligned} \tag{9.68}$$

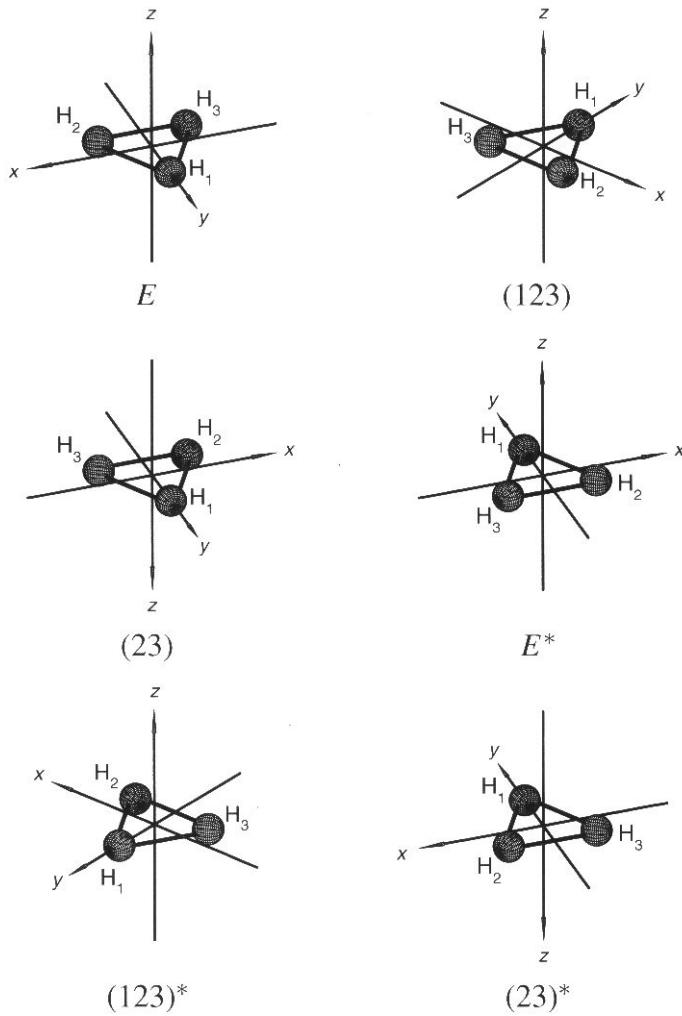


Figure 9-5 – The equivalent rotations associated with the symmetry operations of the $D_{3h}(M)$ group for H_3^+ .

and

$$\begin{aligned}
 E^* |J, \pm K, m\rangle &= R_z^\pi |J, \pm K, m\rangle = e^{\pm iK\pi} |J, \pm K, m\rangle = (-1)^K |J, \pm K, m\rangle \\
 (123)^* |J, \pm K, m\rangle &= R_z^{5\pi/3} |J, \pm K, m\rangle = e^{\pm i5K\pi/3} |J, \pm K, m\rangle \\
 (23)^* |J, \pm K, m\rangle &= R_0^\pi |J, \pm K, m\rangle = (-1)^J |J, \mp K, m\rangle.
 \end{aligned} \tag{9.69}$$

The character generated by these two eigenvectors is easily evaluated if we consider them as part of a two-dimensional vector. That is, the character of a transformation will (not) be zero when the ‘ \pm ’ is (not) inverted after the application of the symmetry operator under study. We now combine the results of equations (9.67) to (9.69) and write the characters for $K = 0$ and $K > 0$

$D_{3h}(M)$:	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$
$K = 0 :$	1	1	$(-1)^J$	1	1	$(-1)^J$
$K > 0 :$	2	$2 \cos(2K\pi/3)$	0	$2(-1)^K$	$2 \cos(5K\pi/3)$	0 $= (-1)^K 2 \cos(2K\pi/3)$

As has now become a habit, we use equation (6.60) to determine the realized irreducible representations. For $K = 0$ we must discern between the cases when J is even or odd, and we find that

$$\begin{aligned}\Gamma(J \text{ even}) &= A'_1 \\ \Gamma(J \text{ odd}) &= A'_2.\end{aligned}\tag{9.70}$$

For $K > 0$, we see that only four different characters are possible corresponding to $2 \cos(2K\pi/3) = \pm 1$ or ± 2 . For example, we have

$$\begin{aligned}\Gamma(K = 1) &= E'' \\ \Gamma(K = 3) &= A''_1 \oplus A''_2.\end{aligned}\tag{9.71}$$

Possible results are summarized in Table 9-6.

Table 9-6 – The realized irreducible representations for the H_3^+ . The $(2J + 1)$ degeneracy in m is ignored, and n is an integer.

K	Γ
0	$J \text{ even } A'_1$
	$J \text{ odd } A'_2$
$6n \pm 1$	E''
$6n \pm 2$	E'
$6n \pm 3$	$A''_1 \oplus A''_2$
$6n \pm 6$	$A'_1 \oplus A'_2$

9.4.1.2 Asymmetric Top Case - H_2O

We saw in Chapter 4 that for an asymmetric rotator it is not possible to label the states of the molecule simply with a pair of quantum numbers J and K , as is the case for a symmetric rotator. Instead, we must study the two limiting cases of prolate (type I' convention) and oblate (type III' convention) molecules by varying the value of B_e . We then get two corresponding sets of energies and eigenvectors $|J, K_a, A^\pm\rangle$ and $|J, K_c, A^\pm\rangle$ that can be used to specify the state of the molecule. Indeed, the states are labeled as $J_{K_a K_c}$. These states are called “ee”, “eo”, “oe”, or “oo” depending on whether K_a and K_c are even or odd. Because of this, we must determine the representations generated by both conventions for the molecule (remember that the conventions differ in the

assignment of the xyz -axes to the abc labels; for a type Γ $abc = zxy$, while for a type III^Γ $abc = xyz$). The process is the same as was done for the symmetric top, but it must be done twice.

For example, the rotations associated to the symmetry operators of the MS group of water determined earlier in this chapter, as well as the transformation properties of the Euler angles, and orbital angular momentum were all done in the type Γ convention. The corresponding eigenvectors transformations and representations are calculated as follows.

When $K = 0$, we have

$$\begin{aligned} E|J,0,m\rangle &= R^0|J,0,m\rangle = |J,0,m\rangle \\ (12)|J,0,m\rangle &= R_0^\pi|J,0,m\rangle = (-1)^J|J,0,m\rangle \\ E^*|J,0,m\rangle &= R_{\pi/2}^\pi|J,0,m\rangle = (-1)^J|J,0,m\rangle \\ (12)^*|J,0,m\rangle &= R_z^\pi|J,0,m\rangle = |J,0,m\rangle. \end{aligned} \tag{9.72}$$

When $K > 0$, we calculate

$$\begin{aligned} E|J,\pm K,m\rangle &= R^0|J,\pm K,m\rangle = |J,\pm K,m\rangle \\ (12)|J,\pm K,m\rangle &= R_0^\pi|J,\pm K,m\rangle = (-1)^J|J,\mp K,m\rangle \\ E^*|J,\pm K,m\rangle &= R_{\pi/2}^\pi|J,\pm K,m\rangle = (-1)^{J+K}|J,\mp K,m\rangle \\ (12)^*|J,\pm K,m\rangle &= R_z^\pi|J,\pm K,m\rangle = (-1)^K|J,0,m\rangle. \end{aligned} \tag{9.73}$$

The characters thus generated are

$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$
type Γ				
$K = 0$:	1	$(-1)^J$	$(-1)^J$	1
$K > 0$:	2	0	0	$2(-1)^K$

And the realized irreducible representations are

$$\begin{aligned} \Gamma(K = 0, J \text{ even}) &= A_1 \\ \Gamma(K = 0, J \text{ odd}) &= B_1 \\ \Gamma(K > 0 \text{ and odd}) &= A_2 \oplus B_2 \\ \Gamma(K > 0 \text{ and even}) &= A_1 \oplus B_1. \end{aligned} \tag{9.74}$$

The same calculations must be performed for a type III^Γ convention. When this is done, both sets of irreducible are combined and the results are shown in Table 9-7.

Table 9-7 – The representations of the $C_{2v}(M)$ group of water molecule generated by the $|J, k_a, m\rangle$ and $|J, k_c, m\rangle$ bases. The $(2J+1)$ degeneracy in m is ignored.

K_a	Γ_a	K_c	Γ_c
$0 \begin{cases} J \text{ even} \\ J \text{ odd} \end{cases}$	A_1	$0 \begin{cases} J \text{ even} \\ J \text{ odd} \end{cases}$	A_1
	B_1		B_2
odd	$A_2 \oplus B_2$	odd	$A_2 \oplus B_1$
even	$A_1 \oplus B_1$	even	$A_1 \oplus B_2$

Because the actual molecule asymmetry is located somewhere between these two limits, the representation realized by a given state $J_{K_a K_c}$ must correlate, or fit, both solutions. We therefore see that it must be that

$$\begin{aligned} J_{ee} &= A_1, & J_{oe} &= B_2, \\ J_{eo} &= B_1, & J_{oo} &= A_2. \end{aligned} \quad (9.75)$$

This result can actually be generalized to any asymmetric top molecule with the so-called **asymmetric top symmetry rule**:

The ‘ee’ functions will transform as the totally symmetric representation, the ‘eo’ functions as the representation having +1 for R_a^π (and -1 for R_b^π and R_c^π), the ‘oe’ functions as the representation having +1 for R_c^π (and -1 for R_a^π and R_b^π), and the ‘oo’ functions as the representation having +1 for R_b^π (and -1 for R_a^π and R_c^π).

9.4.2 The Classification of Vibrational Wave Functions

We have previously shown how to determine the symmetries of the normal coordinates. With this information in hand we can now proceed to the classification of the associated wave functions.

9.4.2.1 Non-degenerate Normal Modes

The fundamental vibrational wave function $\Phi_{v=0}$ of a non-degenerate normal coordinate Q is given by equation (4.10)

$$\Phi_0(Q) = \left(\frac{\lambda^{1/2}}{\pi\hbar} \right)^{1/4} e^{-\frac{\lambda^{1/2}Q^2}{2\hbar}}. \quad (9.76)$$

Because of the fact that the potential energy of the molecule is proportional to Q^2 , then Φ_0 must share the same symmetry as the potential energy, and therefore the Hamiltonian. That is, Φ_0 is totally symmetric. Moreover, the symmetry of an arbitrary wave function Φ_v can be evaluated if we know the symmetry of the ladder operator

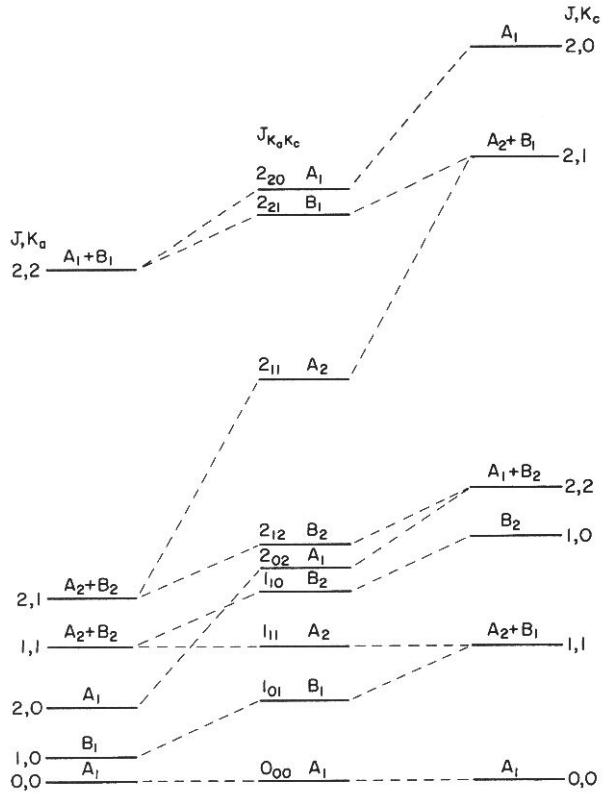


Figure 9-6 – The rotational labels for the water molecule (centre), and their correlation to the prolate (left) and oblate (right) cases.

$$\hat{R}^\pm = \frac{1}{\sqrt{2}} \left(-i\hbar \frac{\partial}{\partial Q} \pm i\lambda^{1/2} Q \right), \quad (9.77)$$

since

$$\Phi_v(Q) = N_v (\hat{R}^+)^v \Phi_0(Q), \quad (9.78)$$

with N_v a normalization constant. Because of equation (9.77), the ladder operator will transform according to the same one-dimensional representation, say Γ^i , as Q does. We can then write

$$\Gamma(\Phi_v) = \underbrace{\Gamma^i \otimes \Gamma^i \otimes \cdots \otimes \Gamma^i}_{v \text{ times}} = (\Gamma^i)^v, \quad (9.79)$$

and therefore

$$\Gamma(\Phi_v) = \begin{cases} \Gamma^{(s)}, & v \text{ even} \\ \Gamma^i, & v \text{ odd.} \end{cases} \quad (9.80)$$

For example, the water molecule has three one-dimensional normal coordinates and, accordingly, the total vibrational wave function is given by

$$\Phi_{\text{vib}} = \Phi_{v_1}(Q_1)\Phi_{v_2}(Q_2)\Phi_{v_3}(Q_3), \quad (9.81)$$

with

$$\Gamma(Q_1) = \Gamma(Q_2) = A_1 \quad \text{and} \quad \Gamma(Q_3) = B_2. \quad (9.82)$$

The generated representation is therefore given by

$$\Gamma_{\text{vib}} = (A_1)^{v_1+v_2} \otimes (B_2)^{v_3} = (B_2)^{v_3}. \quad (9.83)$$

9.4.2.2 Doubly degenerated Normal Modes

A pair of doubly degenerated normal coordinates Q_a and Q_b , of symmetry, say, Γ^j can be transformed into two new coordinates $Q = (Q_a^2 + Q_b^2)^{-1/2}$ and $\alpha = \tan^{-1}(Q_a/Q_b)$ with the states of the wave functions $\psi_{v,l}$ specified with two quantum numbers v and l . In the lowest level the wave function is

$$\psi_{0,0}(Q) = \sqrt{\frac{\gamma}{\pi}} e^{-\frac{\gamma Q^2}{2}}, \quad (9.84)$$

while in general

$$\psi_{v,l}(Q, \alpha) \propto [\hat{R}^{+(-)}]^{(v-l)/2} [\hat{R}^{+(+)})]^{(v+l)/2} \psi_{0,0}(Q), \quad (9.85)$$

where the ladder operators $\hat{R}^{\pm(\pm)}$ are defined in equation (4.44). For similar reasons as was the case for the one-dimensional normal mode, the fundamental wave function $\psi_{0,0}$ is totally symmetric in the MS group. Then the $(v+1)$ degenerate wave functions $\psi_{v,l}$, with $l = v, v-2, v-4, \dots, -v$, respectively transform as the operators

$$(\hat{R}^{+(+)})^v, (\hat{R}^{+(-)}) (\hat{R}^{+(+)})^{v-1}, (\hat{R}^{+(-)})^2 (\hat{R}^{+(+)})^{v-2}, \dots, (\hat{R}^{+(-)})^v. \quad (9.86)$$

That is, they transform, as a whole, as the symmetric v th power of the two-dimensional representation generated by $(\hat{R}^{+(+)}, \hat{R}^{+(-)})$. This is because every product is symmetric in

the interchange of $(\hat{R}^{+(-)})^m$ and $(\hat{R}^{+(+)})^{v-m}$. However, we know from equations (4.42) and (4.44) that the pair $(\hat{R}^{+(+)}, \hat{R}^{+(-)})$ transforms as (Q_a, Q_b) , i.e., as Γ^j . And furthermore, we know from equation (7.57) that the character of the representation generated by the symmetric v th power of a doubly degenerate representation Γ^j is given by

$$\chi^{[\Gamma^j]^v}[R] = \frac{1}{2} \left[\chi^{\Gamma^j}[R] \chi^{[\Gamma^j]^{v-1}}[R] + \chi^{\Gamma^j}[R^v] \right]. \quad (9.87)$$

For example, the symmetry of the normal coordinates of H_3^+ can be shown to be

$$\Gamma_Q = A'_1 \oplus E', \quad (9.88)$$

with the total vibrational wave function

$$\Phi_{\text{vib}} = \Phi_{v_1}(Q_1) \Phi_{v_2, l_2}(Q_2, \alpha_2). \quad (9.89)$$

The representation associated to Φ_{v_1} will be totally symmetric (i.e., A'_1) for any v_1 , and we will therefore ignore it in the following discussion.

For the lowest level $v_2 = 0$ there is only one product $(Q_a)^0 (Q_b)^0 = 1$ and the representation Γ_0 is obviously totally symmetric. That is,

$$\chi^{[E']^0}[R] = \chi^{A'_1}[R]. \quad (9.90)$$

For the next level $v_2 = 1$ there are two functions $l = \pm 1$ and products, and from equation (9.87) we have

$$\begin{aligned} \chi^{[E']}[R] &= \frac{1}{2} \left[\chi^{E'}[R] \chi^{[E']^0}[R] + \chi^{E'}[R] \right] \\ &= \frac{1}{2} \left[\chi^{E'}[R] \chi^{A'_1}[R] + \chi^{E'}[R] \right] = \chi^{E'}[R], \end{aligned} \quad (9.91)$$

and

$$\Gamma_1 = E'. \quad (9.92)$$

For $v_2 = 2$, we have

$$\begin{aligned}
\chi^{[E']^2}[R] &= \frac{1}{2} \left[\chi^{E'}[R] \chi^{[E']^1}[R] + \chi^{E'}[R^2] \right] \\
&= \frac{1}{2} \left[\chi^{E'}[R] \chi^{E'}[R] + \chi^{E'}[R^2] \right] \\
&= \chi^{A'_1 \oplus E'}[R]
\end{aligned} \tag{9.93}$$

since

$D_{3h}(M)$:	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$
$(\chi^{E'}[R])^2$:	4	1	0	4	1	0
$\chi^{E'}[R^2]$:	2	-1	2	2	-1	2
$\frac{1}{2} \left[(\chi^{E'}[R])^2 + \chi^{E'}[R^2] \right]$:	3	0	1	3	0	1

That is,

$$\Gamma_2 = A'_1 \oplus E' = [E']^2. \tag{9.94}$$

By continuing this process for higher values of v_2 it can be shown that

$$\Gamma_{v_2} = [E']^{v_2}. \tag{9.95}$$

In general, the representation of the vibrational wave functions follows the rule that states that *for a molecule with vibrational coordinates of symmetries $\Gamma^{(1)}, \Gamma^{(2)}, \dots, \Gamma^{(f)}$ in a state specified by corresponding quantum numbers v_1, v_2, \dots, v_f the symmetry of the vibrational wave function is given by*

$$\Gamma_{\text{vib}} = [\Gamma^{(1)}]^{v_1} \otimes [\Gamma^{(2)}]^{v_2} \otimes \dots \otimes [\Gamma^{(f)}]^{v_f}, \tag{9.96}$$

where $[\Gamma^{(j)}]^{v_j}$ is the symmetric v th product for a degenerate species and the ordinary v th product for a non-degenerate species.

It should be clear from this rule and the previous examples that the **vibrational ground state**, when $v_1 = v_2 = \dots = v_f = 0$, is always totally symmetric. A **fundamental state**, when $v_j = 1$ and $v_i = 0$ for $i \neq j$, has the symmetry of Q_j .