

## Chapter 6. Hamiltonian Symmetry

### Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (1998), Chaps. 1 to 5, and Bunker and Jensen (2005), Chaps. 7 and 8.*

### 6.1 Hamiltonian Symmetry Operations

In the previous chapter we were concerned with symmetry operations that left unchanged the geometrical appearance of a molecule in its equilibrium configuration. It is, however, unclear how symmetries related to the appearance of a molecule at equilibrium has anything to do with the physics of this same molecule as it rotates, vibrates, or changes its electronic states (and is therefore away from equilibrium). What we should really be focusing on are operations that leave the molecular Hamiltonian unchanged, or commute with it; these we call **Hamiltonian symmetry operations**. We now study these operators, while the relationship between the two sets of operators corresponding to geometrical and Hamiltonian symmetries will be explored later in this chapter.

#### 6.1.1 Nuclear Permutations

A **permutation** operation is one that changes the order of an ordered set of numbers. More precisely, a permutation  $(abcd\cdots yz)$  replaces  $a$  by  $b$ ,  $b$  by  $c$ ,  $c$  by  $d$ , ...,  $y$  by  $z$ , and  $z$  by  $a$ . For example, if the permutation operators  $(12)$  and  $(123)$  are applied to the ordered set  $\underline{321}$ , then we get the following results

$$\begin{aligned}(12)\underline{321} &= \underline{312} \\ (123)\underline{321} &= \underline{132}.\end{aligned}\tag{6.1}$$

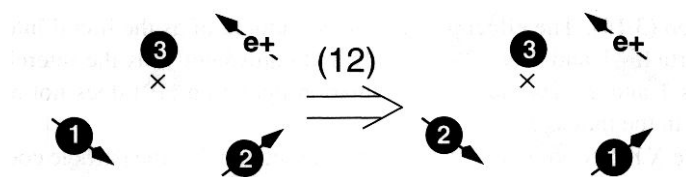
A permutation involving only two elements, e.g.,  $(12)$ , is usually called a **transposition**. From this definition, it should be clear that

$$(12) = (21), \quad (23) = (32), \quad (13) = (31),\tag{6.2}$$

and

$$(123) = (312) = (231), \quad (132) = (321) = (213), \quad \text{etc.}\tag{6.3}$$

When applied to molecules permutation operators act on nuclei only, not electrons. More precisely, in order for a permutation to keep the Hamiltonian of a molecule invariant permutations can only affect identical nuclei. For example, interchanging the positions of the two hydrogen nuclei of a water molecule will not change its energy (i.e., Hamiltonian), but exchanging the position of a hydrogen nucleus with that of the oxygen nucleus completely changes the state of the system. Thus, the permutation of like nuclei is a Hamiltonian symmetry operation, but the permutation of nuclei of different nature is not.



**Figure 6-1** – The effect of the permutation (12) on a water molecule (not necessarily at equilibrium).

Moreover, it is important to realize that the permuted nuclei also exchange their spins. If that were not the case, then the absolute spatial position of the spins would change and, therefore, potentially bring a change in the energy content of the molecule (because of spin-orbit or spin-spin couplings, for example).

An example of a permutation is shown in Figure 6-1 where the effect of the (12) operation on a vibrating water molecule is presented. The hydrogen and oxygen nuclei are respectively labeled 1, 2, and 3, the spins are represented with arrows, and the electron denoted by ‘e’ (the ‘+’ sign signifies that the electron is above the plane of the page; a ‘-’ would indicate that it is below). Finally the centre of mass is represented by the cross ‘×’.

#### 6.1.1.1 *The Effect of a Permutation on a Function*

Let us suppose that we have a function of the positions and spins of the nuclei that compose a molecule upon which we apply a permutation. More precisely, consider the wave function  $\psi$  associated with a water molecule and further define its transformation by the permutation (12) with

$$\psi^{(12)}(\mathbf{R}_1, \sigma_1, \mathbf{R}_2, \sigma_2, \mathbf{R}_3, \sigma_3, \dots, \mathbf{R}_{13}, \sigma_{13}) = (12)\psi(\mathbf{R}_1, \sigma_1, \mathbf{R}_2, \sigma_2, \mathbf{R}_3, \sigma_3, \dots, \mathbf{R}_{13}, \sigma_{13}), \quad (6.4)$$

with  $\mathbf{R}_i$  and  $\sigma_i$  the space-fixed position and spin of particle  $i$ , and where labels 1 to 3 are used for the nuclei and labels 4 to 13 for the ten electrons composing the molecule. Using our previous definition for a permutation we have

$$\begin{aligned} \psi^{(12)}(\mathbf{R}_1, \sigma_1, \mathbf{R}_2, \sigma_2, \mathbf{R}_3, \sigma_3, \dots, \mathbf{R}_{13}, \sigma_{13}) &= (12)\psi(\mathbf{R}_1, \sigma_1, \mathbf{R}_2, \sigma_2, \mathbf{R}_3, \sigma_3, \dots, \mathbf{R}_{13}, \sigma_{13}) \\ &= \psi(\mathbf{R}_2, \sigma_2, \mathbf{R}_1, \sigma_1, \mathbf{R}_3, \sigma_3, \dots, \mathbf{R}_{13}, \sigma_{13}). \end{aligned} \quad (6.5)$$

For example, let us consider the following (totally unphysical) wave function (unrelated to the water molecule)

$$\psi(X_1, X_2, X_3) = X_1 + 2X_2 + 3X_3, \quad (6.6)$$

from which we can calculate the following arbitrary permutation operation

$$\begin{aligned}
\psi^{(123)} &= (123)\psi\left(\underbrace{X_1}_1, \underbrace{X_2}_2, \underbrace{X_3}_3\right) \\
&= \psi\left(\underbrace{X_1}_2, \underbrace{X_2}_3, \underbrace{X_3}_1\right) = \psi\left(\underbrace{X_3}_1, \underbrace{X_1}_2, \underbrace{X_2}_3\right) \\
&= X_3 + 2X_1 + 3X_2,
\end{aligned} \tag{6.7}$$

where the positions and permutations of the labels is made clearer by the curly braces. Alternatively, we can work out this simple problem with the following notation

$$\begin{aligned}
\psi^{(123)} &= (123)[X_1 + 2X_2 + 3X_3] \\
&= X'_1 + 2X'_2 + 3X'_3 \\
&= X_3 + 2X_1 + 3X_2.
\end{aligned} \tag{6.8}$$

In general, for a given operator  $R$  (not necessarily a permutation; see below) we write

$$\begin{aligned}
\psi^R(\mathbf{R}_1, \sigma_1, \dots, \mathbf{R}_l, \sigma_l) &= R\psi(\mathbf{R}_1, \sigma_1, \dots, \mathbf{R}_l, \sigma_l) \\
&= \psi(\mathbf{R}'_1, \sigma'_1, \dots, \mathbf{R}'_l, \sigma'_l),
\end{aligned} \tag{6.9}$$

where  $\mathbf{R}'_i$  and  $\sigma'_i$  are the coordinates and spin of the particle  $i$  after the operation has been effected.

#### 6.1.1.2 *The Successive Applications of Permutations*

Let us consider the following compounded permutation on an ordered set

$$\begin{aligned}
(132)(23)\underline{123} &= (132)[(23)\underline{123}] \\
&= (132)\underline{132} = \underline{321}.
\end{aligned} \tag{6.10}$$

Comparing the starting and final states, i.e.,  $\underline{123}$  and  $\underline{321}$ , it is easy to see that the compounded permutation can be replaced by a simple permutation with

$$(132)(23)\underline{123} = (13)\underline{123} = \underline{321}, \tag{6.11}$$

or

$$(132)(23) = (13). \tag{6.12}$$

In general the product of two permutations does not depend on what ordered set it is applied to, and it is possible to evaluate it without having recourse to an ordered set. For example, it can be said that on the left hand side of equation (6.12): 1 is first replaced by 1 (the (23) permutation) and then by 3 (the (132) permutation); 2 is first replaced by 3

(the (23) permutation) and then by 2 (the (132) permutation); 3 is first replaced by 2 (the (23) permutation) and then by 1 (the (132) permutation). Summarizing all this we have

$$3 \leftarrow 1 \leftarrow 1 = 3 \leftarrow 1, \quad 2 \leftarrow 3 \leftarrow 2 = 2 \leftarrow 2, \quad 1 \leftarrow 2 \leftarrow 3 = 1 \leftarrow 3, \quad (6.13)$$

which is the same as expressed in equation (6.12). It is instructive to reverse the order of the permutations, i.e., consider (23)(132). In this case we have: 1 is first replaced by 3 and then by 2; 2 is first replaced by 1 and then by 1; 3 is first replaced by 2 and then by 3. Combining everything we have

$$(23)(132) = (12). \quad (6.14)$$

It should be clear from this that *two permutations do not commute in general*.

Let us go back to our wave function  $\psi$  of equation (6.6) and transform it with the left hand side of equation (6.14)

$$\begin{aligned} \psi^{(23)(132)} &= (23)(132)\psi\left(\underbrace{X_1}_1, \underbrace{X_2}_2, \underbrace{X_3}_3\right) \\ &= (23)\psi\left(\underbrace{X_1}_3, \underbrace{X_2}_1, \underbrace{X_3}_2\right) = (23)\psi\left(\underbrace{X_2}_1, \underbrace{X_3}_2, \underbrace{X_1}_3\right) \\ &= \psi\left(\underbrace{X_2}_1, \underbrace{X_3}_3, \underbrace{X_1}_2\right) = \psi\left(\underbrace{X_2}_1, \underbrace{X_1}_2, \underbrace{X_3}_3\right) \\ &= X_2 + 2X_1 + 3X_3. \end{aligned} \quad (6.15)$$

Another important aspect to consider is that *any permutation can be expressed as a product of transpositions*. Although there can be many representations for a given permutation, it should be clear from the discussion above that the following holds

$$(abcdef)(gh) = (ab)(bc)(cd)(de)(ef)(gh). \quad (6.16)$$

A given permutation is called **even** or **odd** depending on whether it has an even or odd number of transpositions in its transposition product (the permutation of equation (6.16) is even).

Now consider the operation (123)(132). After a little thought, one will find that 1 is replace by 1, 2 by 2 and 3 by 3; an operation impossible to represent by a permutation! This is the **identity** operation  $E$  that leaves a system unchanged; it is equivalent to “doing nothing”. We therefore write

$$(123)(132) = E, \quad (6.17)$$

and

$$(132) = (123)^{-1}. \quad (6.18)$$

That is, (132) is the inverse of (123). This result leads us to a more general result concerning the inverse of any permutation, i.e.,

$$(abc \cdots yz)^{-1} = (azy \cdots cb). \quad (6.19)$$

A little thought should suffice to convince you of this... It should also be obvious that

$$(abc \cdots yz)E = (abc \cdots yz). \quad (6.20)$$

### 6.1.2 The Complete Nuclear Permutation (CNP) Group of a Molecule

We have introduced in Chapter 5 the four axioms that define a group. Although we did so in the context of point groups, these axioms also apply to groups consisting of permutation operators. We list them here again for convenience

1. The identity  $E$  is an operator of the set.
2. The operators multiply associatively; i.e., given three operators  $R, S$  and  $T$ , then it is true that  $(RS)T = R(ST)$ .
3. If  $R$  and  $S$  are two operators of the set, then  $RS$  is also an operator contained in the set.
4. The inverse of each operator is a member of the set.

If we were to consider the case of the  $\text{H}_3^+$  molecule with the nuclei labeled with 1, 2, and 3, as was done in Chapter 5, and we listed all of the possible permutations of the nuclei that leave the Hamiltonian unchanged in a set, we would get

$$\{E, (12), (23), (13), (123), (132)\}. \quad (6.21)$$

Furthermore, if we build a multiplication table from these operators we have the result shown in Table 6-1. A thorough study on this table will convince the reader that the four axioms are met by this set, which therefore forms a group. Evidently, this would also be the case for any other molecule that possesses three (and no other) identical nuclei, e.g., methyl fluoride ( $\text{CH}_3\text{F}$ ). This set of all possible permutations of identical nuclei is called the **complete nuclear permutation** (CNP) group. This particular CNP group for three identical nuclei is called  $S_3$ ; in general the group  $S_n$  contains  $n!$  operators. As the number of groups of identical nuclei in a molecule increases so does the number of permutations. For example, the CNP of ethylene ( $\text{C}_2\text{H}_4$ ) is made of the so-called *direct product* of the CNP ( $S_4$ ) for the hydrogen nuclei and the CNP ( $S_2$ ) for the carbon nuclei

**Table 6-1** – The multiplication table for the possible permutations of the  $H_3^+$  molecule. The table is calculated by first applying the operator of the top row and then the operator of the left column.

	$E$	(12)	(23)	(13)	(123)	(132)
$E$	$E$	(12)	(23)	(13)	(123)	(132)
(12)	(12)	$E$	(123)	(132)	(23)	(13)
(23)	(23)	(132)	$E$	(123)	(13)	(12)
(13)	(13)	(123)	(132)	$E$	(12)	(23)
(123)	(123)	(13)	(12)	(23)	(132)	$E$
(132)	(132)	(23)	(13)	(12)	$E$	(123)

$$\text{CNP}(C_2H_4) = S_4 \otimes S_2, \quad (6.22)$$

and will contain  $4! \times 2! = 48$  operators. As a trivial example, if we have two  $S_2$  CNP groups with their respective nuclei labeled  $\{1,2\}$  and  $\{3,4\}$

$$\begin{aligned} S_2^a &= \{E, (12)\} \\ S_2^b &= \{E, (34)\}, \end{aligned} \quad (6.23)$$

then the resulting CNP group will be

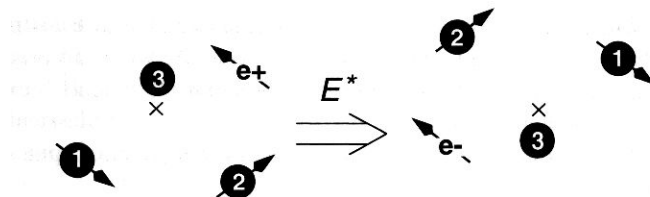
$$S_2^a \otimes S_2^b = \{E, (12), (34), (12)(34)\}. \quad (6.24)$$

Even for relatively small molecules, the CNP group can therefore quickly become enormous and cumbersome to handle.

### 6.1.3 The Inversion Operator $E^*$ and Parity

The permutation operators introduced so far are not the only Hamiltonian symmetry operators. Consider for example the **inversion** operator  $E^*$ , which consists of inverting the spatial coordinates of all nuclei and electrons in a molecule. This is done using the  $(X, Y, Z)$  space-fixed coordinate system that has its origin at the molecular centre of mass. The effect of this operator on the water molecule is shown in Figure 6-2. The inversion leaves the spin of the particles unchanged. That is, the spins stay attached to their corresponding particles. The effect of  $E^*$  on a function can be assessed with equation (6.9)

$$\begin{aligned} \psi^{E^*}(\mathbf{R}_1, \sigma_1, \dots, \mathbf{R}_l, \sigma_l) &= E^* \psi(\mathbf{R}_1, \sigma_1, \dots, \mathbf{R}_l, \sigma_l) \\ &= \psi(\mathbf{R}'_1, \sigma'_1, \dots, \mathbf{R}'_l, \sigma'_l) \\ &= \psi(-\mathbf{R}_1, \sigma_1, \dots, -\mathbf{R}_l, \sigma_l). \end{aligned} \quad (6.25)$$



**Figure 6-2** – The effect of  $E^*$  on the water molecule. The spatial coordinates of all nuclei and electrons are inverted, while the spins stay attached to their corresponding particles.

Going back to our simple earlier example where

$$\psi(X_1, X_2, X_3) = X_1 + 2X_2 + 3X_3, \quad (6.26)$$

we have

$$\begin{aligned} \psi^{E^*} &= -X_1 - 2X_2 - 3X_3 \\ &= -\psi. \end{aligned} \quad (6.27)$$

If a function  $f$  is such that

$$f^{E^*} = f, \quad (6.28)$$

then it is said to have **positive parity**. On the other hand, if

$$f^{E^*} = -f, \quad (6.29)$$

as was the case in the last example, then it has **negative parity**.

The fact that the inversion is symmetry operator can be asserted from the fact that neither the kinetic nor the potential energies of a molecule are affected by a change in the sign of the coordinates.

#### 6.1.4 The Complete Nuclear Permutation Inversion (CNPI) Group of a Molecule

If we intend to define a group for a molecule which includes the permutation and the inversion operators, then by axiom 3 for the definition of a group the operators resulting from the combination of a permutation and the inversion must also be included. For example, the **permutation-inversion** operator

$$(12)^* \equiv E^*(12) = (12)E^* \quad (6.30)$$

must be part of the group. We should, however, ensure that this new operator also leaves the Hamiltonian unchanged. It is trivial to show that this is so in general with  $P^* = E^*P$ , where  $P$  is some permutation,

$$P^* \hat{H}^0 = E^* P \hat{H}^0 = E^* \hat{H}^0 P = \hat{H}^0 E^* P = \hat{H}^0 P^*, \quad (6.31)$$

as both operators  $E^*$  and  $P$  leave the (rovibronic) Hamiltonian unchanged. (Here we use the approximate rovibronic Hamiltonian resulting from the Born-Oppenheimer approximation, the neglect of rotation-vibration coupling, etc.; hence the superscript.) The permutation-inversion operator is therefore a symmetry operation. It is important to note that the statement that an operator  $R$  is a Hamiltonian symmetry operation is equivalent to saying that it commutes with the Hamiltonian

$$[R, \hat{H}^0] = 0, \quad (6.32)$$

as can be inferred from equation (6.31). Incidentally, this also tells us that the transformed wave function  $\psi^R = R\psi$  shares the same energy as the original eigenfunction  $\psi$ , and that it is also an eigenfunction of the Hamiltonian, as

$$\hat{H}^0 \psi^R = \hat{H}^0 R\psi = R \hat{H}^0 \psi = E_\psi^0 R\psi = E_\psi^0 \psi^R, \quad (6.33)$$

where  $E_\psi^0$  is the energy associated with  $\psi$  (i.e., the corresponding eigenvalue of the Hamiltonian). We will come back to this important fact in the next chapter.

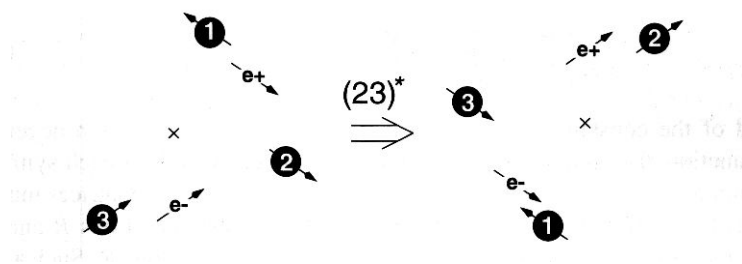
The group formed by combining the elements of the CNP group and the corresponding permutation-inversion operations is the so-called **complete nuclear permutation inversion** (CNPI) group. It is expressible as the direct product

$$\text{CNPI} = \text{CNP} \otimes \mathcal{E}, \quad (6.34)$$

where  $\mathcal{E} = \{E, E^*\}$ . We therefore find that the CNPI group has twice as many elements as the corresponding CNP group. For example, the CNPI group for the  $\text{H}_3^+$  molecule is

$$\{E, (12), (23), (13), (123), (132), E^*, (12)^*, (23)^*, (13)^*, (123)^*, (132)^*\}. \quad (6.35)$$

The effect of the  $(23)^*$  operation on the  $\text{H}_3^+$  molecule is shown in Figure 6-3.



**Figure 6-3** – The effect of the permutation-inversion  $(23)^*$  on the  $\text{H}_3^+$  molecule.



We mentioned earlier that the size of the CNP group can render it cumbersome to use, this comment is even more appropriate for the CNPI group.

## 6.2 The Molecular Symmetry (MS) Group

Although we have established that the CNPI group is a symmetry group of a molecule and, as we will see later, it can be used to specify the molecular state, it is generally best not to use it for this purpose. The reason for this lies in the fact that because of the large number of operators it contains the CNPI group can lead to a larger number of representations for a molecule than can be discerned observationally through experiments of finite precision. It is said that symmetry operations that link two indistinguishable representations are called *unfeasible*. The subset of all *feasible* symmetry operations is that of the so-called **molecular symmetry** (MS) group. The MS group, which we now introduce, is a *subgroup* of the CNPI group.

### 6.2.1 Tunneling and the CNPI Group

Consider the two equilibrium versions of the methyl fluoride  $\text{CH}_3\text{F}$  molecule shown in Figure 6-4. The version on the left has the hydrogen nuclei arranged in a clockwise configuration when looking up the C-F axis, while the one on the right is anticlockwise in character. It should be clear that these two representations of the molecule, and their like deformations, will have similar energy levels.

Indeed, it is usually the case that a potential barrier separates the potential energy minima of two such molecular configurations (see Figure 6-5). A molecule can only pass from one configuration to the other by *tunneling* through the barrier. When this barrier potential is high enough, as is the case for methyl fluoride, we can neglect the possibility of tunneling and these configurations can be considered to exist independently. As these representations are indistinguishable experimentally, there are no advantages in allowing for both their existence when studying the spectroscopy of this molecule. We will bring a significant simplification to the problem by considering only one representation. Molecules that show no tunneling are called **rigid molecules** (please note that this kind of “rigidity” still allows for nuclear vibrations). Those that exhibit tunneling are called **non-rigid molecules**; ammonia ( $\text{NH}_3$ ) is one example.

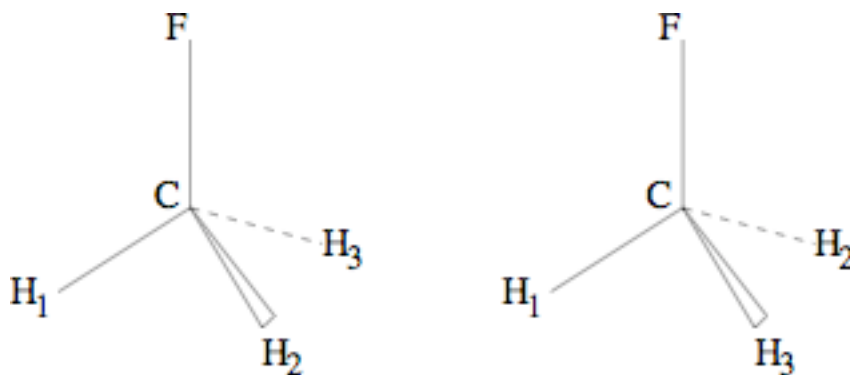
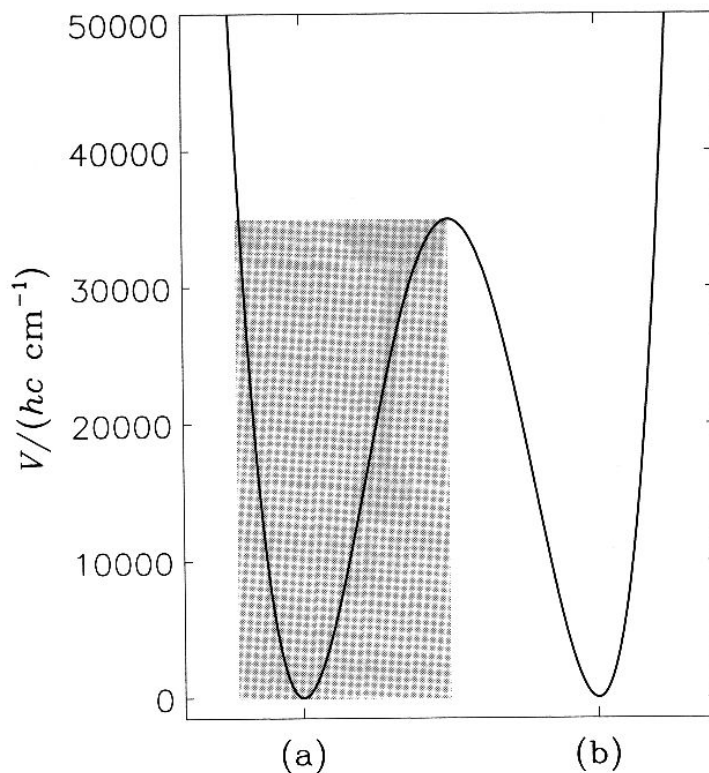


Figure 6-4 – The two versions of methyl fluoride molecule at equilibrium. The version on the left (right) has the hydrogen nuclei arranged in a clockwise (anticlockwise) configuration when looking up the C-F axis. The solid, broken, and thick lines are in, behind, and in front of, the plane of the page, respectively.

The question we must now answer is: how can we identify or recognize equivalent molecular configurations? A careful study of Figure 6-4 will reveal that it is not possible to transform the methyl fluoride molecule from one version to the next by a mere rotation (the  $C_n$  point group symmetry operation). If we therefore define the MS group as containing only permutation and permutation-inversion symmetry operations that leaves the molecule *within* a given configuration, then we must discard any CNPI operator that connect two indistinguishable versions.

For example, since we know that the methyl fluoride possesses the same CNPI group as the  $H_3^+$  ion, we can write from equation (6.35) that

$$\text{CNPI}(\text{CH}_3\text{F}) = \{E, (12), (23), (13), (123), (132), E^*, (12)^*, (23)^*, (13)^*, (123)^*, (132)^*\}. \quad (6.36)$$



**Figure 6-5** – A representation for the potential of the methyl fluoride molecule. The two minima correspond to the two versions shown Figure 6-4. The molecule can go from one version to the other by tunneling through the potential barrier. The MS group of  $\text{CH}_3\text{F}$  (with no tunneling) is determined by using only one part of the potential only (the shaded area).

Since the (12), (13), and (23) permutations change the handedness of a configuration, then they must be excluded from the MS group (i.e., they are *unfeasible*), while (123) and (132) are included (i.e., they are *feasible*). It will be easier to evaluate the effect of the permutation-inversion operators by first visualizing the transformation brought about by the inversion operator. This is shown in Figure 6-6. It is seen that  $E^*$ , like (12), (13), and (23), transforms the clockwise version of the molecule into its anticlockwise version and is, therefore, not part of the MS group. However, combining the inversion with a handedness-changing permutation, such as (12), (13), and (23), will cancel its corresponding effect on the handedness on the molecule and yield a feasible operator. Because of this we determine the MS group of methyl fluoride to be

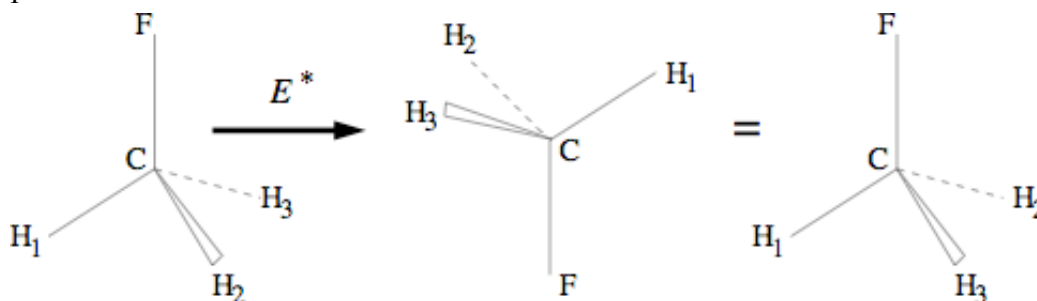
$$\text{MS}(\text{CH}_3\text{F}) = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}. \quad (6.37)$$

Clearly, the MS group of methyl fluoride is significantly smaller than the corresponding CNPI group and will be a lot easier to handle.

Finally, it is important to realize that since the structure of a molecule is dependent on its electronic state, then different electronic states will in general yield different MS groups.

### 6.3 The Relationship between the MS and the Point Groups

We know that both the MS and point groups deal with the symmetry of molecules. It is important to realize, however, that both approaches are very different. On the one hand, a MS group deals with the symmetries of the Hamiltonian, while on the other hand the point group of the molecule under study only considers its geometrical symmetries *at equilibrium*. Since the molecule is rotating and vibrating, we are left to wonder how the latter could ever be of any use for spectroscopy. However, point groups have been around and used for molecular spectroscopy analyses for a much longer period than MS groups have. But MS groups were introduced in part to palliate for the shortcomings of point groups. In fact, on the back cover of their “Fundamentals of Molecular Symmetry” book Bunker and Jensen write “Usually the point group is only useful for isolated, non-rotating molecules, executing small amplitude vibrations in isolated electronics states. However, for the chemical physicist or physical chemist who wishes to go beyond these limitations, the MS group is nearly always required.” So, MS groups are more powerful than point groups... but what is the connection between the two?



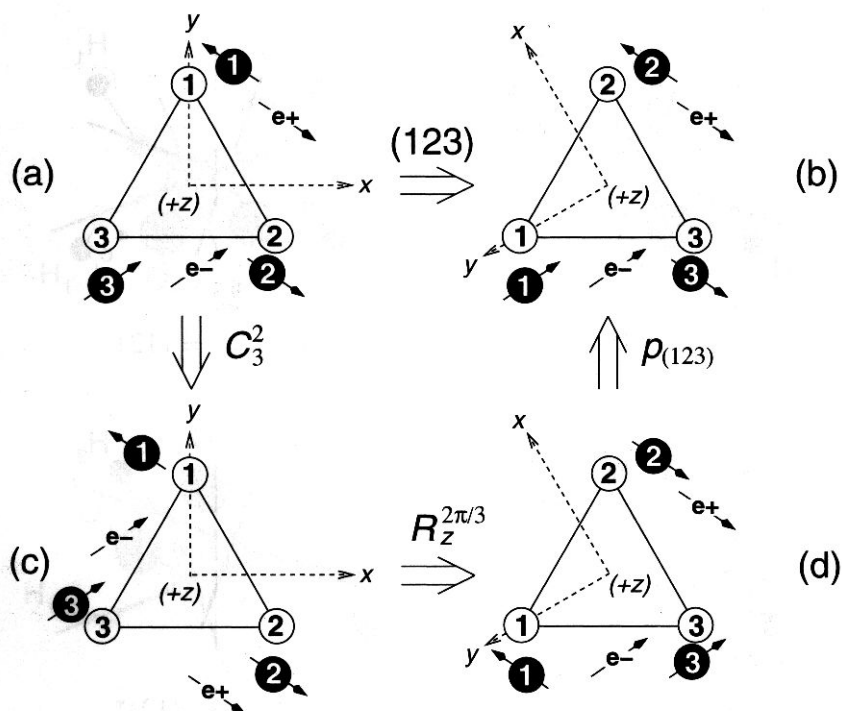
**Figure 6-6** – The effect of the inversion  $E^*$  on the methyl fluoride molecule. It is seen that it transforms the clockwise version of the molecule into its anticlockwise version.

### 6.3.1 Non-linear Rigid Molecules

We first consider non-linear rigid molecules and concentrate on a given MS group operator (i.e., a permutation or permutation-inversion operation) and try to see if it has any connection to some other point group operator. For example, consider the (123) permutation of the  $H_3^+$  molecule shown in Figure 6-7 (a) and (b). We already know the effect of a permutation (i.e., exchange of positions and spins between like nuclei), but we must realize it will also bring a rotation of the molecule-fixed axes (i.e., the  $x$ -,  $y$ -, and  $z$ -axes shown in Figure 6-7) through a change in the Euler angles. However, because we know that point group operations are made about the space-fixed axes we must expect that at least one other type of operators (perhaps more) will be combined with the operators of the point groups to equate a permutation such as the one studied here.

Indeed, it is found that in general two more types of operators are needed. More precisely, any given MS group operator can be broken in three successive operators as follows:

- A point group operation  $R_{ve}$  effected about the space-fixed coordinate axes (which therefore leaves the molecule-fixed unchanged) that transforms the nuclear vibrational coordinates, and electronic coordinates and spins.



**Figure 6-7** – The effect of the (123) permutation on the  $H_3^+$  molecule, and its decomposition in a space-fixed rotation ( $C_3^2$ ), a molecule-fixed rotation ( $R_z^{2\pi/3}$ ), and a nuclear spin permutation ( $p_{(123)}$ ) operators. The filled (open) circles stand for the nuclei positions when the molecule is deformed (at equilibrium).

- b. A rotation operator  $R_{\text{rot}}$  effected about the molecule-fixed coordinate axes, which changes the values of the Euler angles that specify the orientation of the molecule in space.
- c. A nuclear spin permutation operator  $R_{\text{ns}}$ .

Mathematically speaking, any MS group operator  $R$  can be expressed as

$$R = R_{\text{ve}} R_{\text{rot}} R_{\text{ns}}, \quad (6.38)$$

where the order of the three operators on the right hand side is irrelevant, since they all commute with each other. A careful study of Figure 6-7 will, for example, reveal that

$$(123) = C_3^2 R_z^{2\pi/3} p_{(123)}, \quad (6.39)$$

where  $C_3^2$  is the three-fold rotation operator defined in Chapter 5,  $R_z^{2\pi/3}$  is a rotation of  $2\pi/3$  radians about the molecule-fixed  $z$ -axis, and  $p_{(123)}$  consists of a permutation (in the usual fashion) on the nuclear spins. Other examples for the  $\text{H}_3^+$  ion are

$$\begin{aligned} E &= ER^0 p_0 \\ E^* &= \sigma_{\text{h}} R_z^\pi p_0 \\ (23)^* &= \sigma_{\text{xy}} R_x^\pi p_{(23)}, \end{aligned} \quad (6.40)$$

where  $R^0$  and  $p_0$  are identity operators, and  $\sigma_{\text{xy}}$  is for a reflection about the  $xy$ -plane (i.e., it is a  $\sigma_{\text{v}}$  operator, as defined in Chapter 5).

The connection between the MS and point groups can now be better understood, at least for non-linear molecules. That is, the point group is only part of the whole picture: it will only be useful when dealing with vibronic spectroscopy and needs to be complemented with molecule-fixed rotations and nuclear spin permutations to allow a treatment of the full rovibronic spectroscopy of molecules, as the MS group does.

For non-linear rigid molecules, to each elements of the MS group will correspond only one operator  $R_{\text{ve}}$  and vice-versa. The set of all  $R_{\text{ve}}$  forms the **molecular point group**. For that reason, it is common to denote MS groups using the name of the corresponding molecular point group (with a slight modification). For example, the MS group of the  $\text{H}_3^+$  molecule is  $D_{3\text{h}}(\text{M})$ .

The operators  $R_{\text{rot}}$  are part of the so-called **molecular rotation group** (to be considered later); at times they consist of only a subgroup, at other times the whole group. The operators  $R_{\text{ns}}$  are part of the so-called **nuclear spin permutation group**.

### 6.3.2 Linear Rigid Molecules

Linear molecules must be treated differently. The reason is that there is not a one-to-one correspondence between their point and MS groups. For example, the unsymmetrical

HCN molecule has  $C_{\infty v}$  for its point group and  $\{E, E^*\}$  for its MS group. The first one has an infinite number of elements, while the second has only two. Consequently, vibronic states will be labeled (see Chapter 7) using the point group and the rovibronic states using the MS group. However, it is possible to introduce the so-called **extended MS group** of a linear molecule, which can be used for both purposes (see Chapter 12). The extended MS group of HCN is thus denoted by  $C_{\infty v}(EM)$ .

### 6.3.3 The Relationship between $E^*$ and $i$

For a centro-symmetric molecule there will always exist a permutation-inversion operator, say,  $R_i$ , which can be written in the following form

$$R_i = (AA')(BB') \cdots (ZZ')^*, \quad (6.41)$$

where each pair  $AA', BB'$ , etc., consists of identical nuclei positioned symmetrically about the nuclear centre, in the equilibrium configuration. For example, the carbon dioxide and ethylene molecules have

$$\begin{aligned} R_i^{\text{CO}} &= (12)^* \\ R_i^{\text{C}_2\text{H}_4} &= (14)(23)(56)^*, \end{aligned} \quad (6.42)$$

respectively (for  $\text{CO}_2$ , the labels 1 and 2 are for the oxygen nuclei; for  $\text{C}_2\text{H}_4$ , the labels 1 and 4, and 2 and 3, are for the two pairs of hydrogen nuclei (each pair has one nucleus at each end of the molecule), while 5 and 6 are for the carbon nuclei). Because of the relative positions of the nuclei and the combination of the permutation(s) with the inversion  $E^*$  these operators leave the Euler angles unchanged. On the other hand, the vibronic coordinates are inverted and nuclear spins are exchanged within each pair of transposed nuclei. Thus, the operator  $R_i$  is made of the following composition

$$R_i = iR^0 P_{(AA')(BB') \cdots (ZZ')}. \quad (6.43)$$

We conclude from this that the point group inversion operator  $i$  is not the same as the MS group inversion operator  $E^*$ . As stated earlier, the latter one is used to denote the parity ('+' or '-') of a molecule, while  $i$  gives the 'g' and 'u' labels for the vibronic states of a centro-symmetric molecule.

## 6.4 Representations and Character Tables

In this section we list some of the important definitions and results of group theory. Although the material presented here might appear somewhat abstract at first, its usefulness will become clearer when applied to molecular spectroscopy in the following chapters.

### 6.4.1 Matrix Groups

Consider the following set of matrices, which we call  $\Gamma_3$

$$\begin{aligned} \Gamma_3 &= \left\{ M^E, M^{(12)^*}, M^{(23)^*}, M^{(31)^*}, M^{(123)}, M^{(132)} \right\} \\ &= \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}, \right. \\ &\quad \left. \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}, \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}, \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix} \right\}. \end{aligned} \quad (6.44)$$

By forming the multiplication table for these six matrices, it would be easy to verify that  $\Gamma_3$  meets the requirements spelled out by the axioms defining a group (see page 103). That is, it is always possible to represent a group, and all of its abstraction, with a set of matrices;  $\Gamma_3$  in particular is the representation of a group.

### 6.4.2 Isomorphism and Faithful Representations

An **isomorphism** is a one-to-one correspondence between the elements of two sets. To illustrate this concept consider the  $C_{3v}(\text{M})$  MS group of equation (6.21) and the  $\Gamma_3$  matrix group of equation (6.44). It turns out that if we make the following associations

$$\begin{aligned} E &\leftrightarrow M^E, \\ (12)^* &\leftrightarrow M^{(12)^*}, \quad (23)^* \leftrightarrow M^{(23)^*}, \quad (13)^* \leftrightarrow M^{(13)^*}, \\ (123) &\leftrightarrow M^{(123)}, \quad (132) \leftrightarrow M^{(132)}, \end{aligned} \quad (6.45)$$

we find that the two corresponding multiplication tables match perfectly. The multiplication tables for  $C_{3v}(\text{M})$  and  $\Gamma_3$  are said to be isomorphic. A matrix group that is isomorphic to another group is said to be a **faithful representation** of that group.

The same can be said when considering the point group  $D_3$

$$D_3 = \{E, C_2, C_2', C_2'', C_3, C_3^2\}. \quad (6.46)$$

That is, it can be shown that  $\Gamma_3$  is isomorphic to, and a faithful representation of,  $D_3$ . Obviously, from what we have seen in the last section, the MS and molecular point groups of non-linear molecules are also isomorphic to one another.

### 6.4.3 Homomorphism and Unfaithful Representations

A **homomorphism** is a many-to-one correspondence between two sets of different order (i.e., size). For example, consider the two one-dimensional matrix groups  $\Gamma_1$  and  $\Gamma_2$

$$\begin{aligned}\Gamma_1 &: \{1\} \\ \Gamma_2 &: \{1, -1\},\end{aligned}\tag{6.47}$$

and their associations to the  $C_{3v}(\mathbf{M})$  group

$$\begin{aligned}C_{3v}(\mathbf{M}): & E \quad (12)^* \quad (23)^* \quad (13)^* \quad (123) \quad (132) \\ \Gamma_1: & 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \\ \Gamma_2: & 1 \quad -1 \quad -1 \quad -1 \quad 1 \quad 1\end{aligned}\tag{6.48}$$

Clearly any element of  $\Gamma_1$  and  $\Gamma_2$  is mapped to more than one element of  $C_{3v}(\mathbf{M})$ . It is said that the respective mappings of  $C_{3v}(\mathbf{M})$  onto  $\Gamma_1$  and  $\Gamma_2$  are homomorphic. Moreover, if a group is homomorphic onto a matrix group, then the matrix group is said to be an **unfaithful representation** of the group.

#### 6.4.4 Equivalent, Reducible, and Irreducible Representations

Starting from a representation for a group, such as  $\Gamma_3$  for  $C_{3v}(\mathbf{M})$ , it is always possible to obtain an **equivalent representation** through a *similarity transformation*. That is, given a matrix  $A$  we can obtain six new matrices  $M'$  from the six  $M$  matrices defined in equation (6.44) with

$$M' = A^{-1}MA.\tag{6.49}$$

One could easily verify that the new set  $\{M'\}$  is also a matrix group. There are also two important facts concerning matrix representations that we need to know:

- i. Given a representation, it is always possible to find a similarity transformation so that all the matrices in the new representation are unitary.
- ii. A similarity transformation does not change the **trace** of the matrices, which are therefore the same for all representations. This is easily proven as follows

$$\begin{aligned}\text{Tr}(M') &= \sum_j M'_{jj} = \sum_{j,k,l} A_{jk}^{-1} M_{kl} A_{lj} \\ &= \sum_{k,l} M_{kl} \sum_j A_{lj} A_{jk}^{-1} = \sum_{k,l} M_{kl} \delta_{kl} \\ &= \sum_k M_{kk} = \text{Tr}(M).\end{aligned}\tag{6.50}$$

The trace of a matrix is called the **character** of the matrix.

Beside a similarity transformation, it is also possible to obtain a new representation of a group by combining the different representations of that group. For example, starting with the representations  $\Gamma_2$  and  $\Gamma_3$  of  $C_{3v}(\mathbf{M})$  we can form the following three-dimensional **reducible representation**



$$\Gamma_{\text{sum}} = \left\{ \begin{aligned} & \left[ \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right], \left[ \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{array} \right], \left[ \begin{array}{ccc} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{array} \right] \\ & , \left[ \begin{array}{ccc} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{array} \right], \left[ \begin{array}{ccc} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{array} \right], \left[ \begin{array}{ccc} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{array} \right] \end{aligned} \right\}. \quad (6.51)$$

Note that every matrix in  $\Gamma_{\text{sum}}$  is *block diagonal*. From equations (6.44), (6.45), and (6.48), we can see that each matrix is made of two blocks from corresponding matrices of  $\Gamma_2$  and  $\Gamma_3$ . This is symbolically expressed by

$$\Gamma_{\text{sum}} = \Gamma_2 \oplus \Gamma_3. \quad (6.52)$$

Furthermore, it should be clear from our previous discussion concerning the character of matrices that the character of  $\Gamma_{\text{sum}}$  is the sum of the characters of  $\Gamma_2$  and  $\Gamma_3$ . This is expressed as follows

$$\chi^{\Gamma_{\text{sum}}}[R] = \chi^{\Gamma_2}[R] + \chi^{\Gamma_3}[R], \quad (6.53)$$

where  $\chi^{\Gamma_i}[R]$  is the character in the representation  $\Gamma_i$  of the matrix  $D^{\Gamma_i}[R]$  associated with the symmetry operator  $R$  of the corresponding MS group (in this case  $C_{3v}(\text{M})$ ). A representation that cannot be brought into a block diagonal form through any similarity transformation is called an **irreducible representation**. It can be shown from the so-called *Great Orthogonality Theorem* (GOT) of group theory that the matrix elements  $D^{\Gamma_i}[R]_{mn}$  and  $D^{\Gamma_j}[R]_{m'n'}$  of two irreducible representations  $\Gamma_i$  and  $\Gamma_j$  satisfy the following relation

$$\sum_R \sqrt{\frac{l_i}{h}} D^{\Gamma_i}[R]_{mn}^* \sqrt{\frac{l_j}{h}} D^{\Gamma_j}[R]_{m'n'} = \delta_{ij} \delta_{mm'} \delta_{nn'}, \quad (6.54)$$

where  $h$  is the order of the group,  $l_i$  and  $l_j$  are the dimensions of the matrices of the irreducible representations  $\Gamma_i$  and  $\Gamma_j$ , respectively, and the summation is over all the elements  $R$  of the group. Perhaps more important for our purposes is the so-called **little orthogonality theorem** obtained by setting  $m = n$ ,  $m' = n'$  and summing over  $m$  and  $m'$  in equation (6.54) to get

$$\begin{aligned} \sum_{m,m'} \sum_R \sqrt{\frac{l_i}{h}} D^{\Gamma_i} [R]_{mm'}^* \sqrt{\frac{l_j}{h}} D^{\Gamma_j} [R]_{m'm'} &= \sum_R \sqrt{\frac{l_i}{h}} \chi^{\Gamma_i} [R]^* \sqrt{\frac{l_j}{h}} \chi^{\Gamma_j} [R] \\ &= \sum_{m,m'} \delta_{ij} \delta_{mm'} \delta_{mm'} = \sum_m \delta_{ij} \delta_{mm} = l_i \delta_{ij}, \end{aligned} \quad (6.55)$$

or alternatively,

$$\boxed{\sum_R \chi^{\Gamma_i} [R]^* \chi^{\Gamma_j} [R] = h \delta_{ij}} \quad (6.56)$$

It turns out that for finite groups there exist a finite number of irreducible representations (see the discussion on classes below). For example,  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$  are the only possible irreducible representations for  $C_{3v}(\text{M})$ , and therefore any representation  $\Gamma$  can be expressed as follows

$$\Gamma = a_1 \Gamma_1 \oplus a_2 \Gamma_2 \oplus a_3 \Gamma_3, \quad (6.57)$$

with the corresponding characters

$$\chi^\Gamma [R] = a_1 \chi^{\Gamma_1} [R] + a_2 \chi^{\Gamma_2} [R] + a_3 \chi^{\Gamma_3} [R], \quad (6.58)$$

where  $a_i$  is an integer.

#### 6.4.5 Reduction of a Representation

As we will see in the next chapter, irreducible representations are used to label molecular states. Usually, one will have to start with a reducible representation and decompose it into a sum of irreducible representations (as in equation (6.57)) in order to produce the desired labels. That is, we want to evaluate the different coefficients  $a_i$  in equations (6.57) and (6.58). To do so we generalized equation (6.58) to

$$\chi^\Gamma [R] = \sum_j a_j \chi^{\Gamma_j} [R], \quad (6.59)$$

and we multiply by  $\chi^{\Gamma_i} [R]^*$  on both sides of this equation and use the little orthogonal theorem (i.e., equation (6.56)) to get

$$\boxed{a_i = \frac{1}{h} \sum_R \chi^\Gamma [R] \chi^{\Gamma_i} [R]^*} \quad (6.60)$$

Since the reduction depends entirely on the characters of the different representations, the characters of MS groups have been tabulated into so-called **character tables** (see below) to facilitate calculations.

### 6.4.6 Classes of Operators

The operators of a group can always be separated into **classes**. Two elements  $A$  and  $B$  belong to the same class if there exists another group element  $C$  such that

$$B = C^{-1}AC. \quad (6.61)$$

It follows from this definition that the identity  $E$  is always in a class of its own. Equation (6.61) also implies that *operators belonging to the same class have the same character* (see equations (6.49) and (6.50)).

The actual meaning of this separation between the elements of a group is that operators belonging to the same group are of all of a same type of operations. For example, referring to Table 5-2 for the  $D_{3h}$  point group we see that the subsets  $\{C_3, C_3^2\}$ ,  $\{C_2, C_2', C_2''\}$ ,  $\{\sigma_v, \sigma_v', \sigma_v''\}$ , and  $\{S_3, S_3^2\}$  are made of the same kind of operators (i.e., rotations about the symmetry axis, rotations about two-fold axes perpendicular to the symmetry axis, vertical reflection, and improper rotations about the symmetry axis), and therefore form separate classes. The operators  $E$  and  $\sigma_h$  are in classes by themselves. Similarly, the classes of  $C_{3v}(M)$  are  $\{E\}$ ,  $\{(12)^*, (23)^*, (13)^*\}$ , and  $\{(123), (132)\}$  (i.e., the identity, the set of all transposition-inversions, and the set of all permutations of three nuclei). Another important characteristic of classes is the fact that *there are equal numbers of classes and irreducible representations*.

**Table 6-2** – The character table of the  $C_{3v}(M)$  group.

$C_{3v}(M)$ :	$E$	$(123)$	$(23)^*$	
	1	2	3	
$C_{3v}$ :	$E$	$2C_3$	$3\sigma_v$	
Equiv. rotation	$R^0$	$R_z^{2\pi/3}$	$R_{\pi/2}^\pi$	
$A_1$ :	1	1	1	$:T_z, \alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
$A_2$ :	1	1	-1	$:\hat{J}_z, \Gamma(\mu_A)$
$E$ :	2	-1	0	$:(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

### 6.4.7 Character Tables

The characters of the irreducible representations of a group are listed in its character table. In this table the group operators are divided according to their classes, although usually only one operator per class is listed, since they all have the same character. The number of elements in each class is stated, however. For example, the character table of the  $C_{3v}(M)$  group is given in Table 6-2. The first two rows give the classes of elements and the number of elements in each class of the MS group, the third row does the same for the molecular point group, while the fourth row (equivalent rotation) will be discussed later. As there are three classes, we expect to have three irreducible representations, which we find with their corresponding characters in the last three rows. The

representation  $A_1$  has a character of 1 for all classes; it is called the **totally symmetric representation** because of this (it will generally be referred to as  $\Gamma^{(s)}$ ). The last column on the right will also be explained later. Finally, we can guess the dimension of a given irreducible representation by looking at the character of the identity element. It follows from this that both  $A_1$  and  $A_2$  are one-dimensional, while the  $E$  representation is two-dimensional.