

Chapter 11. Non-rigid Molecules

Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (1998), Chap. 15, and Bunker and Jensen (2005), Chap. 13.*

11.1 The Hamiltonian

As was stated before, a rigid molecule is not one for which all the nuclei it contains are rigidly bound to each other, or for which the distance between the atoms cannot change. We know in fact that rigid molecules can rotate and vibrate. On the other hand, non-rigid molecules are different in that they can tunnel through a potential barrier from one configuration to another. We discussed this in Section 6.2 while considering the so-called *feasible* and *unfeasible* operators for a given molecule (see Figure 6-5 for the potential curve of methyl fluoride).

Although the nuclei of rigid molecules generally do not stray too far from the equilibrium configuration, it is possible that one or several internal coordinates of a non-rigid molecule exhibit large excursions from their position of equilibrium; this is necessary to account for the possible tunneling of the molecule. It is, therefore, apparent that we must modify our analysis to correctly account for this type of motions. Most importantly the Hamiltonian must differentiate between normal, small-amplitude, vibrational coordinates (i.e., the normal coordinates) and the so-called **contortional** coordinates that are responsible for the tunneling (e.g., inversion of the molecule or internal rotations). While for rigid molecules we obtained a rotation-vibration Hamiltonian H_{rv} that was a function of the Euler angles (ϕ, θ, χ) and the normal coordinates (Q_1, \dots, Q_{3N-6}) , an in-depth study of non-rigid molecule necessitate the introduction of the so-called rotation-contortion-vibration Hamiltonian H_{rcv} that is a function of the modified set of coordinates $(\phi, \theta, \chi, \rho_1, \dots, \rho_r, Q_1, \dots, Q_{3N-6-r})$, where ρ_i , $i = 1$ to r , are the contortional coordinates. We will not attempt to do this, as it would take us to a level of specialization that is well beyond the level of this course.

However, although the study of the contortional Hamiltonian is necessary to precisely determine the energy levels and transition frequencies, it is possible to understand the tunneling of non-rigid molecules by establishing the correspondence of the parent rigid molecule's MS group to that of the less restrictive tunneling molecule. This is what we endeavor to do in this chapter.

11.2 Correlation and Reverse Correlation Tables

Let us take the example of a molecule for which the MS group is $D_{3h}(M)$, the corresponding character table is given in Table 11-1. Let us also assume that a given matrix representation, Γ , for that group was reduce to a block-diagonal arrangement of irreducible representations with a character of, say,

$$\Gamma[D_{3h}(M)] = A'_1 \oplus A''_2 \oplus E' \quad (11.1)$$

Table 11-1 – The character table for $D_{3h}(\text{M})$, using the system of axes of Figure 11-1.

$D_{3h}(\text{M})$:	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$	
	1	2	3	1	2	3	
D_{3h} :	E	$2C_3$	$2C_3$	σ_h	$2S_3$	$3\sigma_v$	
Equiv. rotation	R^0	$R_z^{2\pi/3}$	R_0^π	R_z^π	$R_z^{5\pi/3}$	$R_{\pi/2}^\pi$	
A_1' :	1	1	1	1	1	1	$:\alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
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	$:T_z$
E' :	2	-1	0	2	-1	0	$:(T_x, T_y), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E'' :	2	-1	0	-2	1	0	$:(\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$

The question we seek to answer is: what would the representation of equation (11.1) transform to if we restricted ourselves to a subgroup of $D_{3h}(\text{M})$? More precisely, imagine that for some considerations (that will become clear later on) we seek to express the representation Γ using the $C_{3v}(\text{M})$ group, which is a subgroup of $D_{3h}(\text{M})$. The character table of $C_{3v}(\text{M})$ is given in Table 11-2.

To answer this question we must first realize that, although Γ as given in equation (11.1) cannot be further reduced within $D_{3h}(\text{M})$, this is not necessarily so in $C_{3v}(\text{M})$. In fact, we should expect that a reduction of the representation is achievable. Fortunately, this is a problem that we have encountered before in Chapter 6 when discussing the reduction of a representation. In this case, the problem can be solved by addressing the more restricted question: given a group G (e.g., $D_{3h}(\text{M})$), how will its irreducible representations, Γ_α , correlate to those, Γ_i , characterizing its subgroup H (e.g., $C_{3v}(\text{M})$)?

Table 11-2 – The character table for $C_{3v}(\text{M})$, using the system of axes of Figure 11-1.

$C_{3v}(\text{M})$:	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	$:(T_x, T_y), (\hat{J}_x, \hat{J}_y), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

We assume that G is of order g with elements $\{G_1, G_2, \dots, G_g\}$, while H is of order $h < g$ with elements $\{H_1, H_2, \dots, H_h\}$, and that $G_j = H_j$, for $j = 1, 2, \dots, h$. This last assumption implies that we know how (the elements of) G transform under (the elements of) H . Our question is then simply answered by the application of equation (6.60) to find the number of times $a_i^{(\alpha)}$ that an irreducible representation Γ_i of H will appear in the reducible representation (within H) Γ_α as follows

$$a_i^{(\alpha)} = \frac{1}{h} \sum_{j=1}^h \chi^{\Gamma_\alpha} [H_j] \chi^{\Gamma_i} [H_j]^*, \quad (11.2)$$

where $\chi^{\Gamma_\alpha} [H_j]$ and $\chi^{\Gamma_i} [H_j]$ are the characters of Γ_α and Γ_i , respectively, for the operator $H_j = G_j$. We then find that

$$\Gamma_\alpha = \sum_i a_i^{(\alpha)} \Gamma_i. \quad (11.3)$$

For example, in the case where $G = D_{3h}(\text{M})$ and $H = C_{3v}(\text{M})$ we have (using Tables Table 11-1 and Table 11-2, and equation (11.2))

$$\begin{aligned} a_{A_1}^{(A_1')} &= a_{A_1}^{(A_2'')} = \frac{1}{6} \{1 \cdot 1 + 2 \cdot (1 \cdot 1) + 3 \cdot (1 \cdot 1)\} = 1 \\ a_{A_2}^{(A_1')} &= a_{A_2}^{(A_2'')} = \frac{1}{6} \{1 \cdot 1 + 2 \cdot (1 \cdot 1) + 3 \cdot [1 \cdot (-1)]\} = 0 \\ a_E^{(A_1')} &= a_E^{(A_2'')} = \frac{1}{6} \{1 \cdot 2 + 2 \cdot [1 \cdot (-1)] + 3 \cdot (1 \cdot 0)\} = 0 \\ a_{A_1}^{(E')} &= a_{A_2}^{(E')} = \frac{1}{6} \{2 \cdot 1 + 2 \cdot [(-1) \cdot 1] + 3 \cdot [0 \cdot (\pm 1)]\} = 0 \\ a_E^{(E')} &= \frac{1}{6} \{2 \cdot 2 + 2 \cdot [(-1) \cdot (-1)] + 3 \cdot (0 \cdot 0)\} = 1, \end{aligned} \quad (11.4)$$

and so on. We therefore find from equations (11.1) and (11.4) that

$$\Gamma[C_{3v}(\text{M})] = 2A_1 \oplus E. \quad (11.5)$$

We can easily verify that Γ has the same character for the elements that are common to both groups.

In general correspondences such as those expressed in equation (11.4) are listed in so-called **correlation tables**. The correlation table for $D_{3h}(\text{M})$ to $C_{3v}(\text{M})$ is given in Table 11-3.

Table 11-3 – The correlation table for $D_{3h}(\text{M})$ to $C_{3v}(\text{M})$.

$D_{3h}(\text{M})$	$C_{3v}(\text{M})$
A_1'	A_1
A_1''	A_2
A_2'	A_2
A_2''	A_1
E'	E
E''	E

Alternatively, we can also ask the related question: given a completely reduced representation, Γ' , in the subgroup H , what is the corresponding representation generated in the group G ? This is the problem of determining the **reverse correlation** from a subgroup to a parent group that was originally addressed (as well as the previous problem of direct correlation) by Watson (1965)¹, who showed that the answer is simply

$$\Gamma'[G] = \sum_i a_i^{(\alpha)} \Gamma_\alpha, \quad (11.6)$$

where $a_i^{(\alpha)}$ is as given in equation (11.2). It is therefore straightforward to write down **reverse correlation tables**. For example, the reverse correlation table for $C_{3v}(\text{M})$ to $D_{3h}(\text{M})$ is given in Table 11-4.

Equation (11.6) is easily understood with our example even without a formal derivation. For example, a comparison of the corresponding character tables (i.e., Table 11-1 and Table 11-2) will show that the character of A_1 in $C_{3v}(\text{M})$ can only be achieved through either A_1' or A_2'' in $D_{3h}(\text{M})$. It should also be noted that the character of elements common between the two groups must always be the same. It therefore follows that the irreducible representation induced in the parent group will be weighted to ensure this. For example, if the totally symmetric representation A_1 is realized n times in $C_{3v}(\text{M})$, then a possible induced irreducible representation in $D_{3h}(\text{M})$ will be $m A_1' \oplus (n - m) A_2''$, where m will take a value between 0 and n depending on the problem at hand.

Table 11-4 – The reverse correlation table for $C_{3v}(\text{M})$ to $D_{3h}(\text{M})$.

$C_{3v}(\text{M})$	$D_{3h}(\text{M})$
A_1	$A_1' \oplus A_2''$
A_2	$A_1'' \oplus A_2'$
E	$E' \oplus E''$

¹ Watson, James K. G. 1965, *Canadian Journal of Physics*, vol. 43, 1996-2007.

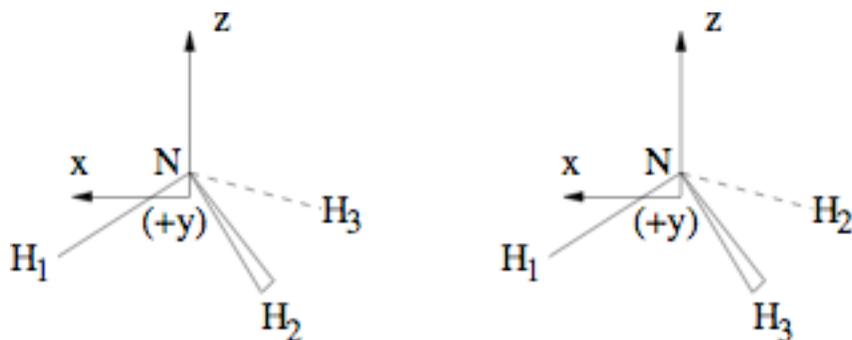


Figure 11-1 – The two equivalent configurations of ammonia (NH_3). This molecule can change from one configuration to the other through tunneling of the nitrogen nucleus.

11.3 An Example: The Inversion of Ammonia

The two possible equivalent configurations of the ammonia molecule are shown in Figure 11-1. If only a rigid version of the molecule is considered, then only one configuration is needed and the associated MS group is $C_{3v}(M)$ (see Table 11-2). The symmetry states of this molecule are essentially the same as for the methyl fluoride molecule (CH_3F) worked out in Problem 1 of the Third Problem List, with the difference that the nitrogen nucleus has a spin of 1 (the corresponding spins of carbon and fluoride are 0 and 1/2, respectively). We therefore have that the internal wave function Φ_{int} can only have the following symmetries

$$\Gamma^+ = A_2 \quad \text{and} \quad \Gamma^- = A_1, \quad (11.7)$$

and that the statistical weights, due to the nuclear spins, associated to the realized symmetry species are

$$\Gamma_{\text{ns}} = 12A_1 \oplus 6E. \quad (11.8)$$

Accordingly, the spin statistical weights for the rovibronic wave functions are given in Table 11-5.

Table 11-5 - Spin statistical weights for the rovibronic wave functions of ammonia without inversion.

NH_3			
Γ_{rve}	$\Gamma_{\text{ns},t}$	Γ_{int}	g_{ns}
A_1	$12A_1$	A_1	12
A_2	$12A_1$	A_2	12
E	$6E$	$\left\{ \begin{matrix} A_1 \\ A_2 \end{matrix} \right\}$	12

Table 11-6 - The realized rotational irreducible representations for NH_3 in the vibronic ground state when treated as a rigid molecule in the vibronic ground state. The $(2J+1)$ degeneracy in m is ignored, and n is an integer.

K	Γ
$0 \begin{cases} J \text{ even} \\ J \text{ odd} \end{cases}$	A_1 A_2
$3n \pm 1$	E
$3n$	$A_1 \oplus A_2$

Furthermore, because $\Gamma(\mu_A) = A_2$ for this MS group it follows that the only transitions allowed for Φ_{int} are of the type

$$A_1 \leftrightarrow A_2. \quad (11.9)$$

This in turn implies that in the totally symmetric vibronic ground state (i.e., $\Gamma_{\text{vib}} = \Gamma_{\text{rot}}$) the only allowed rotational transitions are of the types

$$\begin{aligned} A_1 &\leftrightarrow A_2, & \text{when } \Gamma_{\text{ns}} &= A_1 \\ E &\leftrightarrow E, & \text{when } \Gamma_{\text{ns}} &= E \end{aligned} \quad (11.10)$$

as electric dipole transitions conserve the nuclear spin state. Furthermore, since the realized pure rotational irreducible representations are as given in Table 11-6, the rotational energy levels and allowed electric dipole transitions for $J \leq 3$ are shown in Figure 11-2. All of these transitions have the same statistical weight of 12. The selection rules for pure rotational transitions of symmetric tops (i.e., $\Delta J = \pm 1, \Delta K = 0$) and the corresponding Hamiltonian (equation (4.99)) were also used to make this figure.

If, however, we do allow tunneling of ammonia through inversion, then the two configurations of Figure 11-1 are connected, more permutation and permutation-inversion are feasible, and the MS group becomes $D_{3h}(\text{M})$. Using the corresponding character table (i.e., Table 11-1) we have the only realizable internal wave functions are

$$\Gamma^+ = A_2' \quad \text{and} \quad \Gamma^- = A_2''. \quad (11.11)$$

The statistical weights for this molecule are the same as for H_3^+ given at the end of Chapter 8 (i.e., equation (8.29)) with the exception that the three states of the nitrogen nucleus have to be accounted for. We then have

$$\Gamma_{\text{ns}} = 12A_1' \oplus 6E'. \quad (11.12)$$

The corresponding spin statistical weights for the rovibronic wave functions are as given in Table 11-7.

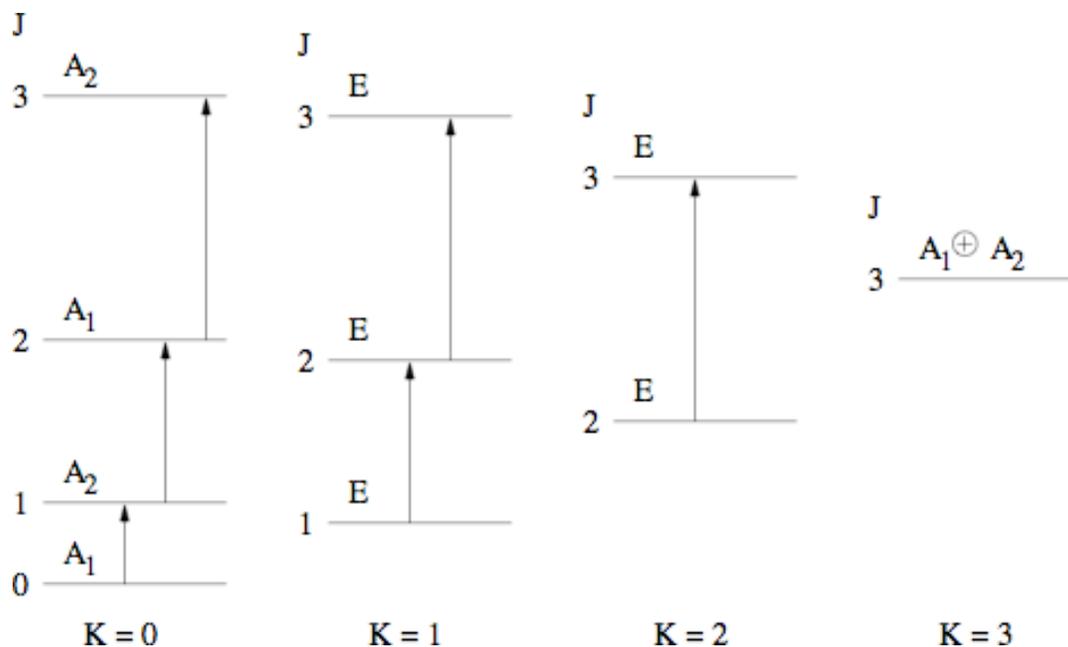


Figure 11-2 – The pure rotational energy levels and allowed electric dipole transitions for $J \leq 3$ when the ammonia molecule is treated as being of the rigid kind. All of these transitions have the same statistical weight of 12.

It is to be noted that because the product

$$\underbrace{E'}_{\Gamma_{rve}} \otimes \underbrace{E'}_{\Gamma_{rve}} = A'_1 \oplus A'_2 \oplus E' \quad (11.13)$$

produces only one of the allowed internal wave function species (i.e., A'_2), then each $\Gamma_{ns} = E'$ contributes a statistical weight of only one even if it contains two nuclear spin functions. The same is true for $E'' \otimes E'$.

Table 11-7 – Spin statistical weights for the rovibronic wave functions of NH_3 when inversion is taken into account. These follow from equation (11.12) and $\Gamma(\mu_A) = A''_1$.

Γ_{rve}	Γ_{ns}	Γ_{int}	g_{ns}
A'_1	—	—	0
A''_1	—	—	0
A'_2	$12A'_1$	A'_2	12
A''_2	$12A'_1$	A''_2	12
E'	$6E'$	A'_2	6
E''	$6E'$	A''_2	6

Considering once again the fact that electric dipole transitions conserve nuclear spin states we find that allowed transitions must obey

$$\begin{aligned}
 A'_2 &\leftrightarrow A''_2, & \text{when } \Gamma_{\text{ns}} = A'_1 \\
 E' &\leftrightarrow E'', & \text{when } \Gamma_{\text{ns}} = E'.
 \end{aligned}
 \tag{11.14}$$

The modifications that must be brought to the rotational energy levels and the allowed electric dipole transitions shown in Figure 11-2 are easily determined by using the reverse correlation table for going from $C_{3v}(\text{M})$ to $D_{3h}(\text{M})$ (i.e., Table 11-4). Indeed, combining this reverse correlation table and Table 11-7 for the statistical weights of the rotational wave functions (we again set ourselves in the vibronic ground state) we find the correlations and statistical weights listed in Table 11-8. We therefore see that the A_1 and A_2 rotational species of $C_{3v}(\text{M})$ do not actually split into $A'_1 \oplus A''_2$ and $A'_2 \oplus A''_1$ of $D_{3h}(\text{M})$, respectively, since A'_1 and A''_1 are not realized (i.e., they have statistical weight of zero). On the other hand, the E species of $C_{3v}(\text{M})$ splits into $E' \oplus E''$ of $D_{3h}(\text{M})$ with equal weights.

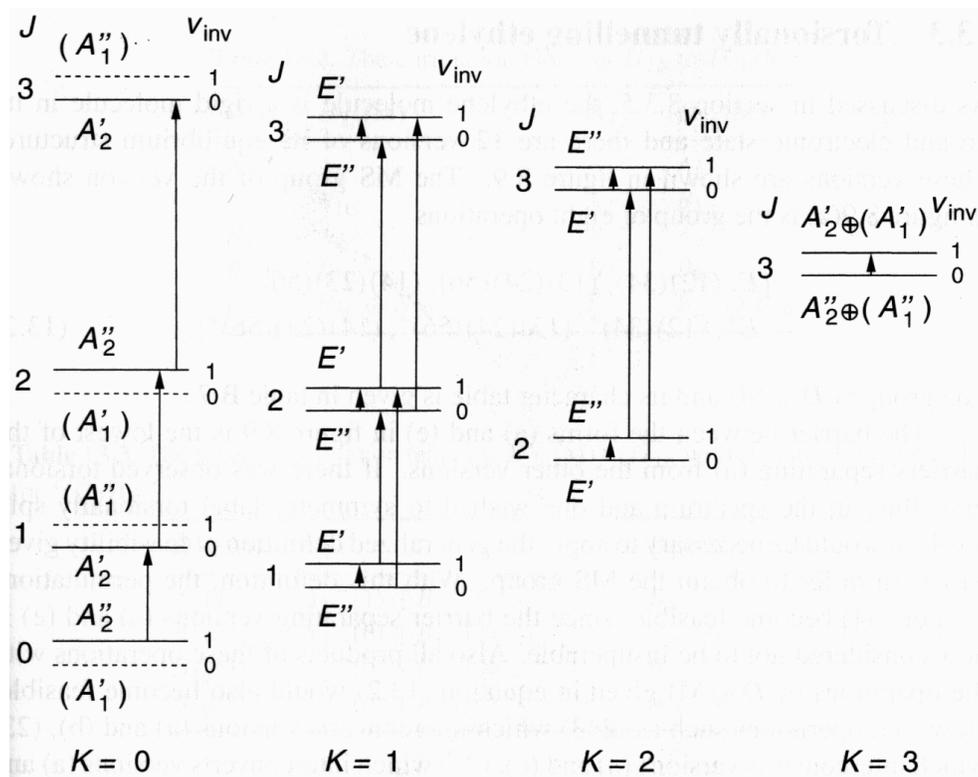


Figure 11-3 - The rotation-inversion energy levels and allowed electric dipole rotation-inversion transitions for $J \leq 3$ and $v_{\text{inv}} = 0$ or 1 of the tunneling ammonia molecule. Missing levels with statistical weights of zero are shown with broken lines and their associated symmetry species in between parentheses. Allowed pure rotational electric dipole transitions are indicated by arrows.

Table 11-8 – The reverse correlation table for ammonia when going from $C_{3v}(\text{M})$ to $D_{3h}(\text{M})$ with the associated statistical weights in parentheses.

$C_{3v}(\text{M})$	$D_{3h}(\text{M})$
$A_1(12)$	$A'_1(0) \oplus A''_2(12)$
$A_2(12)$	$A''_1(0) \oplus A'_2(12)$
$E(12)$	$E'(6) \oplus E''(6)$

These results are presented in Figure 11-3 by displaying the pure rotation-inversion energy levels and allowed electric dipole transitions for $J \leq 3$ of the tunneling ammonia molecule. The inversion splitting of the $C_{3v}(\text{M})$ levels into the $D_{3h}(\text{M})$ levels are labeled with the ν_{inv} ($= 0$ or 1) quantum number. The allowed transitions are indicated by arrows, and follow the aforementioned selection rules for symmetric tops and equations (11.14).

It is important to realize that although group theory allows us to easily investigate the effects of tunneling for this molecule using reverse correlation tables, it does not quantify the splitting of the energy levels or their ordering, nor does it give details as to the introduction of the inversion quantum number ν_{inv} , for example. For this, the rotation-contortion-vibration Hamiltonian H_{rev} must be carefully studied.