12.11: Reducible Representations are Comprised of Irreducible Representations

As we saw in the previous section, the complete motion (translations, rotations, and vibrations) of ammonia (NH_3) can be represented by the following reducible representation:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2

We want to relate the reducible form representation to the irreducible representation. To do this, we use the tabular method. First, create a new table:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2
A_1			
A_2			
E			

We will need the C_{3v} character table for ammonia:

C_{3v}	C_3	C_s
A_1	A	A'
A_2	A	A"
E	E	$A' + A$"

Fill in each number in our table by using the following equation:

$$g_c \chi_i X_r$$

g_e	Number of operations (order) in the class
χ_i	Character of the irreducible representation from the character table
χ_r	Character of the reducible representation from Γ

For example, the top-left value would be:

$$1 \times 1 \times 12 = 12$$

Where:

- 1 is the number of operations in the E class
- 1 is the character of the irreducible representation
- 9 is the character of the reducible representation

The table becomes:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ	12	0	2
A_1	12	0	6

A_2	12	0	-6
E	24	0	0

Sum up each row:

C_{3v}	E	$2C_3$	$3\sigma_v$	$\sum$
Γ	12	0	2	
A_1	12	0	6	18
A_2	12	0	-6	6
E	24	0	0	24

Now divide the summed values by the order of the group to obtain the number of times the irreducible representation appears (n_i). Ammonia has order $h = 6$:

C_{3v}	E	$2C_3$	$3\sigma_v$	$\sum$	$n_i = \frac{\sum}{h}$
Γ	12	0	2		
A_1	12	0	6	18	3
A_2	12	0	-6	6	1
E	24	0	0	24	4

The reducible representation can be broken down to its irreducible forms:

$$\Gamma = 3A_1 + A_2 + 4E$$

Now that we have the irreducible representations for the motion of ammonia, we can determine which are associated with rotations, vibrations, and translations. To start, we turn to the C_{3v} character table:

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(R_x, R_y), (x,y)$	$(xz, yz)\ (x^2-y^2, xy)$

The first column to the right of the characters includes to the terms x, y, z, R_x, R_y, and R_z. The rows with x, y, and z represent the irreducible representations for the translational modes in those directions:

$$\Gamma_{\text{trans}} = A_1 + E$$

The rows with R_x, R_y, and R_z represent the irreducible representations for the rotational modes about those axes:

$$\Gamma_{\text{rot}} = A_2 + E$$

We can subtract the translational and rotational irreducible representations from our \Gamma to get the irreducible representations for the normal vibrational modes:

$$\Gamma_{\text{vib}} = \Gamma - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$$

Doing this, we obtains:

$$\Gamma_{\text{vib}} = 2A_1 + 2E$$