

4.5: Group Theory Considerations

Group theory provides a powerful set of tools for predicting and interpreting vibrational spectra. In this section, we will consider how Group Theory helps us to understand these important phenomena.

Transformation of Axes and Rotations

It is possible to determine the symmetry species or irreducible representation by which each of the three Cartesian coordinate axes transform. This is useful, particularly in determining selection rules in spectroscopy, as the components of a molecule's dipole moment will transform as these axes. The rotations are also useful in understanding the rotational selection rules.

Recall the character table for the C_{2v} point group.

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

It is useful to determine how each axis (x, y and z) is transformed under each symmetry operation. Once this is done, it will be easy to determine the representation that transforms the axis in this way. A table might be useful. Recalling our designation of the σ_v operation as reflection through the xz plane, it can be shown easily that the axes transform as follows:

C_{2v}	E	C_2	σ_v	σ_v'
x	x	-x	x	-x
y	y	-y	-y	y
z	z	z	z	z

The z-axis is unchanged by any of the symmetry operations. Another way of saying this is that the z-axis is symmetric with respect to all of the operations. (In this point group, all of the symmetry elements happen to intersect on the z-axis, which is why it is unchanged by any of the symmetry operations.) The conclusion is that the z-axis transforms with the A_1 representation.

The other axes can be described the same way. Note that the x-axis is symmetric with respect to the σ_v operation and the E operation. (Everything is symmetric with respect to the E operation, oddly enough.) The x-axis is antisymmetric, however, with respect to the σ_v' and C_2 operations. The results for all axes can be summarized in the character table.

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Rotations about the x, y and z axes can be characterized in a similar fashion. Consider the angular momentum vector for each rotation and how it transforms. Such a vector can be constructed using the right-hand rule. If the fingers on your right hand point in the direction of the rotation, your thumb points in the direction of the angular momentum vector.

Rotation about the z-axis (R_z) is symmetric with respect to the operations E and C_2 , but antisymmetric with respect to operations σ_v and σ_v' . Rotation about the x-axis is symmetric with respect to E and C_2 . Clearly, this operation transforms as the irreducible representation A_2 . Rotation about the x-axis and y-axis can also be characterized as following the properties of the B_2 and B_1 representations respectively. As such, the character table for C_{2v} can be augmented to include this information.

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	
A_2	1	1	-1	-1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	y	R_x

Another interpretation of the transformation of the x, y and z-axes is that the representations that indicate the symmetries of these axes in the point group also indicate how the p_x , p_y and p_z orbitals transform. The set of d orbital wavefunctions can also be used. These transformations are generally given in another column in the character table. (This information is also useful for calculating polarizabilities, and hence selection rules for Raman transitions!)

C_{2v}	E	C_2	σ_v	σ_v'			
A_1	1	1	1	1	z		$x^2 - y^2, z^2$
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

Characterizing Vibrational Modes

Vibrational wave functions describing the normal modes of vibrations will be eigenfunctions of the symmetry properties of the group. As such, group theory can be quite useful in determining the vibrational selection rules needed to predict infrared spectra.

The number of vibrational degrees of freedom for a molecule is given by $(3N - 6)$ if the molecule is non-linear and $(3N - 5)$ if it is linear. In these expressions, N is the number of atoms in the molecule. One way to think of these numbers is that it takes 3N Cartesian coordinates (an x, y and z variable) for each atom in the molecule to fully specify the structure of a molecule. As such, 3N is the total number of degrees of freedom.

Since the molecule can translate through space in the x, y or z directions, three (3) degrees of freedom belong to translation. One can also think of these three degrees of freedom being the three Cartesian coordinates needed to specify the location of the center of mass of the molecule – or for the translation of the center of mass of the molecule.

For non-linear molecules, rotation can occur about each of the three Cartesian axes as well. So three (3) degrees of freedom belong to rotation for non-linear molecules. Linear molecules only have rotational degrees of freedom about the two axes that are perpendicular to the molecular axis (which remember is the C axis – and thus the z-axis.) So linear molecules only have two (2) rotational degrees of freedom.

The sum of the irreducible representations by which the vibrational modes transform can be found fairly easily using group theory. The first step is to determine how the three Cartesian axes transform under the symmetry operations of the point group. As an example, let's use water (H_2O), which belongs to the C_{2v} point group since it is familiar. Later, we will work through a more complex example.

Consider the character table for the C_{2v} point group.

C_{2v}	E	C_2	σ_v	σ_v'			
A_1	1	1	1	1	z		$x^2 - y^2, z^2$
A_2	1	1	-1	-1		R_z	xy
B_1	1	-1	1	-1	x	R_y	xz
B_2	1	-1	-1	1	y	R_x	yz

The sum of the representations by which the axes transform will be given by $B_1 + B_2 + A_1$.

C_{2v}		E	C_2	σ_v	σ_v'	
Γ_1	A_1	1	1	1	1	z
Γ_2	B_1	1	-1	1	-1	x
Γ_3	B_2	1	-1	-1	1	y
Γ_{xyz}	$A_1 + B_1 + B_2$	3	-1	1	1	

The reducible representation (Γ_{xyz}) is then multiplied by the representation generated by counting the number of atoms in the molecule that remain unmoved by each symmetry element. This representation for water is generated as follows:

C_{2v}	E	C_2	σ_v	σ_v'
O	✓	✓	✓	✓
H_1	✓	-	-	✓
H_2	✓	-	-	✓
$\Gamma_{unmoved}$	3	1	1	3

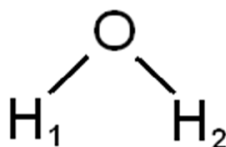


Figure 4.5.1

The reducible representation that describes the transformation of the Cartesian coordinates of each of the atoms in the molecule are given by the product of $\Gamma_{xyz} \cdot \Gamma_{unmoved}$ as shown in the following table.

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{xyz}	3	-1	1	1
$\Gamma_{unmoved}$	3	1	1	3
$\Gamma_{total} = \Gamma_{xyz} \cdot \Gamma_{unmoved}$	9	-1	1	3

Note that the order of Γ_{total} is given by $3N$. This is the sum of representations needed to describe the transformation of each of the Cartesian coordinates for each atom. If the representation for the Cartesian coordinates (Γ_{xyz}) is subtracted from Γ_{total} , the remainder describes the sum of representations by which the rotations and vibrations transform, and this result should be of order $(3N - 3)$. Let's see...

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{total}	9	-1	1	3
Γ_{xyz}	3	-1	1	1
$\Gamma_{vib+rot}$	6	0	0	2

So far, so good. Now let's subtract the sum of the representations by which the rotations transform. The remainder of this operation should be of order $(3N - 6)$ and give the sum of irreducible representations by which the vibrations transform.

C_{2v}	E	C_2	σ_v	σ_v'
$\Gamma_{vib+rot}$	6	0	0	2

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{rot}	3	-1	-1	-1
Γ_{vib}	3	1	1	3

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_1	1	1	1	1
B_2	1	-1	-1	1
Γ_{vib}	3	1	1	3

A quick calculation shows that this result is generated by the sum of $A_1 + A_1 + B_2$. To see this, we can use the Great Orthogonality Theorem. (I told you it was *great*!) In this case, the number of vibrational modes that transform as the i^{th} irreducible representation is given by the relationship

$$N_i = \frac{1}{h} \sum_R \chi_i(R) \chi_{vib}(R)$$

For the A_1 representation, this sum looks as follows.

$$\begin{aligned} N_{A_1} &= \frac{1}{h} (\chi_{A_1}(E) \cdot \chi_{vib}(E) + \chi_{A_1}(C_2) \cdot \chi_{vib}(C_2) + \chi_{A_1}(\sigma_v) \cdot \chi_{vib}(\sigma_v) + \chi_{A_1}(\sigma_v') \cdot \chi_{vib}(\sigma_v')) \\ &= \frac{1}{4} ((1) \cdot (3) + (1) \cdot (1) + (1) \cdot (1) + (1) \cdot (3)) \\ &= \frac{1}{4} (8) \\ &= 2 \end{aligned}$$

The result for the A_2 representation should come to zero since no vibrational modes transform as A_2 . For the A_2 representation, this sum looks as follows.

$$\begin{aligned} N_{A_2} &= \frac{1}{4} ((1) \cdot (3) + (1) \cdot (1) + (-1) \cdot (1) + (-1) \cdot (3)) \\ &= \frac{1}{4} (0) = 0 \end{aligned}$$

For B_1 and B_2 the sum looks as follows:

$$\begin{aligned} N_{B_1} &= \frac{1}{4} ((1) \cdot (3) + (-1) \cdot (1) + (1) \cdot (1) + (-1) \cdot (3)) \\ &= \frac{1}{4} (0) = 0 \\ N_{B_2} &= \frac{1}{4} ((1) \cdot (3) + (-1) \cdot (1) + (-1) \cdot (1) + (1) \cdot (3)) \\ &= \frac{1}{4} (4) = 1 \end{aligned}$$

Let's see if that makes sense! Consider the three normal-mode vibrations in water. These (the symmetric stretch, the bend and the antisymmetric stretch) can be depicted as follows:

It is fairly simple to show that the symmetric stretch and the bending mode both transform as the A_1 representation. Similarly, the antisymmetric stretching mode transforms as the B_2 representation. (Note that we have chosen the xz plane (or the σ_v plane) to lie perpendicular to the molecule!)

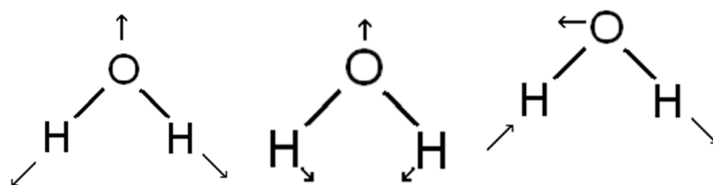


Figure 4.5.2

✓ Example 4.5.1

Find the symmetries of the normal vibrational modes of ammonia.

Solution

Recall the character table for the C_{3v} point group:

C_{3v}	E	$2 C_3$	$3 \sigma_v$		
A_1	1	1	1	z	
A_2	1	1	-1		R_z
E	2	-1	0	x, y	R_x, R_y

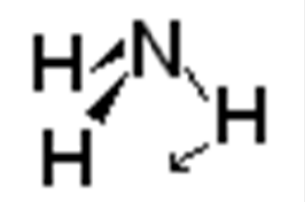
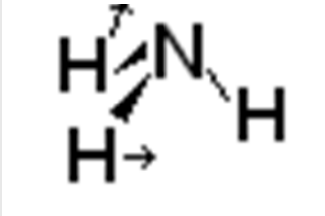
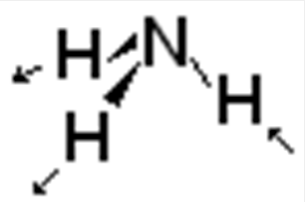
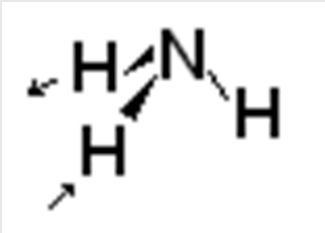
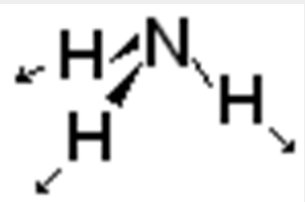
The representation for Γ_{total} can be found in the same way as before. Once we have Γ_{total} , Γ_{vib} is determined as before.

C_{3v}	E	$2 C_3$	$3 \sigma_v$
Γ_{xyz}	3	1	1
$\Gamma_{unmoved}$	4	1	2
Γ_{total}	12	1	2

C_{3v}	E	$2 C_3$	$3 \sigma_v$
Γ_{total}	12	1	2
Γ_{xyz}	3	1	1
Γ_{rot}	3	0	-1
Γ_{vib}	6	0	2

The GOT can be used to find how many modes of each symmetry are present.

Mode	Freq. (cm^{-1})	Sym.
Umbrella	1139	A_1

Mode		Freq. (cm ⁻¹)	Sym.
Bend		1765	E
			
Antisym. Str.		3464	E
			
Sym. Str.		3534	A ₁

$$N_{A_1} = \frac{1}{6}[(1) \cdot (6) + 2(1) \cdot (0) + 3(1) \cdot (2)]$$

$$= \frac{1}{6}(12) = 2$$

$$N_{A_2} = \frac{1}{6}[(1) \cdot (6) + 2(1) \cdot (0) + 3(-1) \cdot (2)]$$

$$= \frac{1}{6}(0) = 0$$

$$N_E = \frac{1}{6}[(2) \cdot (6) + 2(-1) \cdot (0) + 3(0) \cdot (2)]$$

$$= \frac{1}{6}(12) = 2$$

So there are two (2) A₁ modes and two (2) doubly degenerate E modes of vibration. These can be summarized in the table to the right.

✓ Example 4.5.2: The vibrational modes of SF_4

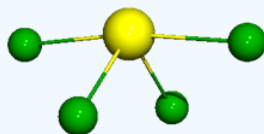


Figure 4.5.3

Solution

SF_4 is an example of a molecule with a “see saw” geometry. It belongs to the point group C_{2v} like water. Let’s find the symmetries of the normal modes of vibration using group theory. First, we must generate Γ_{total} .

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{xyz}	3	-1	1	1
$\Gamma_{unmoved}$	5	1	3	3
Γ_{total}	15	-1	3	3

C_{2v}	E	C_2	σ_v	σ_v'
Γ_{total}	15	-1	3	3
Γ_{xyz}	3	-1	1	1
Γ_{rot}	3	-1	-1	-1
Γ_{vib}	9	1	3	3

Now, subtract Γ_{xyz} and Γ_{rot} to generate Γ_{vib} as shown above.

So this implies that there are nine degrees of freedom due to vibration. This is the result we expect since for the 5-atom non-linear molecule, $(3N-6) = 9$. To generate the number of vibrational modes that transform as the A_1 irreducible representation, the follow expression must be evaluated.

$$\begin{aligned}
 N_{A_1} &= \frac{1}{h} (\chi_{A_1}(E) \cdot \chi_{vib}(E) + \chi_{A_1}(C_2) \cdot \chi_{vib}(C_2) + \chi_{A_1}(\sigma_v) \cdot \chi_{vib}(\sigma_v) + \chi_{A_1}(\sigma_v') \cdot \chi_{vib}(\sigma_v')) \\
 &= \frac{1}{4} ((1) \cdot (9) + (1) \cdot (1) + (1) \cdot (3) + (1) \cdot (3)) \\
 &= \frac{1}{4} (16) \\
 &= 4
 \end{aligned}$$

Similarly,

$$\begin{aligned}
 N_{A_2} &= \frac{1}{4} ((1) \cdot (9) + (1) \cdot (1) + (-1) \cdot (3) + (-1) \cdot (3)) \\
 &= \frac{1}{4} (4) = 1
 \end{aligned}$$

$$\begin{aligned}
 N_{B_1} &= \frac{1}{4} ((1) \cdot (9) + (-1) \cdot (1) + (1) \cdot (3) + (-1) \cdot (3)) \\
 &= \frac{1}{4} (8) = 2
 \end{aligned}$$

$$\begin{aligned}
 N_{B_2} &= \frac{1}{4} ((1) \cdot (9) + (-1) \cdot (1) + (-1) \cdot (3) + (1) \cdot (3)) \\
 &= \frac{1}{4} (8) = 2
 \end{aligned}$$

So there should be 4 vibrational modes of A_1 symmetry, 1 of A_2 symmetry and two each of B_1 and B_2 symmetry. A calculation of the structure and vibrational frequencies in SF_4 at the B3LYP/6-31G(d) level of theory¹ yields the following.

Mode	Freq. (cm ⁻¹)	Symmetry	Mode	Freq. (cm ⁻¹)	Symmetry
1	189	A_1	6	584	A_1
2	330	B_1	7	807	B_2
3	436	A_2	8	852	B_1
4	487	A_1	9	867	A_1
5	496	B_2			

The calculation also allows for the simulation of the infrared spectrum of SF_4 .

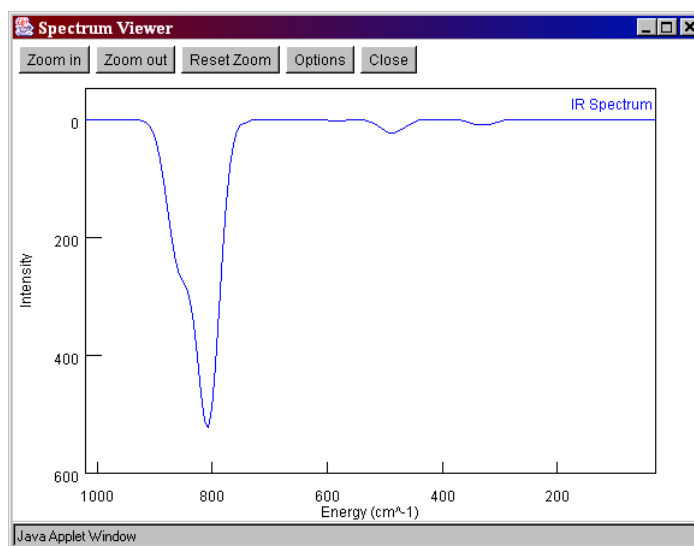


Figure 4.5.4

What would be exceptionally useful is if group theory could help to identify which vibrational modes are active – or if any are inactive. Fortunately, it can! (And *now* how much would you pay?) The tools for determining selection rules depend on direct products.

Intensity

Group theory provides tools to calculate when a spectral transition will have zero intensity, and this will not be seen. In this section, we will see how group theory can help to determine the **selection rules** that govern which transitions can and cannot be seen.

$$\text{Intensity} \propto \left| \int (\psi')^* \vec{\mu} (\psi'') d\tau \right|^2$$

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part $(\psi')^*$, (ψ'') and $\vec{\mu}$. This is helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, let's look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an “odd function” or an “even function.”

Symmetry	definition	Intensity
Even	$f(-x) = f(x)$	$\int_{-a}^a f(x) dx = 2 \int_0^a f(x) dx$

Symmetry	definition	Intensity
Odd	$f(-x) = -f(x)$	$\int_{-a}^a f(x)dx = 0$

Consider the function $f(x) = (x^3 - 3x)e^{-x^2}$. A graph of this function looks as follows:

One notes that the area under the curve on the side of the function for which $x > 0$ has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\begin{aligned}\int_{-a}^a f(x)dx &= \int_{-a}^0 f(x)dx + \int_0^a f(x)dx \\ &= -\int_0^a f(x)dx + \int_0^a f(x)dx = 0\end{aligned}$$

It is also interesting to note that the function $f(x)$ can be expressed as the product of two functions, one of which is an odd function ($x^3 - 3x$) and the other which is an even function (e^{-x^2}). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on x .

$$\hat{i}f(x) = f(-x)$$

“Even” and “odd” functions are eigenfunctions of this operator, and have eigenvalues of either +1 or -1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$$g(x) = x^3 - 3x \text{ and } h(x) = e^{-x^2}$$

Here, $g(x)$ is an odd function and $h(x)$ is an even function. The product is an odd function. This property is summarized for any $f(x) = g(x)h(x)$, in the following table.

$g(x)$	$h(x)$	$f(x)$	$ig(x) = _g(x)$	$ih(x) = _h(x)$	$if(x) = _f(x)$
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or -1) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group C_{2v} as an example. Recall the character table for this point group.

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	y	R_x

The direct product of irreducible representations can be defined by the definition

$$\chi_{prod}(R) = \chi_i(R) \cdot \chi_j(R)$$

So for the direct product of B_1 and B_2 , the following table can be used.

C_{2v}	E	C_2	σ_v	σ_v'
B_1	1	-1	1	-1
B_2	1	-1	-1	1
$B_1 \otimes B_2$	1	1	-1	-1

The product is actually the irreducible representation given by A_2 ! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C_{2v} point group) is given below.

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B				1	2
A	A	B				1	2
B	B	A				2	1

This pattern might seem obvious to some. It stems from the idea that

$$\text{symmetric} * \text{symmetric} = \text{symmetric}$$

$$\text{symmetric} * \text{antisymmetric} = \text{antisymmetric}$$

$$\text{antisymmetric} * \text{antisymmetric} = \text{symmetric}$$

Noting that A indicates an irreducible representation is *symmetric* with respect to the C_2 operation and B indicates that the irreducible representation is *antisymmetric* . . and that the subscript 1 indicates that an irreducible representation is *symmetric* with respect to the σ_v operation, and that a subscript 2 indicates that the irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (i) operator, and the prime/double prime indicates symmetry with respect to a σ plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C_{3v} point group.

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

C_{3v}	E	$2 C_3$	$3 \sigma_v$		
$A_2 \otimes E$	2	-1	0		

Consider the direct product of A_2 and E.

This product is clearly just the E representation. Now one other example – Consider the product $E \otimes E$.

C_{3v}	E	$2 C_3$	$3 \sigma_v$
E	2	-1	0
E	2	-1	0
$E \otimes E$	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$\begin{aligned}
 N_{A_1} &= \frac{1}{6} [(1)(4) + 2(1)(1) + 3(1)(0)] = 1 \\
 N_{A_2} &= \frac{1}{6} [(1)(4) + 2(1)(1) + 3(-1)(0)] = 1 \\
 N_E &= \frac{1}{6} [(2)(4) + 2(-1)(1) + 3(0)(0)] = 1
 \end{aligned}$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

Now that we have a handle on direct products, we can move on to selection rules.

Selection Rules

According to quantum mechanics, transitions will only be allowed (have non-zero intensity) if the squared magnitude of the transition moment ($|\int \psi' * \vec{\mu} \psi \, d\tau|^2$) is not zero. If the integral vanishes by symmetry, obviously the transition moment will have zero magnitude and the transition is **forbidden** and will not be seen. In order to determine if the integral vanishes by symmetry, it is necessary to determine the symmetry by which the dipole moment operator transforms.

This ($\vec{\mu}$) is a vector operator and can be decomposed into x , y and z components. As such, the transition moment is also a vector property that can have x -, y - and/or z -axis components. Clearly, it will be important to determine how the three axes transform. Fortunately, this information is contained in character tables! Consider the following two point groups, C_{3v} and C_{2v} .

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

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1		R_z
B_1	1	-1	1	-1	x	R_y
B_2	1	-1	-1	1	y	R_x

In the case of C_{2v} , it is clear that the x-, y- and z-axes transform as the B_1 , B_2 and A_1 irreducible representations respectively. In the case of C_{3v} , the z-axis transforms as A_1 , but the x- and y-axes come as a pair and transform as the E irreducible representation. It will always require two axes to complete the basis for a doubly degenerate representation.

Under the C_{2v} point group, any vector quantity will transform as the sum of $A_1 + B_1 + B_2$ as we saw for Γ_{xyz} before. Further, one can say that the x-axis component transforms as B_1 , the y-axis component as B_2 and the z-axis component as A_1 . By a similar token, under the C_{3v} point group, a vector quantity transforms as the sum of $A_1 + E$. The z-axis component transforms as A_1 and the x- and y-axis components come as a pair that transform by the E representation. All that is needed to complete the picture is to determine the symmetries of the upper and lower state wave functions.

Infrared Active Transitions

In order for a spectral transition to be allowed by electric dipole selection rules, the transition moment integral must not vanish.

$$\int \psi'^* \vec{\mu} \psi'' d\tau$$

This can be determined by using the irreducible representations by which the two wavefunctions transform and the three components of the transition moment operator, which will be x, y and z.

$$\int \Gamma_{\psi'} \Gamma_{\vec{\mu}} \Gamma_{\psi''} d\tau$$

If the direct product of the integrand does not contain at least a component of the totally symmetric irreducible representation, the integral will vanish by symmetry.

✓ Example 4.5.3

The three vibrational modes of H_2O transform by A_1 (symmetric stretch), A_1 (bend) and B_2 (antisymmetric stretch.) Will the symmetric stretch mode be infrared active?

Solution

For the symmetric stretch, which transforms as A_1 , the transition moment integrand will be have symmetry properties determined by the product

$$\psi' \begin{pmatrix} x \\ y \\ z \end{pmatrix} \psi'' \quad A_1 \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} A_1$$

where one of the irreducible representations from the set in the middle of the product may be used. (They are the irreducible representations by which the x, y and z axes transform.) In this case, the z-axis must be used.

$$A_1 \cdot A_1 \cdot A_1 = A_1$$

This is the only component that will not vanish. When the z-axis component must be used to make the transition moment operator not vanish, the transition is said to be a parallel transition. Transition moments that lie along axis perpendicular to the z-axis are said to be perpendicular transitions. Parallel and Perpendicular Transitions often have very different selection rules and thus very different band contours.

Another Method

Another method that can be used to see if a mode is infrared active is to take the direct product of the irreducible representations of the wavefunction, and use Γ_{xyz} for the transition moment. If the resulting product has a component that is totally symmetric, the

mode will be infrared active.

✓ Example 4.5.4

Is the antisymmetric stretch mode of water predicted to be infrared active?

Solution

This mode transforms as the B_2 irreducible representation. Γ_{xyz} is given by

$$\Gamma_{xyz} = B_1 + B_2 + A_1$$

So:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
B_2	1	-1	-1	1
Γ_{xyz}	3	-1	1	1
Γ_{prod}	3	1	-1	1

The resulting reducible representation will have a component of the totally symmetric irreducible representation.

$$A_1 \cdot \Gamma_{prod} = (1)(3) + (1)(1) + (1)(-1) + (1)(1) = 4$$

So the A_1 irreducible representation appears once in the product reducible representation. In fact, the component that does not vanish is due to the presence of B_2 in Γ_{xyz} . Hence, the transition is predicted to be a perpendicular \perp transition, since the transition moment lies along the y-axis.

✓ Example 4.5.5

Will the E modes in NH_3 be infrared active?

Solution

In the C_{3v} point group, Γ_{xyz} is given by $A_1 + E$

C_{3v}	E	$2 C_3$	$3 \sigma_v$
E	2	-1	0
Γ_{xyz}	3	0	1
Γ_{prod}	6	0	0

Γ_{prod} clearly has the totally symmetric irreducible representation as a component.

$$A_1 \cdot \Gamma_{prod} = (1)(6) + 2(1)(0) + 3(1)(0) = 6$$

In fact, it is the E component of Γ_{xyz} that makes this transition allowed (and so it is a perpendicular (\perp) transition.

C_{3v}	E	$2 C_3$	$3 \sigma_v$
E	2	-1	0
E	2	-1	0
Γ_{prod}	4	1	0

$$A_1 \cdot \Gamma_{prod} = (1)(4) + 2(1)(1) + 3(1)(0) = 6$$

Vibrational Raman Spectra

Vibrational Raman spectroscopy is often used as a complementary R_y method to infrared spectroscopy. The selection rules for Raman spectroscopy can be determined in much the same way, except that a polarizability integral must be used. The polarizability operator can be expressed as a 3x3 tensor of the form

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

This tensor is symmetric along the diagonal, and the elements transform in the same ways as the functions x^2, y^2, z^2, xy, xz and yz .

✓ Example 4.5.6

What are the vibrational mode symmetries for the molecule H_2CCH_2 which transforms as the D_{2h} point group? Which modes will be infrared active? Which will be Raman active?

Solution

Set up the vibrational analysis table in the usual manner.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1		
Γ_{rot}	3	-1	-1	-1	3	-1	-1	-1		

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1	
Γ_{unm}	6	0	0	2	0	6	2	0	
Γ_{tot}	18	0	0	-2	0	6	2	0	
Γ_{xyz}	3	-1	-1	-1	-3	1	1	1	
	15	1	1	-1	3	5	1	-1	
Γ_{rot}	3	-1	-1	-1	3	-1	-1	-1	
Γ_{vib}	12	2	2	0	0	6	2	0	

Decomposing to the individual components:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	sum	#(h)
$A_g \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(1)(0)	(1)(6)	(1)(2)	(1)(0)	24	3

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}	sum	#(h)
$B_{1g} \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(1)(0)	(1)(6)	(-1)(2)	(-1)(0)	16	2
$B_{2g} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(1)(0)	(-1)(6)	(1)(2)	(-1)(0)	8	1
$B_{3g} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(1)(0)	(-1)(6)	(-1)(2)	(1)(0)	0	0
$A_u \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(-1)(0)	(-1)(6)	(-1)(2)	(-1)(0)	8	1
$B_{1u} \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(-1)(0)	(-1)(6)	(1)(2)	(1)(0)	8	1
$B_{2u} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(-1)(0)	(1)(6)	(-1)(2)	(1)(0)	16	2
$B_{3u} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(-1)(0)	(1)(6)	(1)(2)	(-1)(0)	16	2

So

$$\Gamma_{vib} = 3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$

Of these, the 6 gerade modes will be Raman active, and the five B_{nu} modes ($n = 1, 2, 3$) will be infrared active. The A_u mode will be dark.

1. Calculation performed using Gaussian 98 (<http://www.gaussian.com/>) using the WebMO (<http://www.webmo.net/>) web-based interface.

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