Applications of Representation Theory to Vibrational Spectroscopy

Aaron Taylor

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Contents

Introduction

In 1996 the Nobel Prize in Chemistry was awarded to Curl, Kroto and Smalley for their discovery of buckminsterfullerene, named after the geodesic domes of architect Buckminster Fuller. These molecules, denoted C_{60} or simply "buckyballs", were the first new allotropes of carbon to be discovered since graphite and diamond. Since its discovery, research into fullerenes has generated an enormous number of new structures such as carbon nanotubes, now used in diverse applications.

Although the chemical composition, C_{60}, was known at the time of discovery on the basis of mass spectrometry, the molecular structure remained unknown. Graphite sheets, from which the new compound was formed by laser ablation, should be highly unstable due to the number of dangling bonds with unpaired electrons at the edge. And yet, the new compound was highly stable, suggesting strong molecular symmetry. It follows from Euler's formula for a convex polyhedron,

$$V - E + F = 2$$

where V, E and F are the number of vertices, edges and faces, that for a convex polyhedron comprised of pentagonal and hexagon pieces, both chemically stable shapes, the structure must have 12 pentagons and $V/2 - 10$ hexagons. In the case of C_{60}, this results in 12 pentagons and 20 hexagons, or the shape of a soccerball as seen in Figure 1.
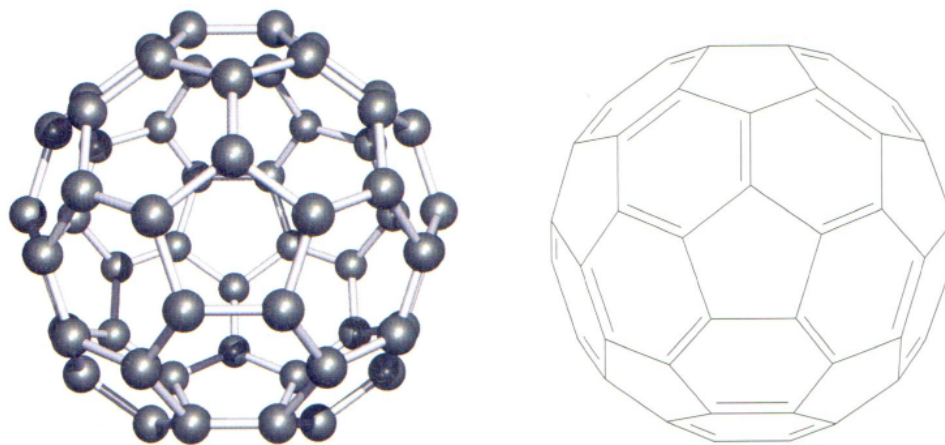

Figure 1. Two structural representations of the fullerene C_{60}. Source: [Housecroft and Sharpe, 2008]

Experimental confirmation of this structure requires testable predictions and it is here that the mathematical theory of groups makes an appearance. The structure shown in Figure 1 belongs to the truncated icosahedron symmetry group or I_h. By applying tools from representation theory, researchers were able to predict the number of spectral lines for various possible structures. After obtaining an experimental spectrum only the structure in Figure 1 was a match.

This paper will develop the mathematical ideas necessary to understand what was done in the buckyball experiment. Due to the large number of symmetry elements in the I_h group we

will instead work with a simple water molecule, or H_2O. A full treatment of the buckyball can be found in [Sternberg, 1994] pages 126–129.

Symmetry Elements and Operations

When considering molecular symmetry, only four categories of symmetry elements and operations need be examined. These categories are presented in Table 1.

Table 1. The four kinds of symmetry elements and operations required to specify molecular symmetry. Source: [Cotton, 1990]

Symmetry Element	Symmetry Operation
Plane	Reflection in the plane
Inversion center	Inversion of all atoms through the center
Proper axis	One or more rotations about the axis
Improper axis	One or more repetitions of the sequence: rotation followed by reflection in a plane perpendicular to the rotation axis

We will restrict ourselves to a superficial treatment of molecular symmetry classification; a full treatment can be found in any inorganic chemistry textbook. Our ongoing example will be the water molecule, H_2O, shown in Figure 2 along with its symmetry elements.
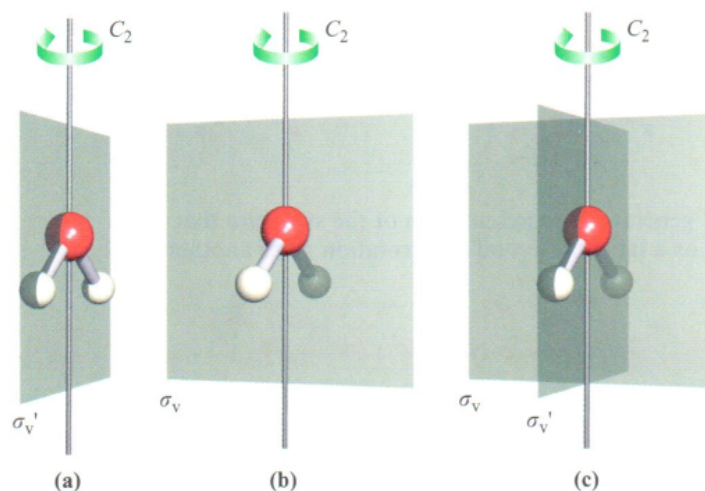

Figure 2. The H_2O molecule possesses one C_2 axis and two mirror planes. (a) The C_2 axis and mirror plane containing the H_2O molecule. (b) The C_2 axis and mirror plane perpendicular to the plane of the molecule. (c) Combination view of all symmetry elements in the H_2O molecule. Source: [Housecroft and Sharpe, 2008]

Proper Axes and Proper Rotations

If rotation of the molecule about an axis passing through the center of the molecule produces an indistinguishable configuration the molecule is said to have a *proper rotation axis*. The symmetry operation involves rotation about an n-fold axis, denoted by the symbol C_n, in which the angle of rotation is $360°/n$ for n a positive integer. In H_2O, Figure 2, we find a single 2-fold proper rotation axis C_2 where rotation by $360°/2 = 180°$ switches the position of the two hydrogen atoms. As this is the axis of highest n, we call it the *principal axis* and consider it the z or vertical axis.

Symmetry Planes and Reflections

If reflection of all parts of a molecule through a plane produces an indistinguishable configuration, then the plane is a *plane of symmetry*; the symmetry operation is reflection through the plane and the symmetry element is the mirror plane, denoted σ. The water molecule contains two mirror planes, one in the plane of the molecule and one perpendicular to it. As both planes contain the principal (or vertical) axis we denote them as σ_v and σ_v'.

Inversion Center

If reflection of all parts of the molecule through the center of the molecule results in an indistinguishable configuration the molecule is said to have an *inversion center*, denoted i. Water has no such symmetry element but the buckyball, Figure 1, does.

Improper Axes and Improper Rotations

If rotation of the molecule about an axis passing through the center followed by reflection through a plane perpendicular to that axis produces an indistinguishable configuration the molecule is said to have an *improper rotation axis*, denoted by the symbol S_n. This can be difficult to spot and again does not appear in water but is present in the buckyball in the form of an S_{10} symmetry element.

Point Groups

Once all symmetry elements have been identified, the corresponding *point group*, or mathematical group of symmetries, can be identified. With symmetry operations considered as functions the group operation is function composition. Although we have not explicitly listed it above, every molecule has a corresponding identity symmetry operation, or E, which fixes all points.

All of the three dimensional point groups are subgroups of the previously encountered[1] orthogonal group $O(3)$. Recall that $O(3)$ is a subgroup of $GL_3(\mathbb{R})$ consisting of the set of orthogonal, 3×3 matrices, or those matrices satisfying $A^{-1} = A^t$. Geometrically, these are matrices which preserve the length of vectors.

We will not dwell on identification of point groups since the process follows a trivial but tedious process as shown in Appendix A, Figure 6. For our example, H_2O, we note from

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[1]The definition and properties of $O(n)$ are explored in [Judson, 2013] pages 167–173.

Figure 2 that the symmetry elements are E, C_2, σ_v, σ_v'. Following the flowchart in Figure 6 we find that the corresponding point group is C_{2v}.

Representations

A representation of the type of groups we shall concern ourselves with is a set of matrices in one-to-one correspondence with the elements of the group such that the result of any combination of group elements parallels the corresponding matrix operations. Thus, if three group elements $\gamma_1, \gamma_2, \gamma_3$ in a group G are related such that $\gamma_1 \gamma_2 = \gamma_3$, and the corresponding matrix for a group element γ_i is g_i, then $g_1 g_2 = g_3$.

Recall that $GL_n(\mathbb{F})$, or the general linear group, is the set of invertible $n \times n$ matrices with entries in $\mathbb{F}$. Given a vector space V there is a similar group $GL(V)$ or $\text{Aut}(V)$ defined as the group of all automorphisms of V, i.e. the set of all bijective linear transformations $V \to V$, with function composition as the group operation. If V has finite dimension n, which for our purposes will always be true, then $GL_n(\mathbb{F})$ is isomorphic to $GL(V)$ and the group $GL(V)$ becomes the group of invertible $n \times n$ matrices.

Let G be a finite group with identity 1 and group operation $(s, t) \mapsto st$. A *linear representation* of G in V is a homomorphism ρ from the group G into the group $GL(V)$. Since group homomorphisms must respect the group operation, for any elements $s, t \in G$,

$$\rho(st) = \rho(s)\rho(t).$$

If follows that

$$\rho(1) = 1 \qquad \text{and} \qquad \rho(s^{-1}) = \rho(s)^{-1}.$$

We will sometimes write $\rho(s)$ as ρ_s.

Suppose that V has finite dimension n; we say that n is the degree of the constructed representation. After choosing a basis for V let R_s be the matrix of ρ_s with respect to this basis. We have

$$\det(R_s) \neq 0 \qquad \text{and} \qquad R_{st} = R_s R_t \qquad \forall s, t \in G.$$

Conversely, given invertible matrices satisfying the preceeding identities, there exists a corresponding linear representation ρ of G in V. This is what it means to give a representation "in matrix form".

As an example, let us work out an explicit representation for C_{2v}, the point group of our example water molecule. We have already established that this group consists of the four elements E, C_2, σ_v, and σ_v'. The tradition is to set the z-axis of our Cartesian coordinate system along the principal axis, C_2 in this case. Additionally, let σ_v be the xz plane and σ_v' be the yz plane. Then the matrices representing the effects of each symmetry operation on a given point are as follows:

$$E : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad\qquad C_2 : \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v(xz) : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad\qquad \sigma_v'(yz) : \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The Cayley table for the C_{2v} group follows as Table 2 and it can be easily shown that the matrices constructed above multiply together in a fashion which respects the composition of symmetry operations detailed below.

Table 2. Cayley table for the group C_{2v}.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

This naturally leads us to wonder if the above representation is unique. Consider that if we assigned three small unit vectors directed along the x, y, and z axes to each of the atoms in H_2O and wrote down the corresponding matrices for each symmetry operation we would have a set of four 9×9 matrices constituting the representation of the group. We could construct a third representation by considering the minimum amount of information necessary to completely describe our representation. It appears that assigning 1 or -1 to to each operation as shown in Table 3, where the operation is component-wise multiplication, both satisfies the Cayley table

Table 3. Alternate representation of C_{2v}.

E	C_2	σ_v	σ_v'
1	1	1	1
1	1	-1	-1
1	-1	1	-1
1	-1	-1	1

and is minimal relative to the 3×3 and 9×9 representations. Clearly then our representation is not unique and the number of representations is limited only by our imagination. This motivates the following definition.

Let ρ and ρ' be two representations of the same group G in vector spaces V and V'. These representations are said to be *similar* (or *isomorphic*) if there exists a linear isomorphism τ :

$V \to V'$ which satisfies the identity

$$\rho'_s = \tau \circ \rho_s \circ \tau^{-1} \qquad \forall s \in G.$$

When ρ and ρ' are given in matrix form by R_s and R'_s respectively, this definition is equivalent to saying there exists an invertible matrix T such that

$$R'_s = T R_s T^{-1} \qquad \forall s \in G.$$

Recall that this is precisely the definition of matrix similarity in linear algebra, corresponding to the idea that similar matrices represent the same linear operator under two different bases, with T being the change of basis matrix. This defines an equivalence relation which partitions the set of representations of a group G into conjugacy classes.

For any group, only a limited number of representations are of fundamental significance. Recall from linear algebra that, given two subspaces U and W of a vector space V, we say that V is a *direct sum* of U and W, written $V = U \oplus W$, if $V = U + W$ and $U \cap W = \emptyset$.

Let $\rho : G \to GL(V)$ be a linear representation of G. We say ρ is *irreducible* if V is not the direct sum of two representations (except for the trivial decomposition $V = 0 \oplus V$). If ρ is not irreducible then we say it is *reducible*.

Since we concern ourselves only with finite groups over the complex numbers, a reducible representation will always decompose into the direct sum of irreducible representations.[2] Hence, a representation of degree 1 is always irreducible.

We can ask if this decomposition is unique, or if two irreducible representations can be in the same conjugacy class. Although the answer may not be immediately obvious, [Serre, 1977] points out that, in the trivial case where all the ρ_s are equal to 1, which we have already seen in the top line of Table 3, the vector subspaces of V are all lines and we have a multitude of decompositions of a vector space into a direct sum of lines.

Character

Since even irreducible representations are not invariant under similarity transformations, it would be useful to have a classification for representations which is invariant in this manner. Since we can always express a representation in matrix form, and since the trace of a matrix, given as the sum of its diagonal elements, is invariant under similarity tranformations, we are motivated to the following definition.

Let $\rho : G \to GL(V)$ be a representation of a finite group G in the vector space V. For each $s \in G$ let

$$\chi_\rho(s) = \text{Tr}(\rho_s).$$

The complex valued function χ_ρ on G is called the *character* of the representation ρ.

Theorem 1. If χ is the character of a representation ρ of degree n, then the following properties are derived from the properties of the trace:

(i) $\chi(1) = n$

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[2]Maschkeś theorem provides a more complete description for determining when a representation is completely reducible. http://en.wikipedia.org/wiki/Maschke%27s_theorem.

(ii) $\chi(s^{-1}) = \chi(s)^*$ $\quad\quad \forall s, t \in G$

(iii) $\chi(tst^{-1}) = \chi(s)$ $\quad\quad \forall s, t \in G$

We see that character is a function which is constant on conjugacy classes; if two representations are similar, they will have identical character. Thus the set of *irreducible characters*, corresponding to the irreducible representations, allows us to fully classify an arbitrary representation.

Results

The Great Orthogonality Theorem

The important properties of representations and their character can be derived from one important theorem concerning the elements of the matrix form for the irreducible representations of the group.

Theorem 2 (The Great Orthogonality Theorem)**.** For a group G of order h let the dimension of the ith representation be denoted l_i. Denote the various operations in the group by R and the element in the mth row and nth column of the matrix corresponding to the operation R in the ith irreducible representation by $\Gamma_i(R)_{mn}$. Then,

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

We will not prove this theorem as it is a non-trivial proof; the full proof can be found in [Eyring et al., 1944] page 371. However, we can interpret the theorem as meaning that, in the set of matrices comprising any single irreducible representation, any set of corresponding matrix elements, one from each matrix, behaves as the components of a vector in h-dimensional space such that all these vectors are mutually orthogonal and each is normalized so the square of its length is h/l_i.

Four Important Rules

In our application of representation theory to chemistry the following four theorems are of prime importance.

Theorem 3. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, that is,

$$\sum l_i^2 = h.$$

Proof. [Cotton, 1990] A complete proof is quite lengthy[3] and will not be given; instead we will give the spirit of the proof by showing that $\sum l_i^2 \leq h$.

In a square matrix of order l there are l^2 elements. Thus each irreducible representation Γ_i will provide l_i^2 h-dimensional vectors (recall the four 3×3 and four 9×9 matrix representations previously mentioned for C_{2v}). By Theorem 2 these vectors must be orthogonal. Since there can be no more than h orthogonal h-dimensional vectors, the sum $\sum l_i^2$ must not exceed h. $\quad\square$

Theorem 4. The sum of the squares of the characters in any irreducible representation is equal to the order of the group, that is,

$$\sum_R [\chi_i(R)]^2 = h.$$

Proof. [Serre, 1977] From Theorem 2 we may write

$$\sum_R \Gamma_i(R)_{mm}\Gamma_i(R)_{m'm'} = \frac{h}{l_i}\delta_{mm'}.$$

Summing the left side over m and m', we obtain

$$\sum_{m'}\sum_{m}\sum_{R} \Gamma_i(R)_{mm}\Gamma_i(R)_{m'm'} = \sum_R \left[\sum_m \Gamma_i(R)_{mm} \sum_{m'} \Gamma_i(R)_{m'm'}\right]$$
$$= \sum_R \chi_i(R)\chi_i(R)$$
$$= \sum_R [\chi_i(R)]^2$$

while summing the right side over m and m', we obtain

$$\frac{h}{l_i}\sum_{m'}\sum_{m}\delta_{mm'} = \frac{h}{l_i}l_i = h.$$

thus proving the desired equality. $\square$

Theorem 5. The vectors whose components are the characters of two irreducible representations are orthogonal, that is,

$$\sum_R \chi_i(R)\chi_j(R) = 0 \qquad \text{when} \qquad i \neq j.$$

Proof. [Cotton, 1990] From Theorem 2, setting $m = n$, we know

$$\sum_R \Gamma_i(R)_{mm}\Gamma_j(R)_{mm} = 0.$$

Using this result in the following chain of equalities we see that

$$\sum_R \chi_i(R)\chi_j(R) = \sum_R \left[\sum_m \Gamma_i(R)_{mm}\Gamma_j(R)_{mm}\right]$$
$$= \sum_m \left[\sum_R \Gamma_i(R)_{mm}\Gamma_j(R)_{mm}\right]$$
$$= 0.$$

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[3]A complete proof can be found in [Serre, 1977], page 18 but requires tracking through a number of other theorems which we have not proven.

□

Theorem 6. The number of irreducible representations of a group is equal to the number of equivalence classes in the group.

Proof. [Cotton, 1990] As for Theorem 3, a complete proof will not be given. We can, however, easily prove that the number of equivalence classes sets an upper limit on the number of irreducible representations. We can combine Theorem 4 and Theorem 5 to state that

$$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}.$$

If we now denote the number of elements in the pth equivalence class by g_p, and if there are k classes altogether, we can restate this as

$$\sum_{p=1}^{k} \chi_i(R_p)\chi_j(R_p)g_p = h\delta_{ij}.$$

where R_p refers to any one of the operations in the pth class. This implies that the k quantities $\chi_l(R_p)$, in each representation Γ_l behave like the components of a k-dimensional vector and that these k vectors are mutually orthogonal. Since only k k-dimensional vectors can be mutually orthogonal, there can be no more than k irreducible representations in a group which has k classes. □

Application

Let us now consider the irreducible representations of our example group, C_{2v}, to see how these four theorems apply. We already know each of the four elements in C_{2v} are in a separate class. Hence, by Theorem 6, there are four irreducible representations for this group. But, by Theorem 3, the sum of the squares of the dimensions of these representations equals h. Thus we seek a set of four positive integers l_i satisfying

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 = 4.$$

Clearly the only solution is

$$l_1 = l_2 = l_3 = l_4 = 1.$$

Thus the group C_{2v} has four one-dimensional irreducible representations.

We can work out the character for each of these irreducible representations based on their vector properties and our theorems. One suitable vector in 4-space with a component of 1 corresponding to E will obviously be

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1

since

$$\sum_R [\chi_1(R)]^2 = 4$$

thereby satifying Theorem 4. All the other representations must also satisfy Theorem 4. Thus,

$$\sum_R [\chi_i(R)]^2 = 4$$

which can only be true if $\chi_i(R) = \pm 1$. Since all four irreducible representations must also be orthogonal in order to satisfy Theorem 5, we find that two elements of each representation must be $+1$ and two must be -1. Therefore the full set of irreducible representations for C_{2v} is

	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1

This result is quite similar to Table 3 which we constructed by considering the minimal amount of information necessary to completely represent the underlying group; how interesting.

Character Tables

Most applications of group theory to molecular symmetry will involve the use of *character tables*. A sample character table[4] for the group C_{2v} can be seen in Table 4, represented exactly as it would appear in a reference text.

Table 4. Character table for the group C_{2v}.

	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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
I		II			III	IV

Area I

Until now we have designated representations with the notation Γ_i. Virtually all books and papers use Mulliken symbols,[5] as shown in Table 4.

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[4] A complete set of character tables for the symmetry groups relevant to real molecules can be found at http://www.webqc.org/symmetry.php.

[5] A summary of Mulliken symbols may be found at http://mathworld.wolfram.com/MullikenSymbols.html.

Area II

Here are the characters of the irreducible representations of the group. These were developed in detail in the previous section and require no additional comment.

Area III

This area consists of the symbols corresponding to the coordinates x, y, and z, as well as the rotations with subscript indicating the corresponding axis. For the group C_{2v} recall the previously developed matrix forms, reproduced below.

$$E : \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad\qquad C_2 : \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v(xz) : \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad\qquad \sigma'_v(yz) : \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Consider the action of each on the vector $\mathbf{v}^T = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix}$, corresponding to the x axis. We find that

$$E\mathbf{v} = \mathbf{v},$$
$$C_2\mathbf{v} = -\mathbf{v},$$
$$\sigma_v(xz)\mathbf{v} = \mathbf{v}, \qquad \text{and}$$
$$\sigma'_v(yz)\mathbf{v} = -\mathbf{v}.$$

Thus, we assign the x coordinate to the B_1 representation. A similar process holds for assignment of the y and z axes.

The transformation properties of rotations can be more complex, but a full treatment is unnecessary for C_{2v}. We proceed geometrically, visualizing a curved arrow about an axis standing for rotation. Given such an arrow around the x axis, we find it is unchanged by E and $\sigma'_v(yz)$ but the direction of the arrow is reversed by C_2 and $\sigma_v(xz)$. Thus we assign the R_x rotation to the B_2 representation. A similar process holds for assignment of the R_y and R_z rotations.

Note that is it possible, both in this section and the next, that certain terms will fail to correspond to any irreducible representation. In such an event, they will not appear in the character table.

Area IV

In this part of the table are listed the quadratic coordinate terms. Assignment of these terms to the correct representation follows the same process as the linear terms in III except that the amount of algebra generally increases. However, that is not always the case. For example, since z goes into itself under all symmetry operations, so does z^2, with corresponding assignment to the A_1 representation. From the Cayley table, shown in Table 2, we see that every group

element is its own inverse. Thus the x^2 and y^2 functions are also unchanged and correspond to the A_1 representation.

Vibrational Spectroscopy

The motion of a molecule containing n atoms can be conveniently described in terms of the Cartesian axes; the molecule has $3n$ degrees of freedom which collectively describe the translational, rotational, and vibrational motions of the molecule. As the molecule must have three degrees of translational and three degrees of rotational freedom, the number of vibrational degrees of freedom must be $3n - 6$. In the case of water we find three vibrational degrees of freedom.

Since water is such a simple molecule we can immediately visualize the three vibrational modes, shown in Figure 3. In more complicated molecules this is rarely the case; one must
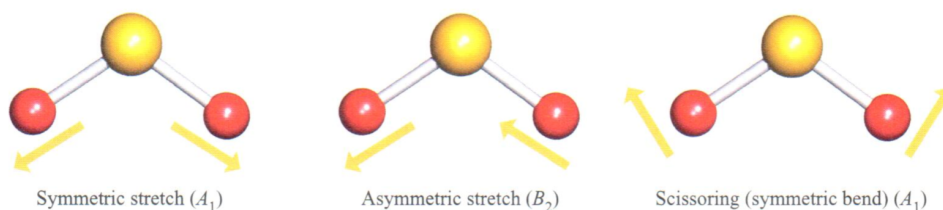

Symmetric stretch (A_1)   Asymmetric stretch (B_2)   Scissoring (symmetric bend) (A_1)

Figure 3. The vibrational modes of H_2O. Source: [Housecroft and Sharpe, 2008]

proceed via purely group theoretic means. For example, consider only the stretching of O–H bonds in the water molecule, without respect to direction, under the symmetry operations of C_{2v}. Ask the question: how many bonds are left unchanged under each operation? The E and σ'_v operations leave two bonds unchanged. However, the C_2 and σ_v operations leave zero bonds unchanged. Thus, stretching of the O–H bonds can be expressed as the representation

	E	C_2	σ_v	σ'_v
Γ_R	2	0	0	2

which, since it does not match any of the irreducible representations of C_{2v}, must decompose into a direct sum of irreducible representations. We can row reduce to find these irreducible representations.

$$
\begin{bmatrix}
1 & 1 & 1 & 1 & 2 \\
1 & 1 & -1 & -1 & 0 \\
1 & -1 & 1 & -1 & 0 \\
1 & -1 & -1 & 1 & 2
\end{bmatrix}
\xrightarrow{\text{RREF}}
\begin{bmatrix}
1 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 1
\end{bmatrix}
$$

This tells us that there are two non-degenerate (orthogonal) stretching modes, one of A_1 symmetry and one of B_2 symmetry. This identifies the symmetric and asymmetric stretch shown in Figure 3, (a) and (b). To identify each mode with its corresponding irreducible representation, again consider the effect of each symmetry operation on the stretch of O–H bonds, but this time

consider with respect to direction (indicated by arrows in Figure 3). We see that the symmetric stretch is left unchanged by all four symmetry operations, or

	E	C_2	σ_v	σ_v'
Γ	1	1	1	1

which, after inspection of the character table, indicates that $\Gamma = A_1$. A similar procedure for the asymmetric stretch indicates correspondence with the B_2 irreducible representation.

Since water has a total of $(3n-6) = 3$ vibrational degrees of freedom, there is one vibrational mode left, corresponding to the scissoring in Figure 3 (c). This mode can be assigned by considering the H–O–H bond angle and repeating the same process used for the other two modes. The result is a correspondence with the irreducible representation A_1.

Having assigned all vibrational modes we can now use the character table to determine which modes are active under IR spectroscopy. Without proof[6] we note the following rule:

> A vibrational mode will be infrared active (i.e., will result in an absorption band) if the corresponding representation corresponds to one or more of the linear coordinate terms in the character table.

Since all three vibrational modes of the water molecule correspond to representations with either z or y linear terms, we see that all three should have IR absorption bands. These are illustrated in the gaseous IR spectrum (neglecting rotational fine structure) of water, shown in Figure 4.
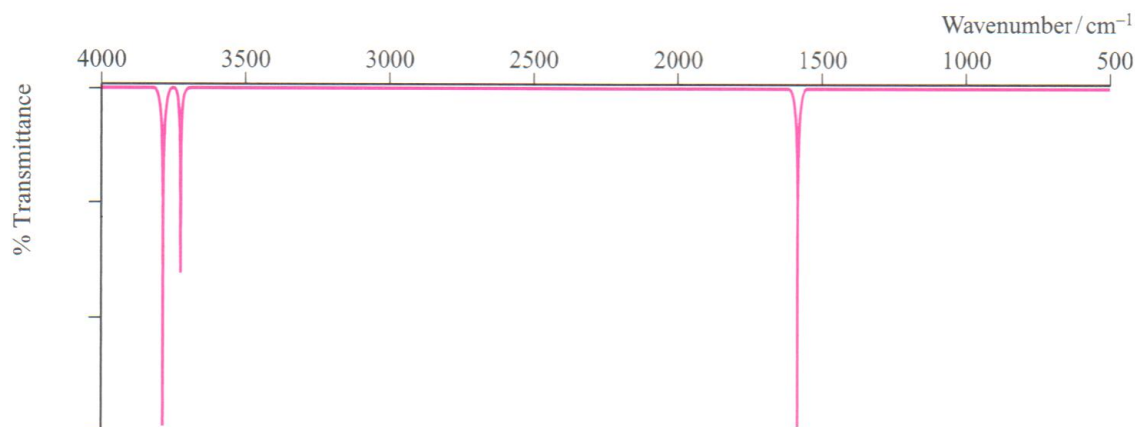

Figure 4. Calculated IR spectrum of gaseous H_2O showing the three fundamental absorptions. Source: [Housecroft and Sharpe, 2008]

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[6]A full development of the *selection rules* which determine if an electronic transition is allowable requires a quantum mechanical treatment beyond the scope of this document. It is based on determining the symmetry of the transition moment function. If this symmetry spans a totally symmetric representation of the molecule's point group then the transition is allowed. A full treatment can be found in [Sternberg, 1994] §3.6 or [Cotton, 1990] §10.6.

Returning in spirit to our opening example of the buckyball, what if we didn't already know the structure of water and wanted to determine if it was bent or linear? We have already predicted that a bent structure will have three IR spectral absorption lines. If instead water was linear it would belong to the point group $D_{\infty h}$ by Appendix A, Figure 6. Although this is an infinite group (since an infinitesimal rotation leaves a linear molecule unchanged) it is one of the few infinite groups which behaves as expected under the mathematical mechanisms we have built. Performing a similar analysis as under the bent case, we find four normal modes of vibration, shown in Figure 5. Of these four, we would find that the symmetric stretch is
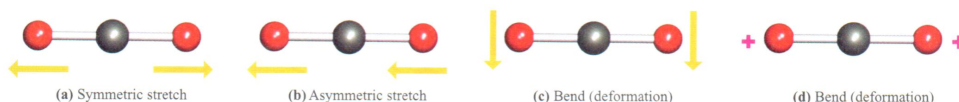

(a) Symmetric stretch   **(b)** Asymmetric stretch   **(c)** Bend (deformation)   **(d)** Bend (deformation)

Figure 5. The vibrational modes of a linear molecule. Vibrations (a) and (b) are stretching modes. Bending mode (c) occurs in the plane of the paper, while (d) occurs in a plane perpendicular to that of the paper; the + signs designate motion towards the reader. The two bending modes require the same amount of energy and are therefore *degenerate*. Source: [Housecroft and Sharpe, 2008]

IR inactive since it does not correspond to an irreducible representation with linear coordinate transformation term. Although the remaining three normal modes are IR active, we would find that the two bending modes are degenerate. Thus a linear molecule would have two IR absorption peaks, allowing easy experimental determination of the structural configuration of water via the power of symmetry and representation theory.

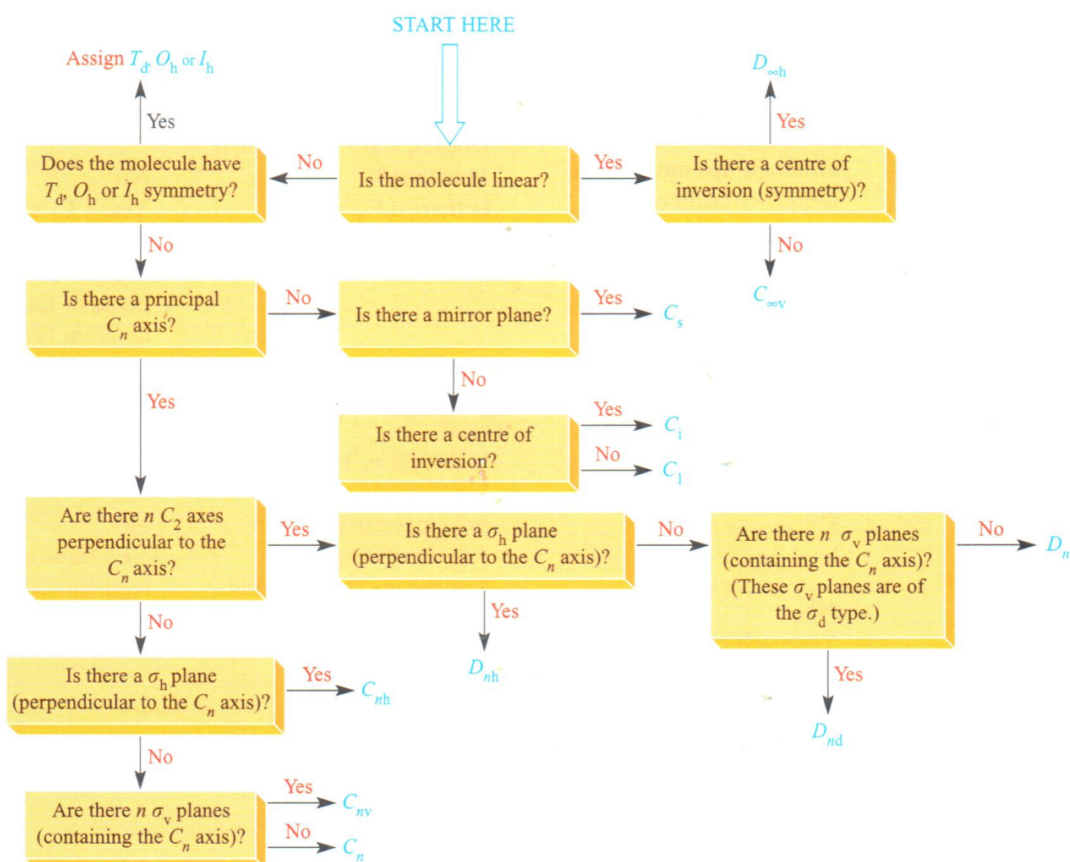## Appendix A – Determination of Point Groups

Figure 6. Scheme for assigning point groups of molecules. Source: [Housecroft and Sharpe, 2008]

Appendix B – Exercises

Problem 1. Prove that a finite group G is abelian if and only if all the irreducible representations of G have degree 1.

Problem 2. Let $\rho^1 : G \to GL(V_1)$ and $\rho^2 : G \to GL(V_2)$ be two linear representations of G, and let χ_1 and χ_2 be their characters. Show that the character of the direct sum representation $V_1 \oplus V_2$ is equal to $\chi_1 + \chi_2$.

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