Utilisation of Group Theory to Determine the Vibrational Modes of the H_2O Molecule

Directed Research Project under the supervision of Dr. Rizwan Khalid

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Abstract

The vibrational modes of the H_2O molecule are identified using techniques from group theory. The symmetry group of the molecule is first determined along with its irreducible representations. The character table of the symmetry group is then constructed. The representations of the symmetry operations of the molecule are then constructed and decomposed in terms of the irreducible representations. Finally, the relevant translational and rotational modes are identified, from which the vibrational modes are determined.

1 Introduction

Group theory is a powerful mathematical tool that has significant applications in physical systems that exhibit some sort of symmetry. This can be seen if we consider the problem of analysing the vibrational modes of chemical molecules. This problem involves the diagonalisation of a $3N$-by-$3N$ matrix in order to determine the normal mode frequencies and their corresponding displacement vectors, where N denotes the number of atoms. Naturally, this becomes significantly more complicated once the number of atoms becomes large, but if the molecule exhibits some sort of symmetry, the tools of group theory allow for a great deal of simplification. As an example, this report considers the problem of determining the vibrational modes of the H_2O molecule. A diagram of this molecule is shown in Figure 1.

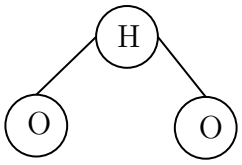

Figure 1: A diagram of the H_2O molecule

2 Identification of the Symmetry Operations

The first step is to identify the symmetry operations of the molecule. For this purpose, it will be helpful to introduce a coordinate system. This is shown is Figure 2.

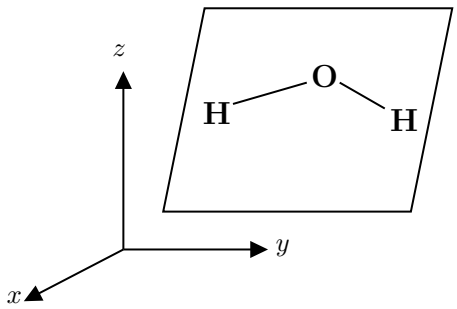

Figure 2: The H_2O molecule and the relevant coordinate system

Recalling that the H_2O molecule is planar (i.e. all of the atoms lie in a single plane), the molecule has been placed on the y–z plane for convenience. A symmetry operation is defined to be an operation that results in an indistinguishable configuration of the molecule after the application of that operation. Hence, the following four symmetry operations can be readily identified [1]:

1. The identity operation (doing nothing to the molecule). This is denoted by the symbol E. Clearly $E(x, y, z) = (x, y, z)$ where (x, y, z) denotes an arbitrary point in 3D space.

2. A rotation of π radians about the z-axis. This is denoted by C_2^z. Clearly $C_2^z(x, y, z) = (-x, -y, z)$.

3. A reflection about the y–z plane. This is denoted by σ_{yz}. Clearly $\sigma_{yz}(x, y, z) = (-x, y, z)$

4. A reflection about the x–z plane. This is denoted by σ_{xz}. Clearly $\sigma_{xz}(x, y, z) = (x, -y, z)$.

We now show that the set $X = \{E, C_2^z, \sigma_{yz}, \sigma_{xz}\}$ satisfy the axioms of a group. We first recall the axioms for a set G equipped with a binary operation $\circ$ to form a group:

1. Closure: $\forall a, b \in G$, $\exists\, c \in G$ s.t. $a \circ b = c$

2. Associativity: $\forall a, b, c \in G$, $(a \circ b) \circ c = a \circ (b \circ c)$

3. Existence of an identity: $\exists\, e \in G$ s.t. $e \circ g = g \circ e = g\ \forall g \in G$

4. Existence of an inverse: $\forall g \in G$, $\exists\, g^{-1} \in G$ s.t. $g \circ g^{-1} = g^{-1} \circ g = e$

Clearly, the element E is the identity element in the set X. Furthermore, we see that

$$\begin{aligned}
(C_2^z)^2(x, y, z) = C_2^z(-x, -y, z) = (x, y, z) &\implies (C_2^z)^2 = E \\
(\sigma_{xz})^2(x, y, z) = \sigma_{xz}(x, -y, z) = (x, y, z) &\implies (\sigma_{xz})^2 = E \\
(\sigma_{yz})^2(x, y, z) = \sigma_{yz}(-x, y, z) = (x, y, z) &\implies (\sigma_{yz})^2 = E
\end{aligned} \tag{2.1}$$

The conclusion is that each element is its own inverse. Hence, the existence and uniqueness of inverses has been shown. For closure we can see that

$$\begin{aligned}
(C_2^z\sigma_{xz})(x, y, z) = C_2^z(x, -y, z) = (-x, y, z) = \sigma_{yz}(x, y, z) &\implies C_2^z\sigma_{xz} = \sigma_{yz} \\
(C_2^z\sigma_{yz})(x, y, z) = C_2^z(-x, y, z) = (x, -y, z) = \sigma_{xz}(x, y, z) &\implies C_2^z\sigma_{yz} = \sigma_{xz} \\
(\sigma_{xz}\sigma_{yz})(x, y, z) = \sigma_{xz}(-x, y, z) = (-x, -y, z) = C_2^z(x, y, z) &\implies \sigma_{xz}\sigma_{yz} = C_2^z
\end{aligned} \tag{2.2}$$

We don't need to look at the identity when considering closure since the identity is defined to combine with any element to simply yield the element back. Hence, the set X also satisfies closure. An additional observation that can be made is that all of the elements commute with each other. Again, we don't need to consider the identity for this case because the identity trivially commutes with all of the elements in the set. Performing an explicit computation, we see that

$$\begin{aligned}
(\sigma_{xz}C_2^z)(x, y, z) = \sigma_{xz}(-x, -y, z) = (-x, y, z) = \sigma_{yz}(x, y, z)\sigma_{xz} &\implies \sigma_{xz}C_2^z = \sigma_{yz} \\
(\sigma_{yz}C_2^z)(x, y, z) = \sigma_{yz}(-x, -y, z) = (x, -y, z) = \sigma_{xz}(x, y, z) &\implies \sigma_{yz}C_2^z = \sigma_{xz} \\
(\sigma_{yz}\sigma_{xz})(x, y, z) = \sigma_{yz}(x, -y, z) = (-x, -y, z) = C_2^z(x, y, z) &\implies \sigma_{yz}\sigma_{xz} = C_2^z
\end{aligned} \tag{2.3}$$

Clearly, Equations (2.2) and (2.3) imply that all of the elements in the set X commute with one another. The only axiom that is left to check now is associativity. Due to the fact that all of the elements commute with one another and the fact that E commutes with all of the elements, we only need to look at three non-trivial cases to fully establish

associativity. These three cases are the permutations of C_2^z, σ_{yz} and σ_{xz}. Performing the explicit computation, we see that

$$\begin{aligned}(C_2^z\sigma_{xz})\sigma_{yz} &= (\sigma_{yz})^2 = E = C_2^z(\sigma_{xz}\sigma_{yz}) = (C_2^z)^2\\ (\sigma_{yz}C_2^z)\sigma_{xz} &= (\sigma_{xz})^2 = E = \sigma_{yz}(C_2^z\sigma_{xz}) = (\sigma_{yz})^2\\ (\sigma_{xz}\sigma_{yz})C_2^z &= (C_2^z)^2 = E = \sigma_{xz}(\sigma_{yz}C_2^z) = (\sigma_{xz})^2\end{aligned} \tag{2.4}$$

Hence, the set X does indeed form a group. It is commonly referred to as the C_{2v} point group. Since all of the symmetry operations commute, we conclude that the C_{2v} group is also Abelian. Using Equations (2.2), (2.3) and (2.4), we can also construct the group multiplication for the C_{2v} point group. This is shown in Table 1.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}
E	E	C_2^z	σ_{xz}	σ_{yz}
C_2^z	C_2^z	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2^z
σ_{yz}	σ_{yz}	σ_{xz}	C_2^z	E

Table 1: Group Multiplication Table for the point group C_{2v}

3 Constructing Representations of C_{2v}

With the symmetry group identified, we now seek to construct representations $\Gamma^{(\sigma)}(g)$ of the group. We know from representation theory that the basic building blocks of any representation are the irreducible representations, and that from the irreducible representations, more complicated representations can be constructed. Hence, it suffices to construct only irreducible representations for the group C_{2v}. An additional simplification in our problem stems from the fact that C_{2v} is Abelian, which implies that all of its irreducible representations are one-dimensional. This also simplifies the determination of the characters of the irreducible representations; since they are all one dimensional, the representations and the characters are equal.

In order to construct the one-dimensional representations, we can begin by considering the action of the elements of C_{2v} on translations in the x, y and z directions separately [2]. Then the relevant basis functions are $\psi_1 = x$, $\psi_2 = y$ and $\psi_3 = z$.

For ψ_1 we have

$$\begin{aligned}E(x) = x &\implies \Gamma^{(x)}(E) = 1\\ C_2^z(x) = -x &\implies \Gamma^{(x)}(C_2^z) = -1\\ \sigma_{xz}(x) = x &\implies \Gamma^{(x)}(\sigma_{xz}) = 1\\ \sigma_{yz}(x) = -x &\implies \Gamma^{(x)}(\sigma_{yz}) = 1\end{aligned} \tag{3.1}$$

For ψ_2 we have

$$\begin{aligned}E(y) = y &\implies \Gamma^{(y)}(E) = 1\\ C_2^z(y) = -y &\implies \Gamma^{(y)}(C_2^z) = -1\\ \sigma_{xz}(y) = -y &\implies \Gamma^{(y)}(\sigma_{xz}) = -1\\ \sigma_{yz}(y) = y &\implies \Gamma^{(y)}(\sigma_{yz}) = 1\end{aligned} \tag{3.2}$$

For ψ_3 we have

$$\begin{aligned} E(z) = z &\implies \Gamma^{(z)}(E) = 1 \\ C_2^z(z) = z &\implies \Gamma^{(z)}(C_2^z) = 1 \\ \sigma_{xz}(z) = z &\implies \Gamma^{(z)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(z) = z &\implies \Gamma^{(z)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.3}$$

Additionally, we can consider how the group elements act on the rotations R_x, R_y and R_z which we define to be ψ_4, ψ_5 and ψ_6 respectively [2]. Here R_x denotes the axis of rotation about the x-axis. This definition carries over for R_y and R_z. The group C_{2v} comprises of the identity, one rotation and two reflections. We can understand the action of the rotation operation on a rotation by rotating the coordinate system, and observing where the new axis of rotation is. Usually, such operations only change the direction of the rotation, which can be checked using the Right Hand Rule. For reflections, the general rule is that if the rotation axis lies along the plane of reflection, then its direction is reversed. Otherwise, it is unchanged.
For ψ_4 we have

$$\begin{aligned} E(R_x) = R_x &\implies \Gamma^{(R_x)}(E) = 1 \\ C_2^z(R_x) = -R_x &\implies \Gamma^{(R_x)}(C_2^z) = -1 \\ \sigma_{xz}(R_x) = -R_x &\implies \Gamma^{(R_x)}(\sigma_{xz}) = -1 \\ \sigma_{yz}(R_x) = R_x &\implies \Gamma^{(R_x)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.4}$$

For ψ_5 we have

$$\begin{aligned} E(R_y) = R_y &\implies \Gamma^{(R_y)}(E) = 1 \\ C_2^z(R_y) = -R_y &\implies \Gamma^{(R_y)}(C_2^z) = -1 \\ \sigma_{xz}(R_y) = R_y &\implies \Gamma^{(R_y)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(R_y) = -R_y &\implies \Gamma^{(R_y)}(\sigma_{yz}) = -1 \end{aligned} \tag{3.5}$$

For ψ_6 we have

$$\begin{aligned} E(R_z) = R_z &\implies \Gamma^{(R_z)}(E) = 1 \\ C_2^z(R_z) = R_z &\implies \Gamma^{(R_z)}(C_2^z) = 1 \\ \sigma_{xz}(R_z) = -R_z &\implies \Gamma^{(R_z)}(\sigma_{xz}) = -1 \\ \sigma_{yz}(R_z) = -R_z &\implies \Gamma^{(R_z)}(\sigma_{yz}) = -1 \end{aligned} \tag{3.6}$$

We can also consider the action of the group elements on functions that involve multiplication of any two functions from x, y and z. We can construct 6 such functions: $\psi_7 = x^2$, $\psi_8 = y^2$, $\psi_9 = z^2$, $\psi_{10} = xy$, $\psi_{11} = xz$ and $\psi_{12} = yz$ [2].
For ψ_7 we have

$$\begin{aligned} E(x^2) = (Ex)(Ex) = x^2 &\implies \Gamma^{(x^2)}(E) = 1 \\ C_2^z(x^2) = (C_2^z x)(C_2^z x) = x^2 &\implies \Gamma^{(x^2)}(C_2^z) = 1 \\ \sigma_{xz}(x^2) = (\sigma_{xz}x)(\sigma_{xz}x) = x^2 &\implies \Gamma^{(x^2)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(x^2) = (\sigma_{yz}x)(\sigma_{yz}x) = x^2 &\implies \Gamma^{(x^2)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.7}$$

For ψ_8 we have

$$\begin{aligned} E(y^2) = (Ey)(Ey) = y^2 &\implies \Gamma^{(y^2)}(E) = 1 \\ C_2^z(y^2) = (C_2^z y)(C_2^z y) = y^2 &\implies \Gamma^{(y^2)}(C_2^z) = 1 \\ \sigma_{xz}(y^2) = (\sigma_{xz} y)(\sigma_{xz} y) = y^2 &\implies \Gamma^{(y^2)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(y^2) = (\sigma_{yz} y)(\sigma_{yz} y) = y^2 &\implies \Gamma^{(y^2)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.8}$$

For ψ_9 we have

$$\begin{aligned} E(z^2) = (Ez)(Ez) = z^2 &\implies \Gamma^{(z^2)}(E) = 1 \\ C_2^z(z^2) = (C_2^z z)(C_2^z z) = z^2 &\implies \Gamma^{(z^2)}(C_2^z) = 1 \\ \sigma_{xz}(z^2) = (\sigma_{xz} z)(\sigma_{xz} z) = z^2 &\implies \Gamma^{(z^2)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(z^2) = (\sigma_{yz} z)(\sigma_{yz} z) = z^2 &\implies \Gamma^{(z^2)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.9}$$

For ψ_{10} we have

$$\begin{aligned} E(xy) = (Ex)(Ey) = xy &\implies \Gamma^{(xy)}(E) = 1 \\ C_2^z(xy) = (C_2^z x)(C_2^z y) = xy &\implies \Gamma^{(xy)}(C_2^z) = 1 \\ \sigma_{xz}(xy) = (\sigma_{xz} x)(\sigma_{xz} y) = -xy &\implies \Gamma^{(xy)}(\sigma_{xz}) = -1 \\ \sigma_{yz}(xy) = (\sigma_{yz} x)(\sigma_{yz} y) = -xy &\implies \Gamma^{(xy)}(\sigma_{yz}) = -1 \end{aligned} \tag{3.10}$$

For ψ_{11} we have

$$\begin{aligned} E(xz) = (Ex)(Ez) = xz &\implies \Gamma^{(xz)}(E) = 1 \\ C_2^z(xz) = (C_2^z x)(C_2^z z) = -xz &\implies \Gamma^{(xz)}(C_2^z) = -1 \\ \sigma_{xz}(xz) = (\sigma_{xz} x)(\sigma_{xz} z) = xz &\implies \Gamma^{(xz)}(\sigma_{xz}) = 1 \\ \sigma_{yz}(xz) = (\sigma_{yz} x)(\sigma_{yz} z) = -xz &\implies \Gamma^{(xz)}(\sigma_{yz}) = -1 \end{aligned} \tag{3.11}$$

For ψ_{12} we have

$$\begin{aligned} E(yz) = (Ex)(Ey) = yz &\implies \Gamma^{(yz)}(E) = 1 \\ C_2^z(yz) = (C_2^z y)(C_2^z z) = -yz &\implies \Gamma^{(yz)}(C_2^z) = -1 \\ \sigma_{xz}(yz) = (\sigma_{xz} y)(\sigma_{xz} z) = -yz &\implies \Gamma^{(yz)}(\sigma_{xz}) = -1 \\ \sigma_{yz}(yz) = (\sigma_{yz} y)(\sigma_{yz} z) = yz &\implies \Gamma^{(yz)}(\sigma_{yz}) = 1 \end{aligned} \tag{3.12}$$

We now consider the problem of how many irreducible representations C_{2v} must have. For this purpose, we need to recall the notion of conjugacy classes. Recall that the number of irreducible representations of a finite group is equal to the number of conjugacy classes. Since the point group C_{2v} is Abelian, each element is in its own conjugacy class. Hence, C_{2v} has 4 conjugacy classes. Hence, we conclude that C_{2v} must have 4 irreducible representations.

However, if we look at the 12 functions that were previously constructed from Equations (3.1) - (3.12), we note some of them transform in the same way under the action of the group elements. We can thus group up the 12 functions according to which of them transform the same way, and use just one symbol to represent all of them. We thus find the following four groups of functions:

1. z, x^2, y^2 and z^2. This is denoted by the symbol A_1.
2. xy and R_z. This is denoted by the symbol A_2.
3. x, xz and R_y. This is denoted by the symbol B_1.
4. y, yz and R_x. This is denoted by the symbol B_2.

The 4 distinct groups correspond to the 4 different irreducible representations we originally needed to determine. All of this information is neatly summarised in the character table for the point group C_{2v}.

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

Table 2: Character Table for the point group C_{2v}

4 Constructing a Representation for the Symmetries of the H_2O Molecule

Now, our task is to explicitly construct a representation for the symmetry operations for the H_2O molecule. We already know how the group elements of C_{2v} act on an arbitrary point in 3D space. If we think of the H_2O molecule as comprising of 9 points in total (3 points for each atom), then we can construct a 9-dimensional representation of C_{2v}. The relevant basis of the representation is then the set $\{x_1, y_1, z_1, \ldots, z_3\}$ as depicted in Figure 3 and the representation is denoted by $\Gamma^{(9)}$.

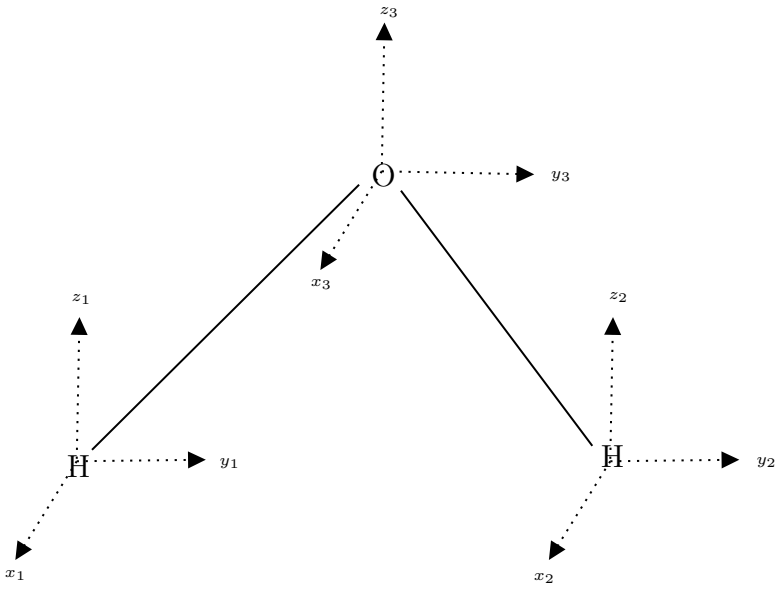

Figure 3: A visualisation of the basis for the $\Gamma^{(9)}$ representation for the H_2O molecule

We first consider the identity E. This does nothing to the molecule. Hence it is represented by the 9-by-9 identity matrix.

$$\Gamma^{(9)}(E) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \implies \chi^{\Gamma^{(9)}}(E) = 9 \tag{4.1}$$

Now consider the operation C_2^z. We already know that how this acts on an arbitrary point in 3D space. Applying it to the molecule, it additionally interchanges the two hydrogen atoms while the oxygen atom stays in place. So (x_1, y_1, z_1) is mapped to $(-x_2, -y_2, z_2)$, (x_2, y_2, z_2) is mapped to $(-x_1, -y_1, z_1)$ and (x_3, y_3, z_3) is mapped to $(-x_3, -y_3, z_3)$. Hence, the C_2^z operation is represented by the following 9-by-9 matrix:

$$\Gamma^{(9)}(C_2^z) = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \implies \chi^{\Gamma^{(9)}}(C_2^z) = -1 \tag{4.2}$$

Now consider the operation σ_{xz}. Again, we know how it acts on one arbitrary point. Additionally, it also exchanges the two hydrogen atoms. So (x_1, y_1, z_1) is mapped to $(x_2, -y_2, z_2)$, (x_2, y_2, z_2) is mapped to $(x_1, -y_1, z_1)$ and (x_3, y_3, z_3) is mapped to $(x_3, -y_3, z_3)$. Hence, the σ_{xz} operation is represented by the following 9-by-9 matrix:

$$\Gamma^{(9)}(\sigma_{xz}) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \implies \chi^{\Gamma^{(9)}}(\sigma_{xz}) = 1 \tag{4.3}$$

Finally, we have the σ_{yz} operation. This does not exchange any atom. All that happens is that the x coordinate for each atom is inverted while the y and z coordinates remain invariant. So (x_1, y_1, z_1) is mapped to $(-x_1, y_1, z_1)$, (x_2, y_2, z_2) is mapped to $(-x_2, y_2, z_2)$

and (x_3, y_3, z_3) is mapped to $(-x_3, y_3, z_3)$. Hence, the σ_{yz} operation is represented by the following 9-by-9 matrix:

$$\Gamma^{(9)}(\sigma_{yz}) = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \implies \chi^{\Gamma^{(9)}}(\sigma_{yz}) = 3 \tag{4.4}$$

Now that we have the characters of the $\Gamma^{(9)}$ representation, we can append it to the C_{2v} character table, as shown in Table 3.

C_{2v}	E	C_2^z	σ_{xz}	σ_{yz}			
A_1	1	1	1	1	z	x^2, y^2, z^2	
A_2	1	1	-1	-1		xy	R_z
B_1	1	-1	-1	1	x	xz	R_y
B_2	1	-1	-1	1	y	yz	R_x
$\Gamma^{(9)}$	9	-1	1	3			

Table 3: Appending the $\Gamma^{(9)}$ representation to the C_{2v} character table

5 Decomposition of the $\Gamma^{(9)}$ Representation

We now seek to decompose the $\Gamma^{(9)}$ representation in terms of the irreducible representations of C_{2v}. This means that we find the unique coefficients a_{A_1}, a_{A_2}, a_{B_1} and a_{B_2} such that

$$\Gamma^{(9)} = a_{A_1} A_1 \oplus a_{A_2} A_2 \oplus a_{B_1} B_1 \oplus a_{B_2} B_2$$

The way the coefficients are determined is by exploiting the orthogonality relations of the characters of the irreducible representations. The general result we have is

$$a_\mu = \frac{1}{h} \sum_g \chi^{(\text{red})}(g) \chi^{(\mu)}(g^{-1}) \tag{5.1}$$

where h is the order of the group (i.e. how many elements there are in the group) and the summation is over all of the group elements [3].

Calculating a_{A_1} we obtain

$$\begin{aligned} a_{A_1} &= \frac{1}{4}\sum_g \chi^{\Gamma^{(9)}}(g)\chi^{(A_1)}(g^{-1}) \\ &= \frac{1}{4}\Big[\chi^{\Gamma^{(9)}}(E)\chi^{(A_1)}(E) + \chi^{\Gamma^{(9)}}(C_2^z)\chi^{(A_1)}(C_2^z) \\ &\qquad + \chi^{\Gamma^{(9)}}(\sigma_{xz})\chi^{(A_1)}(\sigma_{xz}) + \chi^{\Gamma^{(9)}}(\sigma_{yz})\chi^{(A_1)}(\sigma_{yz})\Big] \\ &= \frac{1}{4}(9-1+1+3) = 3 \end{aligned} \tag{5.2}$$

Calculating a_{A_2} we obtain

$$\begin{aligned} a_{A_2} &= \frac{1}{4}\sum_g \chi^{\Gamma^{(9)}}(g)\chi^{(A_2)}(g^{-1}) \\ &= \frac{1}{4}\Big[\chi^{\Gamma^{(9)}}(E)\chi^{(A_2)}(E) + \chi^{\Gamma^{(9)}}(C_2^z)\chi^{(A_2)}(C_2^z) \\ &\qquad + \chi^{\Gamma^{(9)}}(\sigma_{xz})\chi^{(A_2)}(\sigma_{xz}) + \chi^{\Gamma^{(9)}}(\sigma_{yz})\chi^{(A_2)}(\sigma_{yz})\Big] \\ &= \frac{1}{4}(9-1-1-3) = 1 \end{aligned} \tag{5.3}$$

Calculating a_{B_1} we obtain

$$\begin{aligned} a_{B_1} &= \frac{1}{4}\sum_g \chi^{\Gamma^{(9)}}(g)\chi^{(B_1)}(g^{-1}) \\ &= \frac{1}{4}\Big[\chi^{\Gamma^{(9)}}(E)\chi^{(B_1)}(E) + \chi^{\Gamma^{(9)}}(C_2^z)\chi^{(B_1)}(C_2^z) \\ &\qquad + \chi^{\Gamma^{(9)}}(\sigma_{xz})\chi^{(B_1)}(\sigma_{xz}) + \chi^{\Gamma^{(9)}}(\sigma_{yz})\chi^{(B_1)}(\sigma_{yz})\Big] \\ &= \frac{1}{4}(9+1+1-3) = 2 \end{aligned} \tag{5.4}$$

Calculating a_{B_2} we obtain

$$\begin{aligned} a_{B_2} &= \frac{1}{4}\sum_g \chi^{\Gamma^{(9)}}(g)\chi^{(B_2)}(g^{-1}) \\ &= \frac{1}{4}\Big[\chi^{\Gamma^{(9)}}(E)\chi^{(B_2)}(E) + \chi^{\Gamma^{(9)}}(C_2^z)\chi^{(B_2)}(C_2^z) \\ &\qquad + \chi^{\Gamma^{(9)}}(\sigma_{xz})\chi^{(B_2)}(\sigma_{xz}) + \chi^{\Gamma^{(9)}}(\sigma_{yz})\chi^{(B_2)}(\sigma_{yz})\Big] \\ &= \frac{1}{4}(9+1-1+3) = 3 \end{aligned} \tag{5.5}$$

From Equations (5.2) - (5.5) we can conclude that

$$\Gamma^{(9)} = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2 \tag{5.6}$$

6 Determining the Vibrational Modes

Equation (5.6) tells us how the $\Gamma^{(9)}$ representation breaks up into irreducible representations of C_{2v}. Now, group theory tells us that each normal mode of the molecule has a one-to-one correspondence with an irreducible representation; in the decomposition of $\Gamma^{(9)}$ we have 9 irreducible representations, which means that we have 9 normal modes of the H_2O molecule in total [3]. However, we can recognise that 6 of the normal modes correspond to translations and rotations along each of the 3 coordinate axes, which have a frequency of zero. Physically, this just means that moving the molecule around in space or rotating it does not produce an energy difference, which is why the corresponding normal modes just have a frequency of zero. Hence, we need to subtract the 6 trivial modes from Equation (5.6) to determine the true vibrational modes.
From Table 2, we can see that translations in the x direction and rotations about the y axis transform according to the B_1 representation. Translations in the y direction and rotations about the x axis transform according the B_2 representation. Translations in the z direction transform according to the A_1 representation and rotations about the z axis transform according to the A_2 representation. If we subtract all of these from Equation (5.6), we obtain

$$\Gamma^{(9)}_{\text{vib}} = 2A_1 \oplus B_2 \tag{6.1}$$

Equation (6.1) tells us that there are two vibrational modes corresponding to the A_1 representation and one mode corresponding to the B_2 representation. We now need to determine what displacement pattern each representation corresponds to. In order to do this, we need to introduce the projection operator $\hat{P}^{(\sigma)}$ defined as

$$\hat{P}^{(\sigma)}_{ij} = \sum_g \Gamma^{(\sigma)^*}_{ij}(g) \times g \tag{6.2}$$

where $\Gamma^{(\sigma)^*}_{ij}(g)$ denotes the matrix elements of the group element g under the representation σ, and the summation is over all of the group elements. For our specific problem, all of the representations are real and one-dimensional. Hence, we can rewrite $\hat{P}^{(\sigma)}$ as

$$\hat{P}^{(\sigma)} = \sum_g \chi^{(\sigma)}(g) \times g \tag{6.3}$$

6.1 The B_2 Mode

Let's first consider the vibrational mode corresponding to the B_2 representation. The idea is to use Equation (6.3) and act the projection operator on small displacements in the x, y and z dimensions separately for each atom.

If we consider a small displacement of atom 1 in the x direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(x_1) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](x_1) \\ &= \chi^{(B_2)}(E) \times E(x_1) + \chi^{(B_2)}(C_2^z) \times C_2^z(x_1) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(x_1) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(x_1) \\ &= x_1 + x_2 - x_2 - x_1 = 0\end{aligned} \tag{6.4}$$

Hence, the B_2 mode does not involve any displacement of atom 1 in the x direction.
If we now consider a small displacement of atom 2 in the x direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(x_2) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](x_2) \\ &= \chi^{(B_2)}(E) \times E(x_2) + \chi^{(B_2)}(C_2^z) \times C_2^z(x_2) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(x_2) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(x_2) \\ &= x_2 + x_1 - x_1 - x_2 = 0\end{aligned} \tag{6.5}$$

Hence, the B_2 mode does not involve any displacement of atom 2 in the x direction.
For a small displacement of atom 3 in the x direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(x_3) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](x_3) \\ &= \chi^{(B_2)}(E) \times E(x_3) + \chi^{(B_2)}(C_2^z) \times C_2^z(x_3) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(x_3) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(x_3) \\ &= x_3 + x_3 - x_3 - x_3 = 0\end{aligned} \tag{6.6}$$

Hence, the B_2 mode does not involve any displacement of atom 3 in the x direction.
For a small displacement of atom 1 in the y direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(y_1) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](y_1) \\ &= \chi^{(B_2)}(E) \times E(y_1) + \chi^{(B_2)}(C_2^z) \times C_2^z(y_1) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(y_1) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(y_1) \\ &= y_1 + y_2 + y_2 + y_1 = 2(y_1 + y_2)\end{aligned} \tag{6.7}$$

Hence, the B_2 mode involves a displacement of the two hydrogen atoms along the y axis in the same direction.
For a small displacement of atom 2 in the y direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(y_2) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](y_2) \\ &= \chi^{(B_2)}(E) \times E(y_2) + \chi^{(B_2)}(C_2^z) \times C_2^z(y_2) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(y_2) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(y_2) \\ &= y_2 + y_1 + y_1 + y_2 = 2(y_1 + y_2)\end{aligned} \tag{6.8}$$

This corresponds to the same pattern of displacement as the one we found when considering the displacement of atom 1 in the y direction.
For a small displacement of atom 3 in the y direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(y_3) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](y_3) \\ &= \chi^{(B_2)}(E) \times E(y_3) + \chi^{(B_2)}(C_2^z) \times C_2^z(y_3) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(y_3) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(y_3) \\ &= y_3 + y_3 + y_3 + y_3 = 4y_3\end{aligned} \tag{6.9}$$

Hence, the B_2 mode involves a displacement of the oxygen atom along the y direction.
For a small displacement of atom 1 in the z direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(z_1) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](z_1) \\ &= \chi^{(B_2)}(E) \times E(z_1) + \chi^{(B_2)}(C_2^z) \times C_2^z(z_1) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(z_1) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(z_1) \\ &= z_1 - z_2 - z_2 + z_1 = 2(z_1 - z_2)\end{aligned} \tag{6.10}$$

Hence, the B_2 mode involves a displacement of the two hydrogen atoms along the z axis in opposite directions.
For a small displacement of atom 2 in the z direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(z_2) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](z_2) \\ &= \chi^{(B_2)}(E) \times E(z_2) + \chi^{(B_2)}(C_2^z) \times C_2^z(z_2) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(z_2) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(z_2) \\ &= z_2 - z_1 - z_1 + z_2 = 2(z_2 - z_1)\end{aligned} \tag{6.11}$$

This corresponds to the same pattern of displacement as the one we found when considering the displacement of atom 1 in the z direction (both hydrogen atoms moving in opposite directions along the z axis).
For a small displacement of atom 3 in the z direction we have

$$\begin{aligned}\hat{P}^{(B_2)}(z_3) &= \left[\sum_g \chi^{(B_2)}(g) \times g\right](z_3) \\ &= \chi^{(B_2)}(E) \times E(z_3) + \chi^{(B_2)}(C_2^z) \times C_2^z(z_3) \\ &\qquad + \chi^{(B_2)}(\sigma_{xz}) \times \sigma_{xz}(z_3) + \chi^{(B_2)}(\sigma_{yz}) \times \sigma_{yz}(z_3) \\ &= z_3 - z_3 - z_3 + z_3 = 0\end{aligned} \tag{6.12}$$

Hence, the B_2 mode does not involve any displacement of atom 3 along the z axis.
With all of this calculation done, we can see that the B_2 mode involves the two hydrogen atoms moving in the same direction along the y axis and in opposite directions along the z

axis. Additionally, the oxygen atom undergoes some sort of movement in the y direction. We now need to keep physical constraints in mind, which dictate that the centre of mass of the molecule does not move and that both linear and angular momentum are conserved. With these constraints in mind, what we can conclude is that the oxygen atom must move purely along the y axis in a direction opposite to that of the two hydrogen atoms. Diagrammatically, this motion is shown in Figure 4, and corresponds to the asymmetric stretching and bending mode of the molecule.

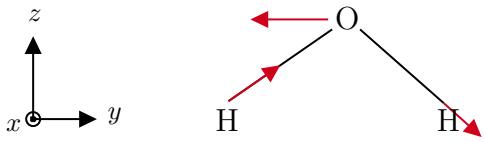

Figure 4: The asymmetric stretching and bending mode of the H_2O molecule

6.2 The A_1 Modes

From Equation (6.1) we know that there are two vibrational modes that correspond to the A_1 representation. Let's label one of them as A_{1a} and the other as A_{1b}. We employ the same procedure as the one that was done for the B_2 mode: apply the projection operator on individual displacements for all of the atoms in the molecule.
For a small displacement of atom 1 in the x direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(x_1) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](x_1) \\ &= \chi^{(A_1)}(E) \times E(x_1) + \chi^{(A_1)}(C_2^z) \times C_2^z(x_1) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(x_1) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(x_1) \\ &= x_1 - x_2 + x_2 - x_1 = 0\end{aligned} \tag{6.13}$$

Hence, atom 1 undergoes no displacement along the x axis.
For a small displacement of atom 1 in the y direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(y_1) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](y_1) \\ &= \chi^{(A_1)}(E) \times E(y_1) + \chi^{(A_1)}(C_2^z) \times C_2^z(y_1) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(y_1) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(y_1) \\ &= y_1 - y_2 - y_2 + y_1 = 2(y_1 - y_2)\end{aligned} \tag{6.14}$$

Hence, atom 1 and atom 2 (i.e. the two hydrogen atoms) move in opposite directions along the y axis.

For a small displacement of atom 1 in the z direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(z_1) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](z_1) \\ &= \chi^{(A_1)}(E) \times E(z_1) + \chi^{(A_1)}(C_2^z) \times C_2^z(z_1) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(z_1) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(z_1) \\ &= z_1 + z_2 + z_2 + z_1 = 2(z_1 + z_2)\end{aligned} \tag{6.15}$$

Hence, atom 1 and atom 2 (i.e. the two hydrogen atoms) move in the same direction along the z axis.
For a small displacement of atom 2 in the x direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(x_2) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](x_2) \\ &= \chi^{(A_1)}(E) \times E(x_2) + \chi^{(A_1)}(C_2^z) \times C_2^z(x_2) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(x_2) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(x_2) \\ &= x_2 - x_1 + x_1 - x_2 = 0\end{aligned} \tag{6.16}$$

Hence, atom 2 undergoes no motion along the x axis.
For a small displacement of atom 2 in the y direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(y_2) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](y_2) \\ &= \chi^{(A_1)}(E) \times E(y_2) + \chi^{(A_1)}(C_2^z) \times C_2^z(y_2) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(y_2) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(y_2) \\ &=\end{aligned} \tag{6.17}$$

Hence, atom 2 undergoes no motion along the x axis.
For a small displacement of atom 2 in the y direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(y_2) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](y_2) \\ &= \chi^{(A_1)}(E) \times E(y_2) + \chi^{(A_1)}(C_2^z) \times C_2^z(y_2) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(y_2) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(y_2) \\ &= y_2 - y_1 - y_1 + y_2 = 2(y_2 - y_1)\end{aligned} \tag{6.18}$$

This corresponds to the same pattern of motion that was seen upon applying the projection operator on a small displacement of atom 1 in the y direction (the two hydrogen atoms move in opposite directions along the y axis).

For a small displacement of atom 2 in the z direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(z_2) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](z_2) \\ &= \chi^{(A_1)}(E) \times E(z_2) + \chi^{(A_1)}(C_2^z) \times C_2^z(z_2) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(z_2) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(z_2) \\ &= z_2 + z_1 + z_1 + z_2 = 2(z_1 + z_2)\end{aligned} \tag{6.19}$$

This corresponds to the same pattern of motion that was seen upon applying the projection operator on a small displacement of atom 1 in the z direction (the two hydrogen atoms move in the same direction along the z axis).
For a small displacement of atom 3 in the x direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(x_3) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](x_3) \\ &= \chi^{(A_1)}(E) \times E(x_3) + \chi^{(A_1)}(C_2^z) \times C_2^z(x_3) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(x_3) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(x_3) \\ &= x_3 - x_3 + x_3 - x_3 = 0\end{aligned} \tag{6.20}$$

Hence, the oxygen atom undergoes no motion along the x axis.
For a small displacement of atom 3 in the y direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(y_3) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](y_3) \\ &= \chi^{(A_1)}(E) \times E(y_3) + \chi^{(A_1)}(C_2^z) \times C_2^z(y_3) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(y_3) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(y_3) \\ &= y_3 - y_3 - y_3 + y_3 = 0\end{aligned} \tag{6.21}$$

Hence, the oxygen atom undergoes no motion along the y axis.
For a small displacement of atom 3 in the z direction we have

$$\begin{aligned}\hat{P}^{(A_1)}(z_3) &= \left[\sum_g \chi^{(A_1)}(g) \times g\right](z_3) \\ &= \chi^{(A_1)}(E) \times E(z_3) + \chi^{(A_1)}(C_2^z) \times C_2^z(z_3) \\ &\qquad + \chi^{(A_1)}(\sigma_{xz}) \times \sigma_{xz}(z_3) + \chi^{(A_1)}(\sigma_{yz}) \times \sigma_{yz}(z_3) \\ &= z_3 + z_3 + z_3 + z_3 = 4z_3\end{aligned} \tag{6.22}$$

Hence, the oxygen atom undergoes some type of motion along the z axis.
With all of the preceding calculations, we can again use physical arguments to obtain a picture of the two A_1 vibrational modes. One mode (which we arbitrarily label as A_{1a}) involves the two hydrogen atoms moving in opposite directions along the y axis while the oxygen atom does not move at all. The other A_{1b} mode then involves the two hydrogen atoms moving in the same direction along the z axis while the oxygen atom moves in

the opposing direction along the z axis. Diagrammatically, the two modes are shown in Figure 5.

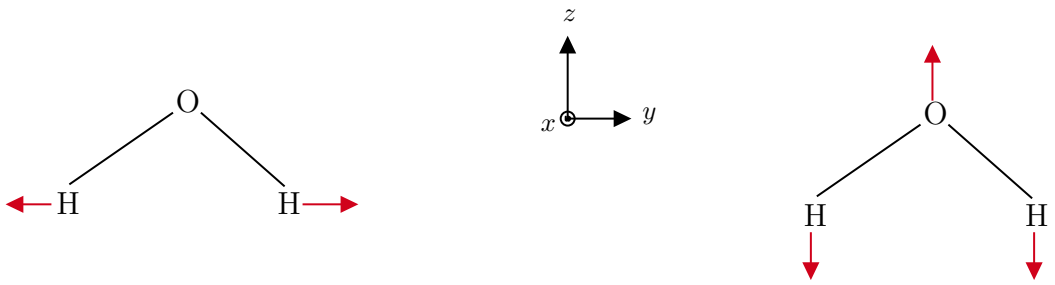

Figure 5: The A_{1a} (left) and A_{1b} (right) vibrational modes of the H_2O molecule

7 Conclusion

Part of the beauty of physics lies in the idea of symmetry; the use of group theory in order to exploit the underlying symmetries of physical problems thus becomes a testament to the aforementioned idea. The generality of the entire procedure that is presented in this report is one of the key reasons why group theory has become an important subject for modern day theoretical physicists to master, and will surely serve us for the years to come.

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