

Re-examining vibrational modes of molecules using crystallographic point groups and character tables

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May 8, 2020

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1 Introduction

All molecules have unique vibrational "fingerprints". The number and type of vibrational modes a molecule possess varies from molecule to molecule depending on the number of atoms and the type of bond between each atom. Since

every molecule has a different composition of atoms and bonds, they will each have different vibrational modes. Raman and IR spectroscopy are spectroscopic techniques which provide information about the vibrational profile of molecules as spectra. Interpreting Raman and IR spectra each provide different information about the molecules vibrations, but when combining the two, the structure can be elucidated. Conversely, knowing the molecules structure and how many vibrational modes it possess can be used to predict and better interpret the Raman and IR spectra.

The focus of this research is on determining the number of vibrational modes a molecule possess utilizing group theory, representation theory, and crystallographic point groups (point groups). When determining vibrational modes using point groups, the number of vibrational modes a molecule has is different than what the literature states it should have. Additionally, the number of vibrational modes of the molecule is dependent on what point group a molecule is classified into. The implication of these results mean the utilizing point groups to determine vibrational modes is more useful than what literature states.

2 Vibrations

Vibrations are internal movements of atoms causing bending, stretching, pushing, and pulling of bonds. Current literature states that non-linear molecules will have $3N-5$ vibrational modes where N is the number of atoms in the molecule, and linear molecules will have $3N-6$ vibrational modes[BH78]. The rationale for this is that every atom can move along three Cartesian axes, contributing $3N$ to the formula. The subtraction components come from removing entire molecule translations and entire molecule rotations. If every atom were to simultaneously move about one axis, the atoms would not move about the bonds of the molecule, but rather would move with the entire molecule. This translation component contributes minus three to the formula. Removing rotations contributes the final remaining three or two component. Similar to translations, if an entire molecule were to rotate about an axis, the orientation of atoms with respect to each other are not changed. For non-linear molecules, this means rotation about any of the three axes does not yield a vibration. For linear molecules, molecules whose atoms all exist along a primary axis, rotation about the primary axis yields no change to the molecule and leaves it in an identical position. Therefore, rotations only contribute minus two instead of three to the formula.

The results of my research show that linear molecules possess $2N-5$ vibrations as opposed to $3N-5$ vibrations. For non-linear molecules, the formula varies depending on the point group the molecule belongs to. However, some non-linear molecules do agree with the $3N-6$ formula, like water.

3 Symmetry Operations

3.1 Symmetry Operations

A symmetry operation is an operation which moves a molecule into a new orientation equivalent to its original one [Cot03]. These will rotate a molecule about a primary axis, reflect atoms through a plane, etc. By utilizing the symmetry possessed by molecules, a group(in the mathematical sense) of symmetry operations that can be applied to a molecule can be created and used to obtain information about vibrational modes.

- 1. **E** - Identity operation, no change to the molecule.
- 2. σ - Reflection through a plane
- 3. C_n^m - Rotation about an axis, where n denotes a fraction of a full rotation, $\frac{2\pi}{n}$, and m denotes how many times that rotation is performed
- 4. S_n^m - Improper rotation, a rotation about an axis followed by a reflection across a plane
- 5. **i** - Inversion, passing each atom through a center and placing it on the opposite side

3.2 Group Theory and Symmetry Operations

A set of elements form a **Group** if they satisfy the following properties

1. **Closure**- The product of any 2 elements must be in the group
2. **Associativity**- The operation of the group is associative; $a(bc) = (ab)c$
3. **Identity**- One element in the group (e) commutes with all elements $ae = ea = a$
4. **Inverses**- Every element of the group possesses an inverse element; $ab = ba = e$

The symmetry operations form a group. The identity operation, E, is necessary because groups need an identity element. Functionally speaking, the most “important” operations are the C and σ because those move the molecule into a new orientation. Similarly to E, the improper rotation operation, S, is necessary because group’s need to have closure. Without the improper rotation operation, applying the rotation and reflection operations would otherwise yield an element (symmetry operation) outside the group.

3.3 Matrix Representation of Symmetry Operations

Each symmetry operation can be represented as a matrix. The symmetry operations are then multiplied to a column matrix where the elements are the x, y, and z coordinates of each atom in the molecule. The resulting product describes the new “location” of each atom’s axis of the molecule. Here are matrix representations of the E and C operations for Water, a molecule in the C_2v point group.

$$\begin{array}{c}
 \text{The E operation water} \\
 \left[\begin{array}{cccccccccc} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right] \cdot \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} \\
 \text{The } C_2 \text{ operation on water} \\
 \left[\begin{array}{cccccccccc} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \cdot \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} -x_3 \\ -y_3 \\ z_3 \\ -x_2 \\ -y_2 \\ z_2 \\ -x_1 \\ -y_1 \\ z_1 \end{bmatrix}
 \end{array}$$

From the matrix representation of a symmetry operation, the trace of the matrix for each operation needs to be calculated to determine the reducible representation. The trace of a matrix is the sum of the diagonal elements, and is also known as the reducible representation. The trace of E is 9 and the trace of C_2 is -1. There are 2 other operations for water, $\sigma(xy)$ and $\sigma(yz)$ which have traces of 3 and 1 respectively.

Another method which is taught to chemistry students first learning this concept is to skip the idea of matrices altogether. Instead ”imagine performing an operation on a molecule, count the number of axis that move and add 0, count the number that did not change and add 1 for each, then subtract 1 for each flipped axis.” This method works for simple molecules but becomes more complex as the orders of symmetry increase. (This technique was from Dr. Matthew Law of UC Irvine at https://www.youtube.com/watch?v=O_KhEpXe6uE)

4 Point Groups and Character Tables

Every molecule can be classified into a crystallographic point group based on the symmetries the molecule possess and the symmetry operations that can be performed on it[BH78]. These point groups all have an associated character table that is used to determine the reducible representation of water.

Table I: Character table for the C_{2v} point group						
C_{2v}	E	C_2	$\nu(xz)$	$\nu'(yz)$	IR Activity	Raman Activity
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

Image from [Tus14]

The columns of the character table are the symmetry operations that are a part of the point group and the rows are irreducible representations. The IR activity column will be used later to determine vibrational modes and the Raman activity column is not used for this purpose. The IR activity column is sometimes referred to as the linear function column and the Raman can be referred to as the quadratic function column.

5 Determining Vibrational Modes Using Character Tables; Water Example

5.1 Reducible Representation of Water

the reducible representation, or trace, of each symmetry operation for water has been determined, $E=9$, $C_2=-1$, $\sigma(xy)=1$, and $\sigma(yz)=1$. Determining the irreducible representation of water is the next step. Using this formula

$$\text{number of irreducible representations} = \frac{1}{\text{order}} \cdot \sum ((\text{number of operations in class}) \cdot (\text{character of irreducible}) \cdot (\text{character of reducible}))$$

5.2 Irreducible Representation of Water

Utilizing the formula, the irreducible representations for each character can be determined. For example,

$$A_1 = \frac{1}{4} ((1 \cdot 1 \cdot 9) + (1 \cdot 1 \cdot -1) + (1 \cdot 1 \cdot 3) + (1 \cdot 1 \cdot 1))$$

$$A_1 = \frac{1}{4} (9 - 1 + 3 + 1)$$

$$A_1 = \frac{1}{4} (12)$$

$$A_1 = 3$$

This process is repeated for the remaining rows of the character table to in total yield

- $A_1 = 3$
- $A_2 = 1$
- $B_1 = 3$
- $B_2 = 2$

This irreducible representation can be considered the total movements of the molecule, the τ_{total} , includes rotations, vibrations and translations,

$$\tau_{total} = \tau_{vibrations} + \tau_{translations} + \tau_{rotations}$$

. For water then

$$\tau_{total} = 3A_1 + 1A_2 + 3B_1 + 2B_2$$

The vibrational modes can then be solved by subtracting the rotations and translations from the total

$$\tau_{vibrations} = \tau_{total} - (\tau_{rotations} + \tau_{translations})$$

The $\tau_{rotations}$ and $\tau_{translations}$ are determined from the IR activity column. The R_x , R_y , R_z represent rotations about x, y, and z axes and the x,y, and z components are the translations.

$$\tau_{translations} = A_1 + B_1 + B_2$$

$$\tau_{rotations} = A_2 + B_1 + B_2$$

$$\tau_{vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - ((A_1 + B_1 + B_2) + (A_2 + B_1 + B_2))$$

$$\tau_{vibrations} = 2A_1 + B_1$$

The results of this mean water has 3 modes of vibration, 2 are A which means symmetric and 1 is B which denotes an anti-symmetric mode of vibration.

6 Results

	Number of Vibrational Modes Determined from Point Groups	Number of vibrational modes from classical formula
$C_{\infty v}$		
$D_{\infty h}$	2N-3	3N-5
S_2		
C_2		
C_{2v}		
C_{2h}	3N-6	3N-6
D_2		
D_{2h}		
C_3		
C_{3v}		
C_{3h}		
D_3	2N-4	3N-6
D_{3h}		
D_{3d}		

The first column shows the formula I derived for determining the number of vibrational modes using the point group representation method and the second is what the literature states. The first two groups, the $C_{\infty v}$ and $D_{\infty h}$ are linear molecules. As mentioned previously, I determined the number of vibrational modes of these molecules to be 2N-3 as opposed to 3N-5. All the point groups with a 2 subscript, with the exception of D_2d , agree with the literature formula for non-linear molecules; where 3N-6 is the number of vibrational modes. The groups with a 3 subscript do not agree with the literature, and all fall under the formula 2N-4 for the number of vibrational modes. These results are significant because they are different than what current literature states and all the molecules in their respective groups agree with the formula I determined. These connections were made by examining molecules using <http://symmetry.jacobs-university.de/> which provides 3-dimensional models and examples of molecules in different point groups. I confirmed that the website agreed with the results I initially had before using it further to explore the relationships between molecules.

7 Plausible Explanation

The most plausible explanation for these results is degenerate vibrational modes. [Tus14] mentions in an article that vibrational modes are those which are energetically equivalent to each other, but are still "unique" vibrational mode. Examining NH_3 for example; according to the literature formula there are 6

vibrational modes of NH_3 . [Tus14] states that 2 of these modes are degenerate, and therefore are energetically equivalent to each other. Removing these vibrational modes to determine the number of energetically unique vibrational modes yields 4. Using the formula I derived from point groups, NH_3 is in the C_{3v} point group which means $2N-4$ should be used. This formula yields 4 vibrational modes, agreeing with the literature if the literature formula accounts for degeneracy.

This is a likely explanation, and if it is the case then point groups are more useful than they currently are stated to be. The important and relevant numbers for spectroscopy are energetically unique vibrational modes. If point groups take those into account then these formulas should be used and the literature on point groups should state that when using point groups in this way, degenerate modes of vibration are removed.

8 Future Work

Study degeneracy further as a plausible explanation for these results. This currently appears to be the most plausible explanation for the discrepancy in the number of vibrational modes. To do this, more molecules in different point groups should be examined to determine if they possess degenerate vibrational modes. If the literature number of vibrational modes agrees with mine after removing degenerate modes, then that would justify and explain the discrepancy. Developing a rigorous proof for why these formulas appear. I derived these formulas by using <http://symmetry.jacobs-university.de/> and manually examining molecules vibrational modes. After determining some did not agree with the literature, I adapted the formula so it worked with every molecule in the group. While this is useful in establishing the relationship, it could be circumstantial that this works. I believe there is a way to prove these formulas, and this would be accomplished by examining the matrix representations of symmetry operations and working from there.

Determine if higher order point groups have unique formulas for number of vibrational modes, and if it differs from literature. Initial research on these groups did not show a consistent formula across molecules of even the same group, ignoring different groups. However if a proof could be derived for the lower order groups, it could potentially be used to determine a formula in the higher order groups.

Conducting real Raman and IR spectroscopic experiments on molecules. Studying the real spectra of molecules can provide useful information about vibrational modes and would justify either the literature's formula or what I derived. These results are interesting and important because the formula's I derived are consistent across multiple groups despite being in disagreement with the literature. Furthermore, if point groups do account for degeneracy when determining number of vibrational modes, then that is an important piece of information which should be added to literature to highlight a benefit of using character tables and point groups to determine vibrational modes.

9 References

References

- [BH78] Michael D Bertolucci and D Harris. *Symmetry and spectroscopy*. 1978.
- [Cot03] F Albert Cotton. *Chemical applications of group theory*. John Wiley & Sons, 2003.
- [Tus14] David Tuschel. “Practical group theory and Raman spectroscopy, part i: Normal vibrational modes”. In: *Spectroscopy* 29.2 (2014), p. 14.