Group Theory: An Application of Discrete Groups

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In order to analyze energy levels, bonding, and spectroscopy, it is of great importance to be able to determine the symmetry of a molecule. The symmetry of a molecule or atom can be analyzed strictly from the molecule itself, or from the environment of the atom. Symmetry properties are classified according to different groups determined by sets of symmetry operations. Different elements are considered when studying symmetry, such as geometrical properties, reflections, and rotations. Symmetries are determined through mathematical tools; these tools are known as Group Theory. Two main distinctions must be made about group theory in terms of the ability of the group to rotate only a finite number of times, or when the rotations depend upon angles which vary in a continuous matter. The first case is known as discrete theory, or finite groups; and the second one is known as continuous, or Lie groups. In this paper, symmetry will be examined from a discrete point of view.

I. INTRODUCTION

Symmetry in molecules is characterized by elements and operations. Among symmetry elements, lines, planes, and centers of rotation are found. Elements are intrinsic to the system to be analyzed; they are not operations. Operations are movements performed on molecules upon their symmetry elements. These movements allow a "before" and "after" to be noticed in the molecule being studied. To clarify, the fact that a molecule possesses a symmetry element does not mean the molecule will actually go through a change. The molecule will show a modification of its original state when an operation is performed upon the element. However, it is important to note that operations can take every point of the molecule into another point in space or back to its original state. The symmetry of a system can be illustrated based on the symmetry operations the system possesses. Operations can be grouped in five main types: identity, rotation, reflection, inversion, and improper rotation. These operations are executed on elements such as, on a line, a plane, a point, or on the object itself. Rotations are performed on lines (axis), reflections on planes, and inversions on points. All symmetry elements intersect in a point at the center of the molecule; therefore, these elements define the point group symmetry of the system being studied.

II. GROUP THEORY

To analyze symmetry, a certain mathematical criteria must be followed. For this, symmetry elements must be defined, and operations generated by these elements will constitute a mathematical group. Symmetry elements are characteristics of a molecule which would allow a transformation; whereas symmetry operations are movements which when applied to a molecule will leave the molecule unchanged. There exists a correspondence between symmetry elements and symmetry operations, as the rotations are transformations by "rotating" the molecule by a certain angle along a proper axis, reflections are "mirror" results through a plane, and inversions are transformations in which atoms exchange positions to the position directly across. Figure 1 summarizes the relationship between elements and operations. These operations can be represented with matrices. To show the matrices reflecting transformations, an (x,y,z) generic point will be used. The identity operation leaves the molecule unchanged. Therefore, for the arbitrary (x,y,z) point, the product of its transformation (x',y',z') is exactly the same as the original point; in which x=x', y=y', and z=z', as shown in Eq.1. Then, the matrix for the identity transformation is the identity matrix.

\[
\begin{bmatrix}
  x' \\
  y' \\
  z'
\end{bmatrix} =
\begin{bmatrix}
  1 & 0 & 0 \\
  0 & 1 & 0 \\
  0 & 0 & 1
\end{bmatrix} \cdot
\begin{bmatrix}
  x \\
  y \\
  z
\end{bmatrix}
\]

(1)

Proper axes of symmetry generate rotations. These n-fold axes denoted by C_n represent a rotation by 2\pi/n. For example, it is easy to see the water molecule has a C_2 (2\pi/2=\pi) axis of symmetry, but it does not possess a C_4 axis, as reflected in Figure 2. One molecule can possess more than one axis of symmetry. For example, XeF_4 has a C_4 axis (perpendicular to the plane in which the Xe and F atoms are contained), and four C_2 axes perpendicular to the main axis of rotation C_4, contained in the Xe-F plane. Consequently, by setting n=2, and n=4, the matrices for a C_2 and a C_4 rotation can be obtained respectively. Then, the general transformation...
FIG. 2: Rotations on water molecule a) C\textsubscript{2}, b) C\textsubscript{4}\textsuperscript{1}

FIG. 3: C\textsubscript{4} and C\textsubscript{2} axis in XeF\textsubscript{4}

matrix for rotations is

\[
\begin{bmatrix}
\cos(2\pi/n) & \sin(2\pi/n) & 0 \\
-sin(2\pi/n) & \cos(2\pi/n) & 0 \\
0 & 0 & 1
\end{bmatrix}
\]  \hspace{1cm} (2)

Reflections are performed on symmetry planes contained in the molecule. Setting the main axis’ direction along the z axis, vertical symmetry planes contain this axis, and are perpendicular to the xy plane; horizontal planes are perpendicular to the z axis, coincident with the xy plane; and dihedral planes are perpendicular to the z-axis, and contain other axis of rotation perpendicular to the main axis of rotation\textsuperscript{1}. For example, a reflections along the two vertical planes in the water molecule in which the hydrogen atoms exchange planes (xy, and xz) are shown in Figure 4. Also, Figure 5 shows the yz vertical plane the water molecule possess, in which the atoms do not exchange positions.

Matrices representing these transformations are shown in equations 3, 4, and 5

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix}, \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}, \begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]  \hspace{1cm} (3)

being the first matrix the representation for \(\sigma_{xz}\) (vertical symmetry plane coincident with the xz plane), the second matrix \(\sigma_{xy}\) (horizontal symmetry plane coincident with the xy plane), and the third one \(\sigma_{yz}\) (vertical symmetry plane coincident with the yz plane)\textsuperscript{1}.

Inversions take place through the center of inversion. Figure 5 reflects how the four B atoms exchange positions in a generic AB\textsubscript{4} molecule. The matrix representing this transformation will then be the negative identity. Improper rotations are denoted as S\textsubscript{n}, and are generated by a rotation and a reflection along the n-axis. Figure 6 shows an S\textsubscript{6} operation performed on staggered ethane\textsuperscript{1}.

Point groups are groups that follow multiplication tables which contain symmetry operations, and comply with the properties of mathematical groups. Figure 7 shows examples for some groups\textsuperscript{5}.

III. APPLICATIONS AND XEF\textsubscript{4} ANALYSIS

Knowing the symmetry of a molecule allows studying vibrational spectroscopy. Following, an application of group theory to spectroscopy will be shown using xenon tetrafluoride (XeF\textsubscript{4}). Through XeF\textsubscript{4}, assignment of modes of vibration to a polyatomic molecule, selection rules for IR and Raman activity\textsuperscript{5}, symmetry coordinates, normal modes, stretching mode analysis, and assignment of real spectra will be exemplified.

FIG. 4: Reflection on a water molecule a) containing plane, b) bisecting plane\textsuperscript{1}

FIG. 5: Inversion operation on a generic AB\textsubscript{4} molecule\textsuperscript{1}

FIG. 6: Relation between operations\textsuperscript{1}

FIG. 7: Examples of different point groups\textsuperscript{4}
A. Normal Modes of Vibration

XeF₄’s point group is D₄h; therefore, by group theory, it is known the symmetry elements the molecule possesses are: E, 2C₂ᵥ, C₂ᵥ, 2C₄, i, 2S₄, σᵥ, 2σᵥ', 2σᵥ''. The geometry of this molecule is square planar, and its z-axis coincides with the C₄ axis (principal axis). The vertical planes (σᵥ) include the Xe-F bonds, and the dihedral planes (σᵥ) bisect the Xe-F bonds. The C₂ axis is coincident with the principal axis, the C₂' axis includes the bonds, and the C₂'' bisect the bonds. Figure 8 shows the elements and coordinate system of XeF₄.

By setting an x-y-z dextro-coordinate system in each atom in the XeF₄ molecule, table 1 can be constructed, showing the reducible representations (Γ) for the unmoved atoms (Γᵤm), and the total reducible (Γₜot). As a note, the results shown for each operation correspond to the trace of the matrix representing the motion. Then, Γₜot=Γᵤm+Γᵤv.

Subtracting the translations (a₁g =a₁g + b₁g + b₂g + e₂ + 2a₂u + b₂u + 3eᵥ) and rotations (a₂g and e₂) from the Mulliken symbols used to identify reducible and irreducible representations according to degeneracy and symmetry. Table II shows the D₄h character table which corresponds to XeF₄. These normal modes of vibrations correspond to 7 different vibrational energies. Figure 9 shows one of each set of the degenerate vibrations.

B. Selection Rules and Polarization

Selection rules indicate the transitions to be expected in the spectrum; they do not indicate intensity. Real spectra show very weak to very strong bands. Selection rules are useful because they can indicate the transitions expected to have zero intensity (forbidden), and the ones that are not zero (allowed). IR activity depends on the dipole moment of the molecule being modified through the vibration; whereas Raman activity is based on the polarizability of the molecule changing throughout the vibration.

It was shown in the previous section that Γᵤv=Γ_u+Γ_v, giving three vibrational modes with seven different energies. In Figure 9, the possible vibrations between the central atom (Xe) and the corner atoms (F) are shown. Each "a" and "b" vibration type corresponds to one kind of energy, and are single-degenerate; however, the "e" vibration types are doubly-degenerate. "e" contributes only one kind of energy (not two). This "e" subindex in Mulliken symbols represents double-degeneracy. Therefore, there are seven possible fundamental transitions because there are only seven different energy values. Then, the only IR active possible fundamentals take the form of a₃ₕ multiplied by the irreducible representation giving the irreducible representation. Consequently, a₂u and e₂ are the only IR active modes of XeF₄, which implies there will be only three fundamental transitions in the IR spectrum. Nonetheless, the Raman active bands will correspond to a₁g, b₁g, and b₂g - giving three allowed fundamental transitions. The study of XeF₄ demonstrates the mutual exclusion rule, in which it is noticeable that a molecule with a center of symmetry will have "u" modes being IR active, and "g" modes being Raman active.
C. Assignment of Real Spectra

Real spectra will not show as many strong bands predicted by theory based on the allowed fundamentals. One solution for this would be to account for the weaker bands; however, it can occur that more bands than expected are found. The study of symmetry of the molecule and prediction of bands can help determine the geometry of a molecule. For example, XeF₄’s geometry could be tetrahedral or square planar. Through group theory and spectral analysis, it can be shown XeF₄’s geometry if square planar corresponding to the D_{4h} point group. If the geometry would be tetrahedral, the corresponding point group would be Tₐ, and as it is indicated in the Figures 10 to 12, the symmetrical properties affect the prediction of bands, and help determine the molecular symmetry. Figure 13 shows a comparison between the fundamental observed frequencies between XeF₄ and XeOF₄.

IV. CONCLUSION

Having used a discrete approach to describe symmetry, in this case, in molecules, elements for the analysis of excitation levels (allowed and forbidden transitions), bonding and spectroscopy, have been given. A description of symmetry properties were given, as of the classification in different groups determined by sets of symmetry operations. For this matter, different elements were considered, in particular, geometrical properties, reflections, and rotations. Knowing that symmetry in molecules is characterized by elements and operations, different operations and elements were explained based on lines, planes, and centers of rotation giving five types of operations: identity, rotation, reflection, inversion, and improper rotation. Nonetheless, the importance of symmetry in molecules in terms of spectral analysis was exemplified through XeF₄. From this molecule, it was also explained how geometries can be selected according to the predictions obtained from analyzing group theory.