

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 Theory¹. 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 groups². 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 studied¹. 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 state³. 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 itself¹. 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 studied³.

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

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

FIG. 1: Elements and operations required in specifying molecular symmetry¹

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 unchanged¹. 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 matrix¹.

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (1)$$

Proper axes of symmetry generate rotations. These n-fold axes denoted by C_n represent a rotation by $2\pi/n$ ¹. 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 respectively¹. Then, the general transformation

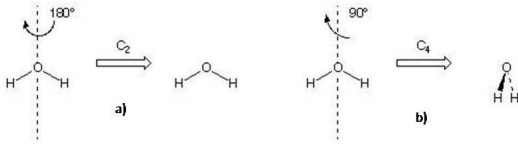


FIG. 2: Rotations on water molecule a) C_2 , b) C_4 ¹

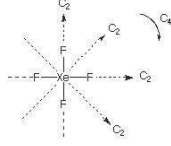


FIG. 3: C_4 and C_2 axis in XeF_4

matrix for rotations is

$$\begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (2)$$

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 rotation¹. 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

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3)$$

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

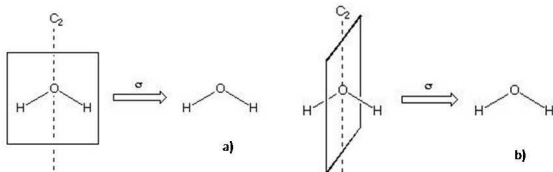


FIG. 4: Reflection on a water molecule a) containing plane, b) bisecting plane¹

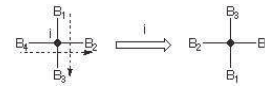


FIG. 5: Inversion operation on a generic AB_4 molecule¹

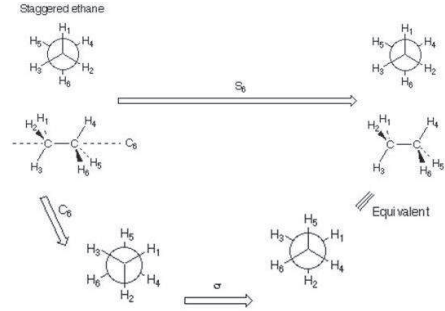


FIG. 6: Relation between operations¹

Inversions take place through the center of inversion. Figure 5 reflects how the four B atoms exchange positions in a generic AB_4 molecule. The matrix representing this transformation will then be the negative identity. Improper rotations are denoted as S_n , and are generated by a rotation and a reflection along the n -axis. Figure 6 shows an S_6 operation performed on staggered ethane¹.

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 groups⁵.

III. APPLICATIONS AND XeF_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_4). Through XeF_4 , assignment of modes of vibration to a polyatomic molecule, selection rules for IR and Raman activity⁵, symmetry coordinates, normal modes, stretching mode analysis, and assignment of real spectra will be exemplified.

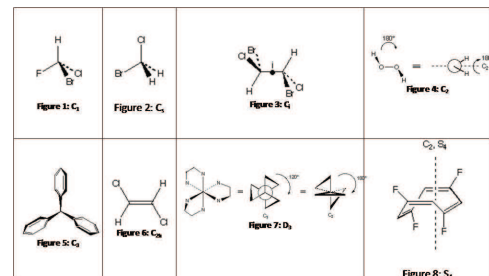


FIG. 7: Examples of different point groups⁴

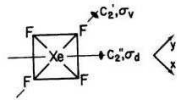


FIG. 8: Coordinate system and symmetry elements of XeF_4^5

TABLE I: Determination of Γ_{vib} for XeF_4^5

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v'$	$2\sigma_d''$
Γ_{xyz}	3	1	-1	-1	-1	-3	-1	1	1	1
Γ_{unm}	5	1	5	3	1	1	1	5	3	1
Γ_{tot}	15	1	-1	-3	-1	-3	-1	5	3	1

A. Normal Modes of Vibration

XeF_4 's point group is D_{4h} ; therefore, by group theory, it is known the symmetry elements the molecule possesses are: $E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v', 2\sigma_d''$. The geometry of this molecule is square planar, and its z -axis coincides with the C_4 axis (principal axis). The vertical planes (σ_v) include the Xe-F bonds, and the dihedral planes (σ_d) bisect the Xe-F bonds. The C_2 axis is coincident with the principal axis, the C_2' axis includes the bonds, and the C_2'' bisect the bonds⁵. Figure 8 shows the elements and coordinate system of XeF_4 .

By setting an x - y - z dextro-coordinate system in each atom in the XeF_4 molecule, table 1 can be constructed, showing the reducible representations (Γ), for the general (x,y,z) point (Γ_{xyz}), for the unmoved atoms (Γ_{unm}), and the total reducible (Γ_{tot})¹. As a note, the results shown for each operation correspond to the trace of the matrix representing the motion¹.

Then, $\Gamma_{tot} = a_{1g} + a_{2g} + b_{1g} + b_{2g} + e_g + 2a_{2u} + b_{2u} + 3e_u$. Subtracting the translations (a_{2u} and e_u) and rotations (a_{2g} and e_g), it is found that XeF_4 has 9 normal modes of vibration: $\Gamma_{vib} = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$ ⁵. Being $a_{1g}, a_{2g}, b_{1g}, b_{2g}, e_g, a_{2u}, b_{2u}$, and e_u the Mulliken symbols used to identify reducible and irreducible representations according to degeneracy and symmetry¹. Table II shows the D_{4h} character table which corresponds to XeF_4 ¹. These normal modes of vibrations correspond to 7 different vibrational energies⁵. 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

TABLE II: Character table for D_{4h} group¹

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v'$	$2\sigma_d''$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	0
E_g	2	0	-2	0	0	2	0	-2	0	-1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

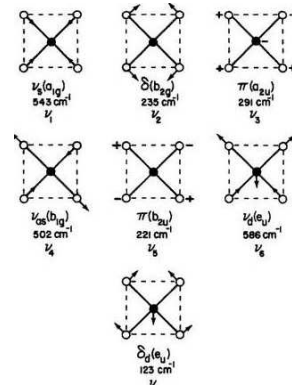


FIG. 9: Normal modes of vibration of a square planar XeF_4 molecule⁵

vibration⁵.

It was shown in the previous section that $\Gamma_{vib} = a_{1g} + b_{1g} + b_{2g} + a_{2u} + b_{2u} + 2e_u$, showing nine vibrational modes with seven different energies¹. 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-degenerate¹; 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-degeneracy¹. 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 a_{1g} multiplied by the irreducible representation, giving the irreducible representation. Consequently, a_{2u} and e_g are the only IR active modes of XeF_4 , which implies there will be only three fundamental transitions in the IR spectrum. Nonetheless, the Raman active bands will correspond to a_{1g}, b_{1g} , and b_{2g} - giving three allowed fundamental transitions⁵. The study of XeF_4 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.

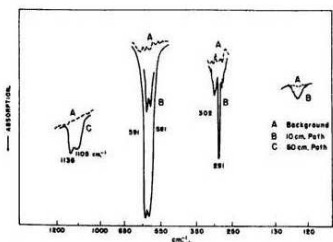


FIG. 10: IR spectrum of XeF₄ vapor⁵

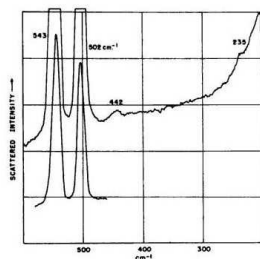


FIG. 11: Raman spectrum of XeF₄ solid⁵

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 group⁵. If the geometry would be tetrahedral, the corresponding point group would be T_d, 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 XeOF₄⁵.

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,

Xe F ₄ Fundamentals (D _{4h} Symmetry)						
a _{1g}	ν ₁	R	543 cm ⁻¹			✗
a _{2u}	ν ₂	IR	291 cm ⁻¹			✗
b _{1g}	ν ₃	R	235 cm ⁻¹			✗
b _{1u}	ν ₄	Inactive	221 ?			✗
b _{2g}	ν ₅	R	502 cm ⁻¹			✗
e _u	ν ₆	IR	586 cm ⁻¹			✗
e _u	ν ₇	IR	123 cm ⁻¹ ?			✗

FIG. 12: Numbering, spectral activity, and assignment of fundamentals of XeF₄ solid⁵

XeF ₄			XeOF ₄			
Frequency (cm ⁻¹)	Designation	Spectrum observed	Frequency (cm ⁻¹)	Designation	Spectrum observed	Description
			926.3	ν ₁ (a ₁)	R, ir	Xe - O stretch
554.3	ν ₁ (a _{1g})	R	576.9	ν ₂ (a ₁)	R, ir	XeF ₄ in-phase stretch
291	ν ₂ (a _{2u})	ir	285.9	ν ₃ (a ₁)	R, ir	XeF ₄ out-of-plane bend
218	ν ₃ (b _{1g})	R	225	ν ₄ (b ₁)	R	XeF ₄ in-plane scissor
524	ν ₅ (b _{2g})	R	543	ν ₅ (b ₂)	R	XeF ₄ out-of-phase stretch
(216)	ν ₄ (b _{1u})	inactive	(219)	ν ₆ (b ₂)	none observed	F ₄ out-of-plane pucker
586	ν ₆ (e _u)	ir	609	ν ₇ (e)	R, ir	F ₄ degenerate stretch
			362	ν ₈ (e)	R, ir	Xe - O bend
(161)	ν ₇ (e _u)	none observed	161	ν ₉ (e)	R, ir	F ₄ degenerate bend

FIG. 13: Fundamental frequencies of XeF₄ and XeOF₄⁵

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.

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