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Prediction of Vibrational Spectra of a Molecule of C_{3v} Point Group with the Help Symmetry and Group Theory

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Abstract

Group Theory and Symmetry helps us to understand molecular structure, some chemical properties, and characteristics of physical properties (spectroscopy) of molecules. Group Theory is also used to predict vibrational spectra for the identification of molecular shape, as well as a tool for understanding electronic structure and bonding of a molecule of different point group. In this paper we understand how Group Theory helps to predict vibrational spectra of NH_3 an example of C_{3v} point group. The combination of C_3 & σ_v (vertical mirror plane) leads to C_{3v} point group, which leads to the C_{3v} character table. From the character table predictions can be made for which symmetries can exist. Character table of the point table also contains the irreducible representation of that group along with its corresponding matrix characters. A vibrational mode is active in the infrared if it corresponds to an irreducible representation that has the same symmetry as the Cartesian coordinates x, y, or z because a vibrational motion that shifts the center of charge of the molecule in any of the x, y, or z directions results in a change in dipole moment. Otherwise, the vibrational mode is not infrared active.

Keywords: Symmetry, vibratioal spectra, character table

1. INTRODUCTION

The concept of symmetry and group theory are important to study the structure of molecules. The measurement of crystal structures, infra– red spectra, ultra–violet spectra, dipole moments and optical activities, all these are properties which depend on molecular symmetry [1-2]. Symmetry is present in geometrical figures, crystalline solids and molecules C_n (axis of symmetry), σ (plane of symmetry), i (centre of symmetry) and S_n (improper axis of symmetry) is the element of symmetry. The symmetry operations are rotation about axis, reflection in a plane, inversion about point and rotation– reflection or reflection–rotation, we have to know about the total symmetry operations present in a certain molecules. All the

symmetry operations present in a molecule form a group. Groups have four requirements i.e., closure, associative, identity, and inverse. There requirements are judged by the multiplication table, subgroup is the smaller group within a group which also obey all the requirements of group. Classes of operations, similarity transformation, conjugate have very important points of group theory. Point group of a molecule is determined using the total symmety operations present in that molecule. Point group of molecule is just abbreviation of total symmetry operations of a molecule. Optical activity and dipole moment may also be determined using the point group of the molecule. Symmetry elements in a point group may also be represented by matrix representations may be reducible or irreducible[3]. Great orthogonality[4] theorem in concerned with the irreducible representation of a point group. This theorem is useful for the construction of character table. Character table is self explanatory and is used to solve the problem of chemical importance. Character table predict the effect of a molecule's symmetry on its vibrational modes [5] and other important properties. Each point group has a character table listing its essential symmetry operations. Each row contains an irreducible representation of the operations, along with the corresponding atomic orbital and linear movements.

In present paper we take NH_3 an example of C_{3v} point group and generate its reducible representations.

Reducible representations are generated by evaluating how these symmetry operations affect molecular properties. Reducing this representation gives the contributing irreducible representations.

Then decompose the reducible representations as the sum of irreducible representations with the help of character tables. Now subtract rotational and translational representations to obtain the vibrational degree of freedom. The number of degrees of freedom[6-7] depends on the number of atoms (N) in a molecule. Each atom in the molecule can move in three dimensions (x, y, z), and so the number of degrees of freedom is three dimensions times N number of atoms, or $3N$. The total degrees of freedom include a number of vibrations, three translations $(x,\ y, and\ z)$, and either two or three rotations. Linear molecules have two rotational degrees of freedom, while non-linear molecules have three. The vibrational modes are represented by the following expressions:

For Linear Molecule degrees of freedom = $3N - 5$

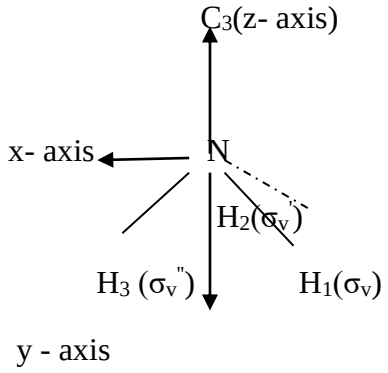
For Nonlinear Molecule degrees of freedom =$3N - 6$.

By the character table we can predict vibrational modes are IR-active[9-10] those having symmetry of the $x,\ y, and\ z$ axes. Also we can recobnise the vibrational modes that are Raman- active by those with the symmetry of any of the binary products or linear combination of binary products.

Material and Method

In this study we illustrate first the procedure and general results to form character table for Ammonia molecule NH_3 belongs, in its ground-state equilibrium geometry, to the C_{3v} point group.

C_{3v} point group has six element E, C_3, $C_3^2 = C^2$, σ_v , σ_v' , σ_v'' i.e. order of the group is '6'.



Also these symmetry operations have been divided into three classes (E), (C_3, C_3^2)and(σ_v , σ_v' , σ_v''). Therefore, there will be three irreducible representation in this point group and let these be Γ_1, Γ_2, and Γ_3, . Partial character table for C_{3v} group is

	E	$2C_3$	$3\sigma_v$
Γ_1			
Γ_2			
Γ_3			

We know by Great Orthogonality Theorem that $\sum_R [\chi_i(R)]^2$ = h i.e. sum of the squares of χ(R) equal to order of the group. If d_1, d_2 and d_3 are the dimension of these three irreducible representation

Then $d_1^2 + d_2^2 + d_3^2 = 6.$ …… (A)

The above rule relating reducible and irreducible representation will only be satisfied when $d_1 = d_2 = 1$ and $d_3 = 2$. As dimension of irreducible representation equals to the character of all operations in the same class.

	E	$2C_3$	$3\sigma_v$
Γ_1	1		
Γ_2	1		
Γ_3	2		

We also know that in a point group, there is always an irreducible representation for which the character for all operations is +1. Let it be Γ_1.

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1		
Γ_3	2		

Now we take element of cell a_{22} as x, cell a_{23} as y, cell a_{32} as z and cell a_{33} as w.

∴

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	x	y
Γ_3	2	z	w

Now from equation (A) for Γ_2 $1^2 + 2x^2 + 3y^2 = 6$ ……(B)

Now we use rule of orthogonality for these irreducible representation $\sum_R g_i[\chi_i(R)]\ [\chi_j(R)] = 0$; i≠j.

Applying the orthogonality rule between Γ_1 and Γ_2

$$1.1\,.\,1 + 2.\,1.\,x + 3.1.\,y = 0.$$
$$1 + 2x + 3y = 0 \qquad \text{……(C)}$$

As Γ_1 and Γ_2, are one dimensional the value of can x and y be +1 or -1. Therefore from equation (B) and (C) $x = 1$ & $y = -1$.

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	z	w

Similarly for Γ_1 and Γ_3 $1.1.2 + 2.1.z + 3.1.w = 0$ or, $2 + 2z + 3w = 0$ …….(1)

And for Γ_2 and Γ_3 $1.1.2 + 2.1.z + 3.(-1)w = 0$

Or, $2 + 2z - 3w = 0$ …….(2)

On solving equation (1) and (2) we get $z = -1\ and\ w = 0$

Hence the final character table for C_{3v} group is

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

	E	**$2C_3$**	**$3\sigma_v$**	**linear functions, rotations**	**Quadratic functions**
$\boldsymbol{A_1}$	1	1	1	z	x^2+y^2,z^2
$\boldsymbol{A_2}$	1	1	-1	R_z	
E	2	-1	0	$(x,y),(R_x,R_y)$	$(x^2-y^2, xy)(xz,yz)$

Matrix representation of Ammonia: We know the matrix representation of NH_3 (C_{3v} group) is

$$E=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix};\quad C_3=\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix};\quad C_3^2=\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix};\quad \sigma_v=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}$$

$$\sigma_v'=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix};\quad \sigma_v''=\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}$$

Therefore $\Gamma_{3N} = 3\,A_1 + A_2 + 4\,E$

Translations are $\Gamma_x, \Gamma_y, \Gamma_z$ listed in the character table $\Gamma_T = A_1 + E$

Rotation are R_x, R_y, R_z listed in the character table $\Gamma_R = A_2 + E$

We know $\Gamma_{vib} = \Gamma_{3N} - \Gamma_T - \Gamma_R$

$\therefore \quad \Gamma_{vib} = 3\,A_1 + A_2 + 4\,E - A_1 + E - A_2 + E$

$\Gamma_{vib} = 2A_1 + 2E$

IR active modes have the same symmetry as the translational vectors, thus $\Gamma\,(IR) => \{A_1, E\}$

The Raman modes have the same symmetry as the binary functions, thus

$\Gamma\,(Raman) => \{A_1, E\}$.

Conclusion:

From the above we conclude that Ammonia is nonlinear molecule hence it has 3N-6 i.e $(3 \times 4 - 6) = 6$ fundamental modes of vibration .Since irreducible representation has same symmetry as x, y, z coordinate , therefore it is *IR* active. Also A_1 and E has component($x^2 + y^2$),($z^{2)}$, (x^2- y^2, xy)(xz,yz), therefore Ammonia is also *Raman* active.

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