

Group theory Character Table Enhancement by Introducing the Partial Molecular Symmetry Principle in the Molecular Spectroscopy

Ahmed S. Abdel-Rahman

Physics Department, Faculty of Science, Cairo University, Giza, Egypt.

Corresponding author: asabry@sci.cu.edu.eg

Group theory character table is a very useful tool to know important information about molecular activities and their spectra but suffers different defects such as the physical meaning of ω , the entire levels of degenerate states and the atomic motion through molecular vibration. On the way to define the infrared spectra, Raman spectra and natural frequency of molecules; it is important to split degenerate states and determine the motion of each atom through molecular vibration. While symmetry can be seen as the most basic and important concept in physics, the higher n -fold rotation axis C_n symmetry element can be represented as a full or partial symmetric rotation axis and governs other symmetry elements in the molecule through the vibrational motion. Symmetry states and Omega-table which hold all possible symmetry states of the molecule will solve the character table defects. Selection rules judge some of the symmetry states to be forbidden. Omega-table illustrates the relation between symmetry elements in the molecule through its translation, rotation and vibration processes and separates the degenerate states as well as can be reduced to point group character table. Based on omega-table, the description of the atomic motion of NH_3 molecule or any other molecules through vibration was so clear according to ω mathematical value and its physical meaning.

1. Introduction:

Molecules can be classified into point groups according to their symmetry elements. Molecules with similar symmetries are put into the same point group. Symmetry elements are mirror planes, axes of rotation (n -fold rotation axis), centers of inversion, etc.

On a given physical system, the eigenstate properties and the degeneracy of eigenvalues are governed by symmetry considerations. The symmetry properties

of each point group are summarized in a character table. Character table lists all symmetry elements of the group, along with a complete set of irreducible representations [1].

The point group character table is useful to investigate the polarity, chirality, orbitals used in σ bonds and symmetry properties of all molecular motions in molecules [1-4]. But suffers some defects in its construction, and they are:

- The physical and mathematical meaning of ω ,
- Combined symmetry elements,
- Degenerate states,
- Meaning of characters rather than ± 1 .

The character ω was very important as predicted by F. Hegelund *et al.* [5], it is the n -th root of unity and being a complex quantity:

$$\omega_n = e^{2\pi i/3} \quad (1)$$

Application of character table leads to define the infrared and Raman spectra relation to the different vibration modes, but cannot determine the spectrum frequency and intensity where character table fails to describe the atomic motion through molecular vibration. The application of character table and finding the corresponding spectral line in IR and Raman studies are investigated on many molecules [6-8].

In the present work, the physical definition of ω will be investigated besides the building of omega-table as the general case of character table, which solves character table defects and will show the vibration motion of each atom in ammonia molecule as the C_{3v} example in contrast with what is illustrated in [1,2].

2. Defects in the Character Table:

Table 1 shows the character table of the C_3 point group.

Table (1): Character table for the group C_3 .

	E	C_3	C_3^2
A	1	1	1
$E\{$	1	ω	ω^2
	1	ω^2	ω

2.1. Physical and Mathematical Meaning of ω

Some characters as in Table (1), take complex values (ω), its physical and mathematical meanings are not so clear. The mathematical meaning is not that its value but what is meant by character to be a complex quantity.

2.2. Combined Symmetry Elements

Some symmetry elements in character tables are combined in one column (such as $2C_3$ in the C_{3v} point group Table 2) and their characters represent collected values of its symmetry elements. The character table cannot illustrate each symmetry element value and then its case in molecular motions.

Table (2): Character table for group C_{3v} .

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

2.3. Degenerate States:

Some irreducible representations displayed in double or triple or higher degenerate states, E double degenerate state in the C_{3v} table 2, they do not show characters of the entire states.

2.4. Meaning of characters rather than ± 1

It is well known, Characters of +1 indicate that the basic function is unchanged by the symmetry operation. While characters of -1 indicate that the basic function is reversed. Another character indicates that the basis function undergoes a more complicated change.

3. Method

3.1 Symmetry elements in molecular motion

The symmetry elements such as mirror planes, axes of rotation, centers of inversion are defined clearly for static molecules [3,4]. The molecular motions (translation, rotation and vibration) will show new symmetry modes rather than static due to the mutual motion of atoms in the molecule. The three-fold axis in the C_{3v} point group (ammonia as an example) can be discussed in three classes. The normal full symmetry axis C_3 is shown in Fig. (1. a), where all atoms move in-phase. If one atom gets out from in-phase motion, the C_3 symmetry element is not completely saved but shows a mid-way class between full symmetric and asymmetric classes. And then displays a new order of symmetry, this is called partial symmetry state and shown in Fig. (1. b). It is important to consider the motion of Nitrogen atom to conserve the center of mass in front of the Hydrogen plan (the plan of the paper). The two in-phase motions (two hydrogen atoms) should have vibration paths to conserve the angle of the C_3 axis on 120° .

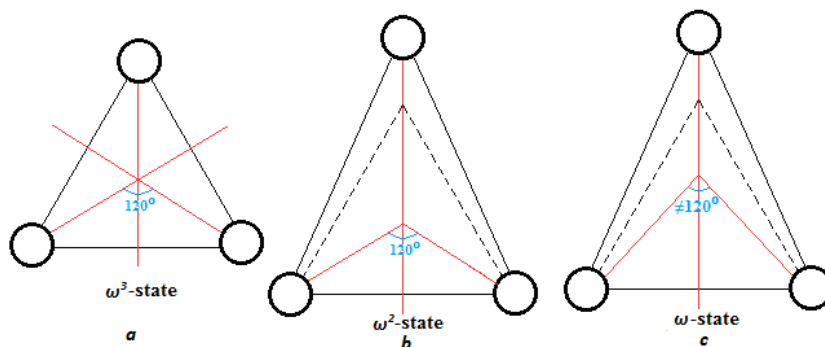


Fig. (1): The C_3 fold axis states in molecular motion. (a) Full symmetry state, (b) partial symmetry state and (c) asymmetry state.

But it is forbidden for the three atoms to lose their in-phase motion totally while they must show a little amount of symmetry such as breaking the C_3 angle condition only and keeping the two atoms on the same distance from rotation axis. Thus the C_3 axis disappears and this case is denoted by asymmetry state (Fig. 1. c).

Based on this hypothesis, the new concept can be defined as the n -fold axis has n symmetry states (these states are only applicable in the case of molecular vibration or generally in molecular motion). Two-fold rotation axis (or mirror plane and center of inversion) has two allowed states. First is the symmetric state while the molecule coincides itself through 180° rotation and other is the asymmetric state. The identity E is valid anyway and takes single state (symmetric state).

3.2 Omega Definition:

All symmetry elements in the molecule will be denoted mathematically by ω_n^m , while n is the index of omega and takes values $1, 2, \dots, 6$; m is the order of omega and takes the values $1, 2, \dots, n$ where omega ω is the n^{th} root of unity (Eq. 1). Mirror planes and center of inversion have the index $n=2$, while the n -fold axis has the index of n . The order of omega defines the symmetry ratio to the full symmetry state or in other words, $m=n$ is the full symmetric and $m=1$ is the asymmetric state.

3.3 Symmetry States:

As the molecular motions happen, all permutations of symmetry states are considered to form molecular symmetry states. Each symmetry element is labeled in a separate column while the rows will hold all possible permutations of omega values. Table (3) represents the molecular symmetry states for the C_{3v} point group and three mirror planes in the direction of the major three-fold rotation axis C_3 , the C_3^2 axis is the rotation axis as C_3 in the opposite rotation direction.

Table 3: C_{3v} symmetry States.

E	$C_3(z)$	$C_3^2(z)$	$\sigma_v(xz)$	σ_{v2z}	σ_{v3z}
ω_1	$\omega_3^3 / \omega_3^2 / \omega_3$	$\omega_3^3 / \omega_3^2 / \omega_3$	ω_2^2 / ω_2	ω_2^2 / ω_2	ω_2^2 / ω_2

$$\begin{aligned} \omega_1 &= e^{i2\pi/1} = 1 \\ \omega_2 &= e^{i2\pi/2} = -1, \omega_2^2 = e^{2i2\pi/2} = 1 \\ \omega_3 &= e^{i2\pi/3} = -\frac{1}{2} + i\frac{\sqrt{3}}{2}, \omega_3^2 = e^{2i2\pi/3} = -\frac{1}{2} - i\frac{\sqrt{3}}{2}, \omega_3^3 = e^{3i2\pi/3} = 1 \end{aligned} \quad (2)$$

Not of all these symmetry states are allowed for the molecule to hold, some of these states are forbidden and they can be determined by selection rules.

3.4. Selection Rules:

All permutations of omega values in the C_{3v} ω -table are 72 symmetry states; the main symmetry rotation axis judges the other symmetry elements' values throughout selection rules as following:

- 1- The opposite direction z-fold rotation axis (C_3^2) is, in reality, is the C_3 twice and then it must be equal to the square value of C_3 ω -value. So if any symmetry state has $C_3 = \omega_3^m$ and $C_3^2 \neq \omega_3^{2m}$, this state will be forbidden.
- 2- When the C_3 is in ω_3^3 -state (full symmetry) that defines two cases for lower elements (i.e. $3\sigma_v$). In the first case, all of these planes are symmetric, and the other case all of them are anti-symmetric, then this state is being degenerate to two mutual states as above A_1 and A_2 while A_1 the symmetric state called ω_a^3 -state and A_2 the symmetric/asymmetric state called ω_b^3 -state.
- 3- If the C_3 is in ω_3 -state (asymmetric state) that defines at least one symmetric state of lower elements ($3\sigma_v$); this is the asymmetric state called ω -state.
- 4- If the C_3 in ω_3^2 -state (partial symmetric state) this state requires one symmetric of the lower elements; this is the semi-symmetric/semi-symmetric state called ω^2 -state.
- 5- The application of selection rules on the C_{3v} ω -table reduces states from 72 to 4 allowed states as shown in Table (4). Table (5) illustrates the allowed states with their omega-equivalent values.

Table (4): The C_{3v} ω -table with all allowed/forbidden states.

	E	$C_3(z)$	$C_3^2(z)$	$\sigma_v(xz)$	σ_{v2z}	σ_{v3z}	State
A_1	ω_1	ω_3^3	ω_3^3	ω_2^2	ω_2^2	ω_2^2	allowed
A_2	ω_1	ω_3^3	ω_3^3	ω_2	ω_2	ω_2	allowed
E_1	ω_1	ω_3^2	ω_3	ω_2^2	ω_2	ω_2	allowed
E_2	ω_1	ω_3	ω_3^2	ω_2^2	ω_2	ω_2	allowed
	Else						forbidden

Table 5: The C_{3v} detailed ω -table.

	E	$\sigma_v(xz)$	$\sigma_v(yz1)$	$\sigma_v(yz2)$	$C_3(z)$	$C_3^2(z)$
A_1	1	1	1	1	1	1
A_2	1	-1	-1	-1	1	1
E_1	1	1	-1	-1	ω_3^2	ω_3
E_2	1	1	-1	-1	ω_3	ω_3^2

4. Results and Discussion:

3.1. Reducing Omega-table to Character Table:

Omega-table (Table 5) can be reduced to the well-known character table by merging the same type elements (columns) and degenerate states (rows) as following:

- 1- While the value of the C_3^2 axis just directly obtained from C_3 axis values, one can merge these two elements in one element ($2C_3$) and only mention the value of the C_3 axis.
- 2- The independent elements $\sigma_v(xz)$, $\sigma_v(yz1)$ and $\sigma_v(yz2)$ can be merged to one column ($3 \sigma_v$) by numerically adding uncommon values, where if there duplicated values are added the second value will be dropped; thus the result of combining the A_1 state is summing of three minus ones, the second and third minus ones will be dropped and the resultant is -1.

To get the character table (Table 2), one should represent real (non-imagery) values, where ω_3 and ω_3^2 should be disappeared. The two degenerate states E_1 and E_2 should be merged in one row called double degenerate state E, the same procedure in step 2 is applied to columns rather than identity while this column values summed in the regular method. Taking into account the imagery omega values will be disappeared where $\omega_3^2 + \omega_3 = -1$.

In this methodology, we can say omega-table is the generalized form of the character table and can be applied to describe information (like atomic vibration) that cannot be deduced from the character table.

3.2. Vibration Modes in Ammonia:

Character table can describe the vibration modes of ammonia by finding the reducible representation Γ_{3N} and reduce it to irreducible representations [1,9,10].

Decomposition theory can be applied to Table (2) as:

$$\chi_{A_1}(\Gamma_{3N}) = \frac{1}{6}[12 + 0 + (3 \times 2)] = 3$$

$$\chi_{A_2}(\Gamma_{3N}) = \frac{1}{6}[12 + 0 - (3 \times 2)] = 1$$

$$\chi_E(\Gamma_{3N}) = \frac{1}{6}[24 + 0 + 0] = 4$$

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

$$\Gamma_{\text{trans}} = A_1 + E$$

$$\Gamma_{\text{rot}} = A_2 + E$$

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

while $E = E_1 + E_2$,

$$\Gamma_{\text{vib}} = 2A_1 + 2E_1 + 2E_2 \tag{3}$$

3.3. Stretching Vibration and Atomic Motion

By the same algorithm of decomposition, stretching and bending modes can be found; considering the stretching vibration modes:

$$\Gamma_{\text{stretches}} = A_1 + E_1 + E_2 \tag{4}$$

Stretching vibration mode is associated with the motion of atoms along with their bonds between them; but also creating change in the angle between bonds. The simplest stretching case for ammonia is that all hydrogen atoms move directly towards N-atom along their N-H bonds, and then nitrogen atom should move perpendicular to H atoms plane towards the center c to reserve center of mass (Figs 2 and 3) and thus the angles between bonds will be changed.

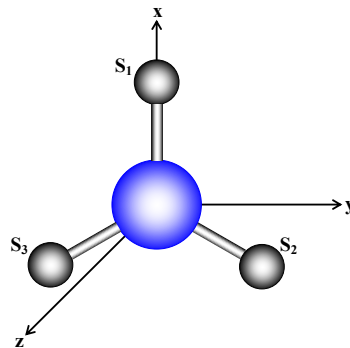


Fig. (2): Stretching vibration in Ammonia.

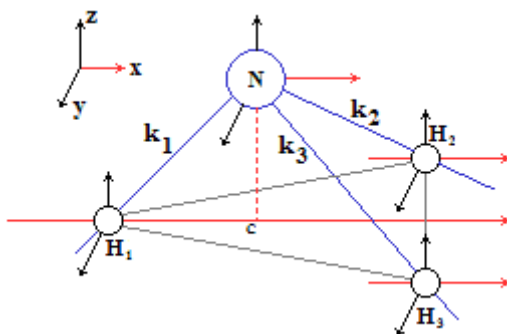


Fig. (3): Stretching vectors in Ammonia.

The reducible representation ($\chi_{A_1}(Q_{S1})$) for the stretching mode A_1 from the S_1 atom is:

$$\chi_{A_1}(Q_{S1}) = \frac{1}{6}[S_1 + S_2 + S_3 + S_1 + S_2 + S_3] = \frac{1}{3}[S_1 + S_2 + S_3] \quad (5)$$

This represents a simple symmetric stretching mode A_1 , where all atoms move in regular motion with constant amplitude along with their bonds.

$$\begin{aligned} \chi_{E_1}(Q_{S1}) &= \frac{1}{6}[S_1 + \omega_3^2 S_2 + \omega_3 S_3 + S_1 - S_2 - S_3] = \frac{1}{6}[2S_1 + (\omega_3^2 - 1)S_2 + (\omega_3 - 1)S_3] \\ &= \frac{1}{6}\left[2S_1 + \left(-\frac{3}{2} - i\frac{\sqrt{3}}{2}\right)S_2 + \left(-\frac{3}{2} + i\frac{\sqrt{3}}{2}\right)S_3\right] \end{aligned} \quad (6)$$

This vibration mode E_1 formed of moving S_1 atom $1/3$ points in $+x$ direction (along bond; i.e. \mathbf{k}_1 -vector in Fig. 3) while S_2 atom moves $1/4$ points in $-x$ -direction (\mathbf{k}_2) and $\sqrt{3}/12$ points in $-y$ -direction (perpendicular to the bond \mathbf{k}_2 -vector), S_3 atom moves $1/4$ points in $-x$ -direction (\mathbf{k}_3) and $\sqrt{3}/12$ points in $+y$ direction (perpendicular to the bond \mathbf{k}_3 -vector).

To get the equation of motion of each atom, we choose the axis x to be set in the direction of an active mirror plane ($\sigma_{v,xz}$ in Table 5). \mathbf{k} vector is the stretching vector of each bond toward the N atom.

Taking the projection of the molecule on xy -plan (the plan holds all hydrogen atoms) and nitrogen atom in front of the page as shown in Fig. (4) while the black circles define the static location of Hydrogen atoms and denoted by H while the gray circles define the atom location at maximum amplitude and denoted by H'.

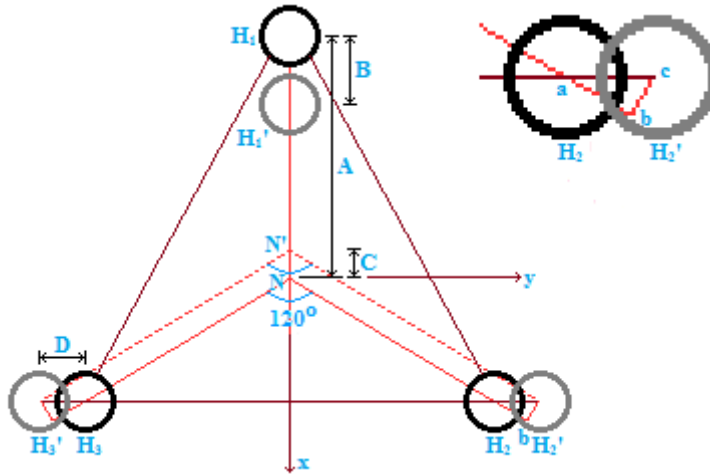


Fig. (4): Ammonia molecule projection on xy-plan.

The motion of H_2 is $-3/2-i\sqrt{3}/2$ or in other words $3/2$ in the direction of k_2 vector (projection is **ab**) and $\sqrt{3}/2$ in the perpendicular direction (projection is **bc**), it is clear that the motion of H_2 and H_3 atoms lie in the y-direction outwards to each other to keep the angle to the N-atom (N') 120° through vibration and hence partial symmetry of C_3 axis was saved. While the atoms H_1 , H_2 , H_3 , and N have their vibration amplitudes (xy-plane projection) as B , D , D , and C , respectively and they share the same frequency of vibration. And A represents the NH bond projection on **xy**-plane.

The stretching equation (6) describe the motion of atoms; H_1 moves stretching towards N atom, while H_2 and H_3 move to expand each other, the x component of H_2' can be calculated by two methods:

1) The motion of H_2' atom is being in the y-direction and hence the x-component should be same as H_2 atom, or $x[H_2'] = x[H_2] = A \sin 60 = A/2$

$$2) \quad x[H_2'] = \frac{1}{2}[N'H_2'] - C = \frac{1}{2}\left[\frac{C}{2} + A + \frac{\sqrt{3}}{2}D\right] - C = -\frac{3}{4}C + \frac{1}{2}A + \frac{\sqrt{3}}{4}D \quad (7)$$

Now, these values must be equal, and then:

$$\frac{D}{C} = \sqrt{3} \quad (8)$$

This equation relates the amplitude of vibration of atoms H_2 (or H_3) to N atom; while the motion of Nitrogen atom defined from the molecule center of mass which is kept at constant location ($z=0.31426\text{\AA}$ above c-point) through the molecule vibration, i.e. N atom moves in $-x$ -direction, x_{cm} represents the x-component of center of mass, Hydrogen atoms are set in the order illustrated in Fig. (4):

$$x_{cm} = \frac{1}{M} \sum_i x_i m_i = \frac{1}{(3H + N)} \left[(-A + B)H + \left(\frac{A}{2}\right)H + \left(\frac{A}{2}\right)H - CN \right] = 0 \quad (9)$$

$$\frac{B}{C} = \frac{N}{H} \quad (10)$$

And hence;

$$\frac{B}{D} = \frac{1}{\sqrt{3}} \frac{N}{H} \quad (11)$$

In ammonia, the H₁ atom vibrated with x-component of amplitude 14 times than Nitrogen vibrates, and 8.08 times than other Hydrogen atoms vibrates.

E₂ stretching mode is typical to the E₁ mode but the atoms H₂ and H₃ move towards each other to keep σ_{v1} but do not verify the C₃ rotation condition where the angle between H₂cH₃ is not 120°.

$$\begin{aligned} \chi_{E_2}(Q_{S1}) &= \frac{1}{6} [S_1 + \omega_3 S_2 + \omega_3^2 S_3 + S_1 - S_2 - S_3] = \frac{1}{6} [2S_1 + (\omega_3 - 1)S_2 + (\omega_3^2 - 1)S_3] \\ &= \frac{1}{6} \left[2S_1 + \left(-\frac{3}{2} + i\frac{\sqrt{3}}{2}\right)S_2 + \left(-\frac{3}{2} - i\frac{\sqrt{3}}{2}\right)S_3 \right] \end{aligned} \quad (12)$$

3.4. Bending Vibration and Atomic Motion

The bending vibration motion is associated with the change of bond angles and may be classified into two classes; in-plane and out-of-plane motions. In the case where Hydrogen atoms move towards each other in H-plane, the Nitrogen atom is not moved, and bond angles decrease simultaneously (vibration mode A₁), see Fig. (5).

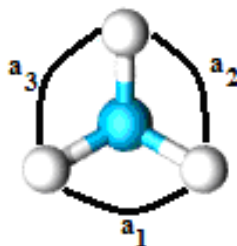


Fig. (5): Bending vibration in Ammonia.

$$\text{and } \Gamma_{\text{ip}} + \Gamma_{\text{oop}} = A_1 + E$$

$$\Gamma_{\text{bends}} = \Gamma_{\text{vib}} - \Gamma_{\text{stretches}} = A_1 + E = A_1 + E_1 + E_2 \quad (13)$$

$$\chi_A(Q_{a1}) = \frac{1}{6}[a_1 + a_3 + a_2 + a_1 + a_2 + a_3] = \frac{1}{3}[a_1 + a_2 + a_3]$$

$$\chi_{E1}(Q_{a1}) = \frac{1}{6}[a_1 + \omega_3^2 a_2 + \omega_3 a_3 + a_1 - a_2 - a_3] = \frac{1}{6}\left[2a_1 + \left(-\frac{3}{2} - i\frac{\sqrt{3}}{2}\right)a_2 + \left(-\frac{3}{2} + i\frac{\sqrt{3}}{2}\right)a_3\right]$$

$$\chi_{E2}(Q_{a1}) = \frac{1}{6}[a_1 + \omega_3 a_2 + \omega_3^2 a_3 + a_1 - a_2 - a_3] = \frac{1}{6}\left[2a_1 + \left(-\frac{3}{2} + i\frac{\sqrt{3}}{2}\right)a_2 + \left(-\frac{3}{2} - i\frac{\sqrt{3}}{2}\right)a_3\right]$$

The bending mode E_1 just like the E_1 stretching mode but the atoms move in H's plane, also E_2 mode like the stretching one.

Symmetric state A_1 : This vibration state is symmetric and the vibration motions are shown in Fig. (6).

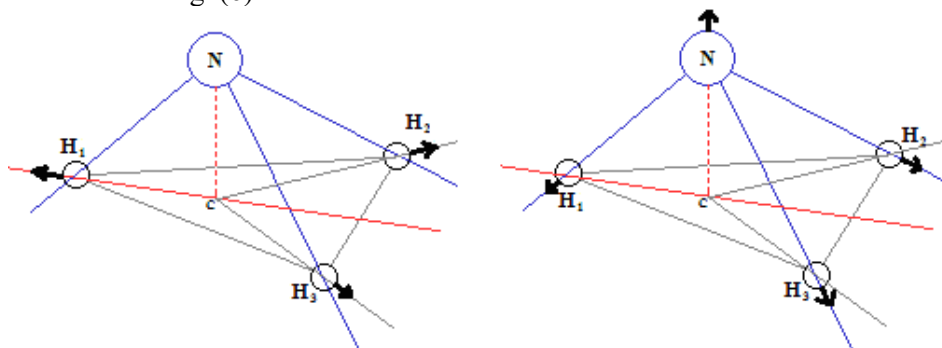


Fig. (6): A_1 vibration modes in Ammonia.

Degenerate state E_1 : While this state partially loses the C_3 rotation state (Fig. 7), the bond angle H_2cH_3 is always 120° , and the bond lengths of cH_2 and cH_3 are equally in all these vibration motions.

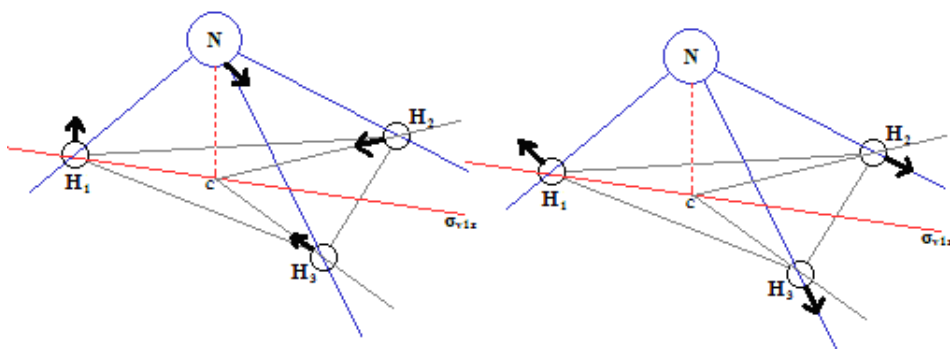


Fig. (7): E_1 vibration modes in Ammonia.

Degenerate state E_2 : While this state loses the C_3 axis and all vertical mirror plans except $\sigma_v(xz)$. The bond angle H_2cH_3 is not saved at 120° and then C_3 rotation lost (Fig. 8).

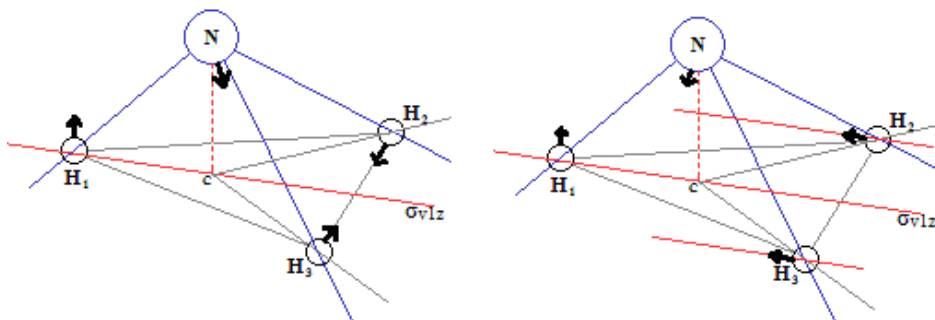
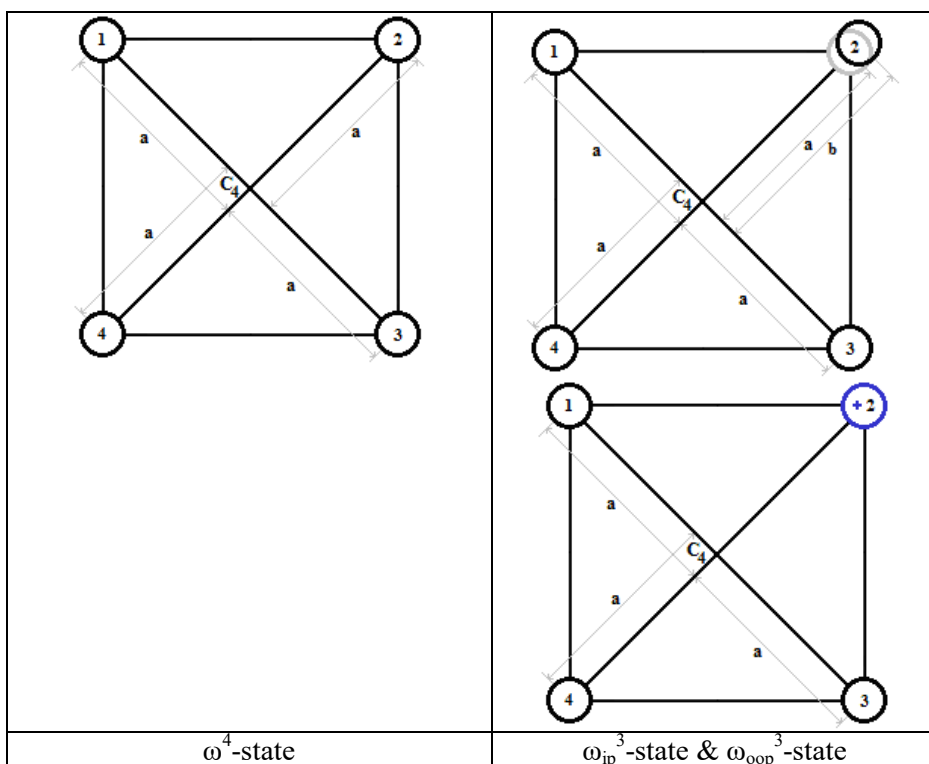
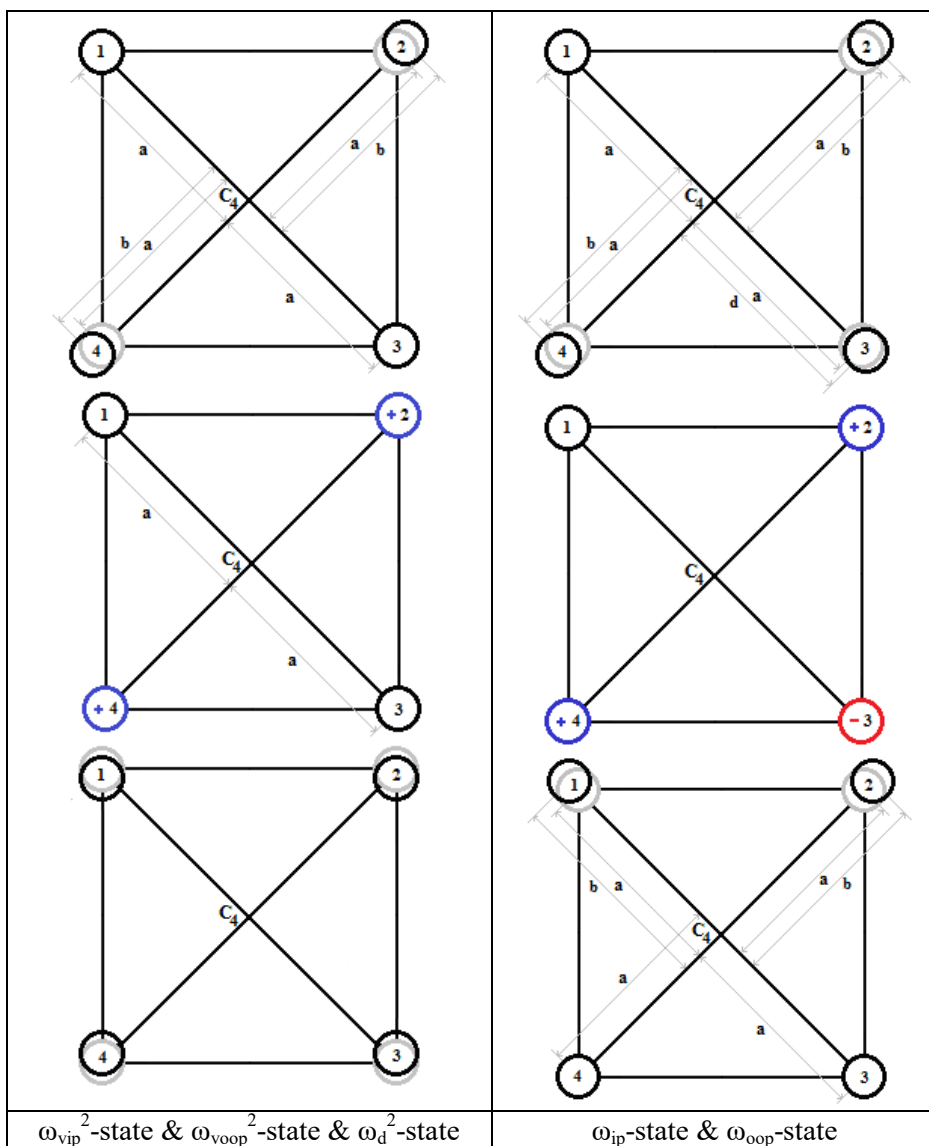


Fig. (8): E_2 vibration modes in Ammonia.

On the same methods, C_4/C_{4v} point groups can be treated (but requires more restrictions in selection rules) and resulting in the vibration modes shown in Table (6). This point is postponed to future work. The Gray circles represent in-plane motion while signs (+/-) represent out-of-plane in-front/behind the page plane.

Table (6): ω states for C_4/C_{4v} point groups.





4. Conclusion

The concept of partial symmetry is the base of defining the vibrational symmetry states which differs than static one where each symmetry element can possess various levels depending on its order, the building of Omega-table upon the combined vibrational symmetry states and by application of selection rules result in separation the degenerate states and these tables can be reduced to point group character tables. The discussed method of atomic motion shows how molecule partially loses its symmetry but must possess at least very low symmetry value in the lowest symmetry state

Omega-table describes the atomic motion of the molecule through vibration according to ω mathematical value and its physical meaning. Then the usage of field theory may discuss the molecular IR and Raman spectra frequency and intensity.

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