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Construct the Character Table of D_{7h} Point Group and Apply it for Classify the (3N-6) Modes of Vibration for the [7] Cyclacene (Linear) Monoring Molecule

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Abstract

The character table or the table of eigen values for the D_{7h} point group, which is not found in the literature was constructed. The constructed table is used to classify all modes of the vibrational frequencies of the IR and Raman spectra for any compound or molecule that has the D_{7h} symmetry in the Point Group. For that, it was used for classifying all the modes of vibrational frequencies of the [7] cyclacene (linear) monitoring molecule, possessing D_{7h} symmetry. The constructed table was used to classify the symmetry species for the total degrees of freedom, total degrees of transition, total degrees of rotation and for the total degrees of modes of vibration (3N-6) for this tube. The character table was also used to determine the active and inactive modes of vibration in the IR and Raman spectra. Also, determining the polarized and non-polarized vibrational frequencies in the Raman spectrum, and used for describing the complete physical structure of the studied molecule after extracting its geometric shape. The methods of quantum mechanics calculations PM3 and DFT were used for this purpose applying the Gaussian 09 program.

Keywords: Character table, monoring molecule, modes of vibration, PM3, DFT.

بناء جدول القيم الذاتية لمجموعة النقطة D_{7h} وتطبيقه لتصنيف أنماط الحركة الاهتزازية بعدد

(3N-6) لانبوب نانوي احادي الحلقة (جزئية سايكلاسين 7)

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الخلاصة

تم بناء جدول القيم الذاتية (character table) لمجموعة النقطة D_{7h} غير موجود في الادبيات، المعتمد عليه عند استخراج تماثلات الانماط الاهتزازية، والذي يمكن الاستفادة منه لغرض استخراج وتصنيف جميع انماط الحركة الاهتزازية في طيف الاشعة تحت الحمراء و طيف رامان لأي مركب أو جزئية تمتلك التماثل D_{7h} في مجموعة النقطة (Point Group). وقد تم تطبيقه على انبوب نانو احادي الحلقة نوع zig zag (جزئية سايكلاسين 7) يمتلك التماثل D_{7h} ، ومنه أمكن استخراج الاصناف التماثلية لدرجات الحرية الكلية و لدرجات الحرية للحركات الدورانية و لدرجات الحرية للحركات الانتقالية و لدرجات الحرية لانماط الحركة الاهتزازية بعدد (3N-6) لهذا الانبوب. أيضا أمكن من خلاله تحديد أنماط الترددات الفعالة وغير الفعالة في طيفي IR و رامان و انماط الترددات الاهتزازية المستقطبة و غير المستقطبة في طيف رامان. أمكن أيضا وصف الصورة الفيزيائية التامة لهذا الانبوب بعد استخراج الشكل الهندسي التوازني لهذا الانبوب وفق طريقة حسابات ميكانيك الكم DFT وباستخدام برنامج Gaussian 09 وفقا لتماثله من أطوال وزوايا التآصر والقيم الطاقية وتوزيع الشحنات.

Introduction

Each molecule has a Symmetry Group that specifies ownership or non-possession of the five symmetry elements: E (Identity), the proper rotation axis (n), the level of symmetry (the plane of symmetry), the axis of rotation (rotation reflection axis) (n) and inversion center (i). The group is similar to symbols called SchÖnflies symbols, such as C_1 , C_{2v} , D_{2h} ...etc [1-2]. Each point group returns all the molecules that have the same analog geometrical form, the same symmetry elements. Using the Character Table in the literature [3] and the Molecular Group, the undifferentiated analog type can be assigned to a particular vibration pattern [4-5], where $3N-6$ is produced from the basic vibrational patterns of each nonlinear molecule. The effectiveness of these patterns can also be determined in the Raman IR spectra. These patterns are polarized or nonpolarized in the Raman spectra and are located relative to the surface of symmetry, as they are at the surface level of symmetry. In case the molecule has a homogeneous surface (σ_h) [6].

The idea of symmetry is familiar, and the relationship of the symmetry of an object to its aesthetic appeal has been understood from the earliest ages. The aim of the scientist was to make the idea of symmetry quantitative so that they could use the symmetry properties of a molecule to simplify many of the problems concerning the structure (internal coordinates of bonds and angles) of molecules. Symmetry dealing mainly with applications that concern isolated, finite molecules, but the extension to objects that can be regarded as infinite (e.g., crystal lattices) is not difficult. It is possible to classify the symmetry of any molecule in terms of the symmetry operations that can be carried out on that molecule. It could be seen that symmetry operations involve;

1-the rotation (a simple rotation or a proper rotation) of the molecule about a certain axis, a rotation axis is given the symbol C_n , where n is an integer, and $(360/n)$ is the minimum rotation necessary to give an equivalent configuration (such an axis is said to be an n -fold axis or an axis of order n).

2-The mirror planes of the molecule (including horizontal planes of symmetry σ_h , so called because it is perpendicular to the main axis or axis of the highest order, a vertical planes of symmetry σ_v , contains the highest order axis of the molecule or any object. Such planes are known as dihedral planes, σ_d , if they bisect the angles between the σ_v planes or bisect the angles between two secondary axes of C_2).

3-The center of inversion of the object (including the identity as a special case of rotation by 0° or 360°) or reflections. The operation of inversion can be regarded as a composite movement comprising rotation by 180° and reflection in a plane perpendicular to this axis. The symmetry operation of improper rotation consists of a clockwise rotation about an axis, followed by a reflection in a plane perpendicular to the axis.

4- The associated symmetry element is a rotation-reflection axis (sometimes known as an alternating axis of symmetry). The symbol for such an axis is S_m where the angle of rotation is $(360/n)^0$, and the operation of rotation by $(m \times (360/n))^0$ with m reflections in the perpendicular plane is given the symbol S_n^m .

5- Finally, the identity of the object E , which could be regarded as rotation by 360^0 . The essential property of such operations is that they bring the object into an equivalent configuration. Such a configuration cannot be distinguished from the original one, but it need not be identical with it, as some equivalent parts of the object may have been interchanged.

The symbols for point groups (the collections of symmetry operations possessed by molecules) used usually are the SchÖnflies symbols; these are used in most applications of group theory, except crystallography, where an alternative nomenclature, the international system, is used [7-9].

The Utilized Programs

Both Gaussian 09 program of Pople et al. [10] and the Molek9000 program of P. Bischof, Heidelberg, were applied throughout the present work.

Results and discussion

The intrinsic value table of the D_{7h} group was built on the knowledge of the exact concept of the elements and processes of symmetry that belong to this group, from the knowledge of the supposed number of symmetries, the nature of the returned analogue items and the analogue classes of rotational and transitional movements, Spectral infrared and spectrum Raman. The construction of this table also requires a deep knowledge of the concept of symmetries, which include vibrational patterns located at the surface of the molecule and outside, and the determination of the rotation angle of the axes. It is also very important to predict the intrinsic values produced by the transformation matrix solution for

the symmetry operations of the point set concerned. The constructed table below represents all of the expected symmetry elements and operations represented for the D_{7h} point group.

Table 1- The constructed character table of D_{7h} point group

D_{7h}	E	$2C_7$	$2C_7^2$	$2C_7^3$	$7C_2$	σ_h	$2S_7$	$2S_7^3$	$2S_7^5$	$7\sigma_v$	IR	Raman
A'_1	1	1	1	1	1	1	1	1	1	1		x^2-y^2, z^2
A'_2	1	1	1	1	-1	1	1	1	1	-1	R_z	
E'_1	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	T_x, T_y	
E'_2	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0		
E'_3	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0		x^2-y^2, xy
A''_1	1	1	1	1	1	-1	-1	-1	-1	-1		
A''_2	1	1	1	1	-1	-1	-1	-1	-1	1	T_z	
E''_1	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	-2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	R_x, R_y	xz, yz
E''_2	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	-2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0		
E''_3	2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0	-2	$\frac{2\cos 360/7}{360/7}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	$\frac{2\cos 360/7 \times 3}{360/7 \times 3}$	0		

Where

D_{7h} : Schönflies symbol (Point group).

E: The identity

C_7, C_2 : The symmetry axes of proper rotation

S_7 : The symmetry axis of improper rotation (rotation-reflection axis).

σ_h : The horizontal plane of symmetry.

σ_v : The vertical plane of symmetry.

IR: Infra-red (the active modes of vibration in Infra-red spectrum).

Raman: (the active modes of vibration in Raman spectrum).

A: One dimension matrix.

E: Two dimension matrix

$A'_1, A'_2, E'_1, E'_2, E'_3$: Symmetry species with respect to σ_h (irreducible representations of Mulliken symbols).

$A''_1, A''_2, E''_1, 9E''_2, E''_3$: Antisymmetry species with respect to σ_h (irreducible representations of Mulliken symbols).

R_x, R_y, R_z : Rotation toward x, y and z axis respectively.

T_x, T_y, T_z : Translation toward x, y and z axis respectively.

x^2-y^2, z^2 : For polarized symmetry species,

x^2-y^2, xy, xz, yz : For depolarized symmetry species.

There aren't found the symmetry species labels from the results calculations of D_{7h} point group. This is where the projection operator comes in. The formula for a projection operator is:

$$a_i = \frac{1}{g} \sum n X_R X_i \quad (1)$$

Where a_i is the projection operator for the irreducible representation, or the number of the symmetry species.

g : is the number of symmetry operations for the concerned point group.

n : the number of repeatable of the symmetry operation.

X_R : is the character of operation R in the irreducible representations/ un-shifted atoms.

X_i : is the transformation number.

In practice, we need to take one of the basis vectors (or functions) and carry out all of the symmetry operations of the point group on that vector (or function). Then we multiply the result for each symmetry operation by the character of that operation in the irreducible representation for which we are forming the symmetry species. Finally, these products are all summed, and the result gives the required total degree of freedom (Γ_{tot}).

For the [7] cyclacene (linear) monoring molecule Figure-1, the number of the symmetry species can be calculated depending on the constructed character table of D_{7h} point group and by applying equation 1 [1, 2] on the geometrical structures of the studied molecule:

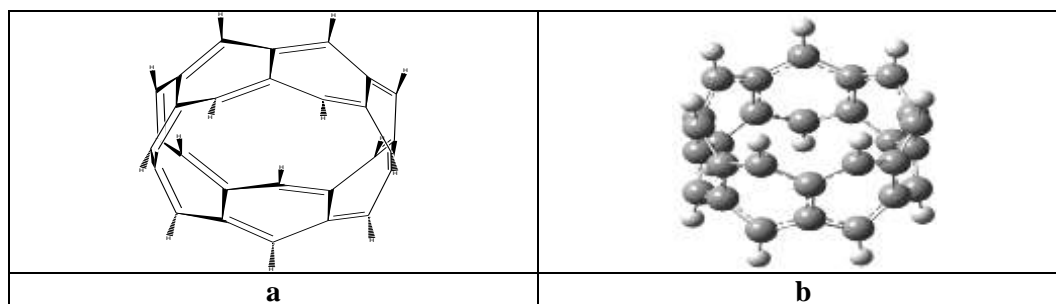


Figure 1- Equilibrium geometry structure of [7] cyclacene (linear) monoring molecule: a) Two dimensions, b) Three dimensions

$$a_{(\dot{A}1)} = (1/28)[(3 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (7 \times 6 \times 1 \times 1)] = (126 + 42)/28 = 168/28 = 6Q \text{ (normal coordinates for the vibration frequencies)}$$

$$a_{(\dot{A}2)} = (1/28)[(3 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (7 \times 6 \times 1 \times (-1))] = (126 - 42)/28 = 84/28 = 3 = 1A'_2(R_z) + 2Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}1)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9 = 1\dot{E}_1(T_x, T_y) + 8Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}2)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}3)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9Q \text{ (vibration frequencies)}$$

$$a_{(A''1)} = (1/28)[(3 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (-42)] = (126 - 42)/28 = 84/28 = 3Q \text{ (vibration frequencies)}$$

$$a_{(A''1)} = (1/28)[(3 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (-42)] = (126 - 42)/28 = 84/28 = 3Q \text{ (vibration frequencies)}$$

$$a_{(A''2)} = (1/28)[(3 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (7 \times 6 \times 1 \times (+1))] = (126 + 42)/28 = 3 = 1A''_2(T_z) + 5Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}''1)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9 = 1\dot{E}''_1(R_x, R_y) + 8Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}2)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9Q \text{ (vibration frequencies)}$$

$$a_{(\dot{E}3)} = (1/28)[(3 \times 2 \times 42 \times 1 \times 1) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0) + (0)] = (126 \times 2)/28 = 9Q \text{ (vibration frequencies)}$$

The net results are:

$$\Gamma_{tot} = 3N = 3 \times 42 = 126$$

$$\Gamma_{tot} = 6A'_1 + 3A'_2 + 9\dot{E}_1 + 9\dot{E}_2 + 9\dot{E}_3 + 3A''_1 + 6A''_2 + 9\dot{E}''_1 + 9\dot{E}''_2 + 9\dot{E}''_3$$

Γ_{tot} : Total degrees of freedom.

N: Number of atoms of the calculated molecule.

Γ_{Rot} : Total degrees of rotation.

$$\Gamma_{Rot} = A'_2(R_z) + \dot{E}''_1(R_x, R_y) = 3$$

$$\Gamma_{Trans.} = 1A''_2(T_z) + 1\dot{E}_1(T_x, T_y) = 3$$

$\Gamma_{Trans.}$: Total degrees of translation

$\Gamma_{vib.}$: Total degrees of vibration

$$\Gamma_{vib.} = \Gamma_{tot} - (\Gamma_{Rot} + \Gamma_{Trans.}) = 3N - 6 = 126 - 6 = 120$$

$$\Gamma_{vib.} = 6A'_1 + 2A'_2 + 8\dot{E}_1 + 9\dot{E}_2 + 9\dot{E}_3 + 3A''_1 + 5A''_2 + 8\dot{E}''_1 + 9\dot{E}''_2 + 9\dot{E}''_3 = 120$$

$\Gamma_{+\sigma h}$: Symmetric modes of vibrations (with respect to σh).

$$\Gamma_{+\sigma h} = 6A'_1 + 2A'_2 + 8\dot{E}_1 + 9\dot{E}_2 + 9\dot{E}_3 = 60$$

$\dot{\prime}$: In-plane of the molecule.

$\Gamma_{-\sigma h}$: Asymmetric modes of vibrations (with respect to $+\sigma h$).

$$\Gamma_{-\sigma h} = 3A''_1 + 5A''_2 + 8\dot{E}''_1 + 9\dot{E}''_2 + 9\dot{E}''_3 = 60$$

$\dot{\prime\prime}$: Out-of-plane of the molecule.

To study the vibration motions of [7] cyclacene monoring molecule, one has to define its geometric parameters and has to distinguish between the axial CC_a (C-C_{axial}) and circumferential CC_c (C-C_{circumferential}) bonds. Figure-2, Table-2. This was done after calculating the geometrical optimization of

the molecule using PM3 and DFT method with the level of (B3LYP/ 6-31G and 6-311G bases set) [11-17]. Table 1 shown the following relationship:

- Length of circumferences bonds < length of axial bonds.
- K (force constant) of the circumferences bonds > K (force constant) of the axial bonds.
- Zero value of cis dihedral angle bonds for CCCC indicates that the surface included carbon atoms is a planar surface, unlike the surface included the CCCH atoms, it is not planar surface (of different values than zero for its cis dihedral angle bond).
- Lower value for $\Delta E_{\text{HOMO-LUMO}}$ of the [7] cyclacene nanotube molecule indicates to be a very good conductor for electronic charge [18].

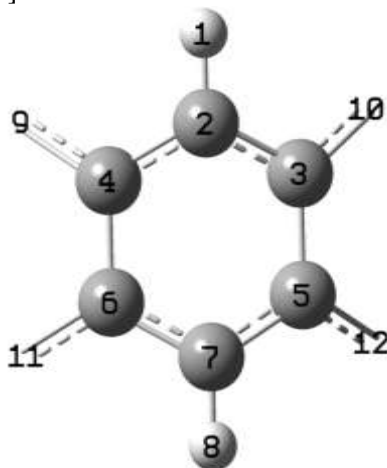


Figure 2- Repetitive sections of bonds and angles of [7]cyclacene (zigzag or linear); monoring molecule of D_{7h} point group, with the numbering of atoms

Table 2- PM3 and DFT calculations of the bond distances, angles, dihedral angles and some of the physical properties of the linear [7]cyclacene monoring molecule.

Bond length (Å) and bond angles (deg.) and dihedral angle bond (deg.) description	PM3	DFT [19-21] B3LYP/ 6-31G	DFT [19-21] B3LYP/ 6-311G
C2-H1	1.09539	1.08670	1.08341
C2-C3, C2-C4 (circumferences bonds)	1.40838	1.41815	1.41564
C3-C5, C4-C6 (axial bonds)	1.44490	1.47358	1.47347
<C3C2H1, <C4C2H1	118.19543	118.19189	118.19539
<C3C2C4	117.59046	117.44495	117.59047
<H1C2C3C5(trans)	-178.06437	-178.06437	-178.06513
<H1C2C3C10 (cis)	31.72869	23.23397	23.23212
<C2C4C6C11, < C2C3C5C12 (trans)	-157.80963	-154.71581	-154.64502
<C2C3C5C7, < C2C4C6C7 (cis)	0.0000	0.0000	0.0000
Molecular formula	$C_{28}H_{14}$		
Point group	D_{7h}		
M.wt. (gm/mol)	350.4		
ΔH_f^0 (kcal/mol)	340.074	-----	-----
E_{total} (a. u)	1075.07816	-1075.78040	-1075.07816
Electronic energy (eV)	-32416.59007	-----	-----
Ionization potential (eV)	4.4323	4.1443	4.43229
E_{HOMO} (eV)	-6.9296	-4.1443	-4.43229
E_{LUMO} (eV)	-2.5028	-2.5021	-2.82134
$\Delta E_{\text{HOMO-LUMO}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	4.4268	1.6422	1.6109
Dipole moment (Debye)	0.0000	0.0000	0.0000
Diameter (Å)	5.57186	5.63296	5.62630
Length (Å)	4.97913	5.00636	4.99476

Classification of vibration frequencies

The infrared spectrum of the (3N-6) normal modes of vibration for the [7] cyclacene monoring molecule was calculated and classified (symmetrically and equivalently) according to the character table of D_{7h} point group. They are 60 ($2A'_2, 6A'_1, 9E'_3, 9E'_2, 8E'_1$) symmetric modes of vibrations (with respect to σ_h) and 60 ($6A''_2, 2A''_1, 9E''_3, 9E''_2, 8E''_1$) asymmetric modes of vibrations (with respect to σ_h), Table 3. Relative to the σ_h reflection the modes of vibration are classified to:

a- Modes of vibrations with ($+\sigma_h$) symmetry operation

They are 60 modes of vibration in number, of which 18 are Raman active ($6A'_1$ (*polarized*) + $9E'_3$ (*depolarized*)), and 16 IR active ($8E'_1$). The rest are both IR and Raman inactive.

$$\Gamma_{+\sigma_h} = 6A'_1 + 2A'_2 + 8E'_1 + 9E'_2 + 9E'_3 = 60$$

$\Gamma_{+\sigma_h}$: Symmetric modes of vibrations (with respect to $+\sigma_h$).

They are classified as the following:

The (C-H) stretching vibrations

They are 14 modes of vibration. The frequency values range from (3066-3067 cm^{-1}) on using PM3 method, and range from (3056-3066 cm^{-1}) on using DFT method Table 3, showing the following correlations:

$$v_{\text{sym}}(\text{CH str.})(3066\text{cm}^{-1}) < v_{\text{asym}}(\text{CH str.})(3067\text{cm}^{-1}) \text{ (PM3)}$$

$$v_{\text{sym}}(\text{CH str.})(3066\text{cm}^{-1}) > v_{\text{asym}}(\text{CH str.})(3056\text{cm}^{-1}) \text{ (DFT)}$$

The highest intensity is (70.6065 km/mol) for ν_{64} .

The CC stretching vibrations

They are 13 modes of vibration of (Nc-1) in number, where Nc: is the number of carbon atoms in the molecule. The frequency values range from (1638-1681 cm^{-1}) on using PM3 method, and range from (1584-1474 cm^{-1}) on using DFT method Table 3, showing the following correlations:

$$v_{\text{sym}}(\text{CC str.})(1659\text{cm}^{-1}) < v_{\text{asym}}(\text{CC str.})(1661\text{cm}^{-1}) \text{ (PM3)}$$

$$v_{\text{sym}}(\text{CC str.})(1515\text{cm}^{-1}) > v_{\text{asym}}(\text{CC str.})(1507\text{cm}^{-1}) \text{ (DFT)}$$

The highest intensity is (1.4881km/mol) for ν_{11-12} , Table-3.

Ring (CCC) stretching vibrations

The CCC modes of vibration (unlike the C-C vibration modes), are not located at definite C atoms as can be seen from the atomic displacement vectors Figure-2. Their frequencies are usually lower than those of C-C vibration modes.

According to the calculated results, the range of these frequencies is (1402-1600 cm^{-1}) on using PM3 method, and range from (1387-1411 cm^{-1}) on using DFT method. The highest intensity is (45.1853 km/mol) for ν_{65} , Table-3.

The bending (δCH) vibrations

They are 14 modes of vibration of (N_H) in number, where N_H is the number of hydrogen atoms in the molecule. The frequency values range from (1121-1337 cm^{-1}) on using PM3 method, and range from (1035-1311 cm^{-1}) on using DFT method. The highest intensity is (2.8088km/mol) for ν_{15-16} , Table-3.

The bending (δCCC) vibrations

The frequency values range from (492-1419 cm^{-1}) on using PM3 method, and range from (488-1321 cm^{-1}) on using DFT method. The highest intensity is (0.0974km/mol) for ν_{19-20} , Table 3.

b- Modes of vibrations with ($-\sigma_h$) symmetry operations

They are 60 modes of vibration in number, of which 18 are Raman active ($8E''_1$ (*depolarized*)), and 5IR active ($5A''_2$). The rest are both IR and Raman inactive.

$\Gamma_{-\sigma_h}$: Asymmetric modes of vibrations (with respect to $-\sigma_h$).

$$\Gamma_{-\sigma_h} = 3A''_1 + 5A''_2 + 8E''_1 + 9E''_2 + 9E''_3 = 60$$

They are classified as the following:

The (γCH) out of plane of the molecule bending vibrations

They are 14 modes of vibration. The frequency values range from (859-996 cm^{-1}) on using PM3 method, and range from (851-957 cm^{-1}) on using DFT method. The highest intensity is (275.5610 km/mol) for ν_{17-18} , Table-3.

The (γCC) and (γCCC) out of plane of the molecule bending vibrations

They have the lowest values for modes of vibration. The frequency values range from (146-821 cm^{-1}) on using PM3 method, and range from (151-801 cm^{-1}) on using DFT method. The highest intensity is (40.6089km/mol) for ν_{21-22} , Table-3.

The intensity for the active modes of vibration is obtained only for the IR spectrum when using the Gaussian calculations program. Figure-3 shown the graphical pictures of some vibration modes for [7]cyclacene (zigzag) nanotube molecule as calculated applying the DFT (B3LYP/ 6-31G) method. Scheme 1 shows the IR spectrum for [7]cyclacene (zigzag) molecule as calculated applying the (DFT/ 6-31G) method.

Note: There isn't any description for symmetry species or modes of vibration could be obtained from the result calculations of the IR vibration spectrum on using PM3 neither DFT method.

Table 3-The calculated vibration frequencies and IR absorption intensities for [7]cyclacene (linear) molecule using PM3 and DFT methods

Symmetry & description		Frequency cm ⁻¹ PM3 [22]	Frequency cm ⁻¹ DFT/ 6-31G	Intensity km/ mol
A₁'			Raman active	
v₁	CH_{Str.}	3066	3066	-----
v₂	CC_{Str.}	1659	1516	-----
v₃	γCH(Wag.)	956	957	-----
v₄	γring (γCCC) (Pack)	887	899	-----
v₅	γring (γCCC) (Pack)	501	502	-----
v₆	γring (γCCC) breathing	415	410	-----
A₂'				
v₇	δCH(Rock.)	1151	1069	-----
v₈	γring (γCCC) (Pack)	821	800	-----
E₁			IR active	
v_{9, 10}	CH_{Str.}	3066	3064	53.1728
v_{11, 12}	CC_{Str.}	1661	1507	1.4881
v_{13, 14}	CCC_{Str.}	1445	1387	23.8781
v_{15, 16}	δCH (Rock.)	1149	1224	2.8088
v_{17, 18}	γCH (Wag.)	935	941	275.5610
v_{19, 20}	δring(δCCC)	891	746	0.0974
v_{21, 22}	γCC (Pack)	552	542	40.6089
v_{23, 24}	γring (γCCC) (Pack.)	440	478	16.3685
E₂				
v_{25, 26}	CH_{Str.}	3066	3059	-----
v_{27, 28}	CC_{Str.}	1652	1485	-----
v_{29, 30}	CCC_{Str.}	1599	1411	-----
v_{31, 32}	δCH (Rock.)	1246	1224	-----
v_{33, 34}	γCC (Pack.)	954	941	-----
v_{35, 36}	γring + γCH (Twist.)	886	814	-----
v_{37, 38}	δring(δCCC)	633	646	-----
v_{39, 40}	γring (γCCC) (Puck.)	422	463	-----
v_{41, 42}	γring (γCCC) (Pack.)	108	112	-----
E₃'			Raman active	
v_{43, 44}	CH_{Str.}	3067	3060	-----
v_{45, 46}	CC_{Str.}	1638	1500	-----
v_{47, 48}	CCC_{Str.}	1600	1409	-----
v_{49, 50}	δCH (Sciss.)	1374	1311	-----
v_{51, 52}	γCH (Twist)	996	925	-----
v_{53, 54}	γring + γCH (Twist)	842	843	-----
v_{55, 56}	δring (δCCC)	617	631	-----
v_{57, 58}	γring (γCCC) (Puck.)	390	377	-----
v_{59, 60}	γring (γCCC) (Puck.)	256	284	-----

A_1''				
ν_{61}	CC _{Str.} axial	1562	1486	-----
ν_{62}	δ CH (<i>Rock</i>) + δ ring (clock-anticlock)	1121	1035	-----
ν_{63}	γ ring (γ CCC) clock-anticlock	453	428	-----
A_2''			IR active	
ν_{64}	CH _{Str.}	3064	3063	70.6065
ν_{65}	δ ring elongation	1419	1321	45.1853
ν_{66}	γ CH (<i>Twist.</i>)	951	897	664.795
ν_{67}	γ ring (γ CCC) (<i>Puck.</i>)	790	801	152.1273
ν_{68}	γ ring (γ CCC) (<i>Puck.</i>)	379	358	16.5256
E_1''			Raman active	
$\nu_{69, 70}$	CH _{Str.}	3064	3056	-----
$\nu_{71, 72,}$	CC _{Str.}	1638	1574	-----
$\nu_{73, 74}$	δ CH (<i>Sciss.</i>) + CCC _{Str.}	1402	1483	-----
$\nu_{75, 75}$	δ CH	1145	1209	-----
$\nu_{77, 78}$	γ CH (<i>Wag.</i>)	942	911	-----
$\nu_{79, 80}$	γ ring + γ CH (<i>Twist.</i>)	802	814	-----
$\nu_{81, 82}$	δ ring (δ CCC)	625	642	-----
$\nu_{83, 84}$	γ ring (γ CCC)	306	326	-----
E_2''				
$\nu_{85, 86}$	CH _{Str.}	3065	3057	-----
$\nu_{87, 88}$	CC _{Str.}	1649	1584	-----
$\nu_{89, 90}$	CCC _{Str.}	1415	1408	-----
$\nu_{91, 92}$	δ CH (<i>Sciss.</i>) + δ ring	1196	1262	-----
$\nu_{93, 94}$	γ CH (<i>Twist.</i>)	902	907	-----
$\nu_{95, 96}$	γ CH (<i>Twist.</i>)	859	851	-----
$\nu_{97, 98}$	γ ring (γ CC) (<i>Puck.</i>)	688	715	-----
$\nu_{99, 100}$	γ ring (γ CCC) (<i>Puck.</i>)	394	431	-----
$\nu_{101, 102}$	γ ring (γ CCC) (<i>Puck.</i>)	146	151	-----
E_3''				
$\nu_{103, 104}$	CH _{Str.}	3065	3063	-----
$\nu_{105, 106}$	CC _{Str.}	1681	1574	-----
$\nu_{107, 108}$	CC _{Str.}	1541	1515	-----
$\nu_{109, 110}$	δ ring + δ CH (<i>Sciss.</i>)	1220	1299	-----
$\nu_{111, 112}$	γ CH (<i>Wag.</i>)	872	897	-----
$\nu_{113, 114}$	δ ring (δ CCC)	813	815	-----
$\nu_{115, 116}$	γ ring (γ CCC) (<i>Puck.</i>)	678	679	-----
$\nu_{117, 118}$	δ ring (δ CCC)	492	488	-----
$\nu_{119, 120}$	γ ring (γ CCC) (<i>Puck.</i>)	308	326	-----

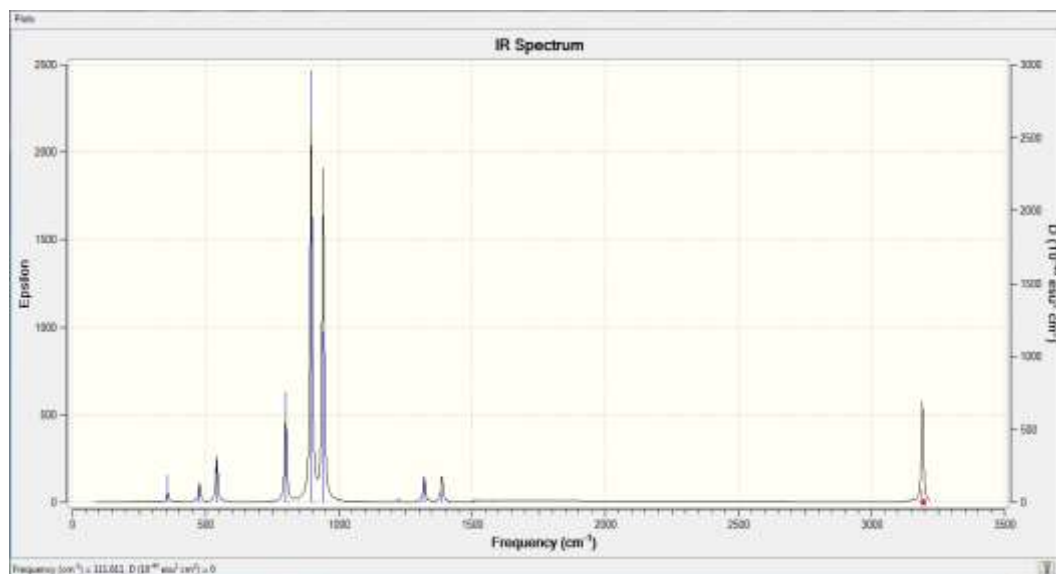
γ : Out of-plane of the molecule., δ : In-plane of the molecule.

(*Breath.*): ring breathing mode, (*Puck.*): ring puckering mode, (*Sciss.*): CH scissoring mode.(*Rock.*): CH rocking mode. (*Twist.*): CH twisting mode, (*Wag.*): CH wagging Mode.

Scaling factors: 0.96 (CH str.) for all DFT (B3LYP/6-31G) frequencies, [22].

$A_2''/\gamma_{ring} (\gamma CCC)$ (<i>Puck.</i>)(358 cm^{-1})	$E_1'/\gamma_{CC} (Pack.)$ (542 cm^{-1})	$E_1'/\gamma_{ring} (\gamma CCC)$ (<i>Puck.</i>) (679 cm^{-1})
$A_2''/\gamma_{CH} (Twist.)$ (897 cm^{-1})	$E_1'/\gamma_{CH} (Wag.)$ (941 cm^{-1})	$A_2''/\delta_{ring} \text{ elongation}$ (1321 cm^{-1})
$E_1'/\delta_{CH} (Rock.)$ (1224 cm^{-1})	$A_2''/CH_{str.}$ (3063 cm^{-1})	$E_1'/CH_{str.}$ (3064 cm^{-1})

Figure 3- The graphical pictures of some IR modes of vibration for [7]cyclacene (linear) molecule as calculated applying Gauss view program



Scheme 1- IR spectrum for [7]cyclacene (zigzag) molecule as calculated applying the (DFT/ 6-31G) method.

The arrow in the center of the molecule indicates the direction of the dipole moment of the active mode of vibration in the infrared spectrum].

And similarly to the single wall carbon nanotubes (SWCNs) [18, 23-26], the calculations of electronic charge for [7]cyclacene (linear) molecule (regardless of the calculation method, PM3, DFT (B3LYP/6-31G) or DFT (B3LYP/6-311G)) also shown that the Mulliken electronic charge densities are mainly concentrated at the outer circumferential carbon atoms, and the axial carbon atoms have diminishing charges. The H atoms are of positively charged, whereas the C atoms are of the negative charge, Figure-4.

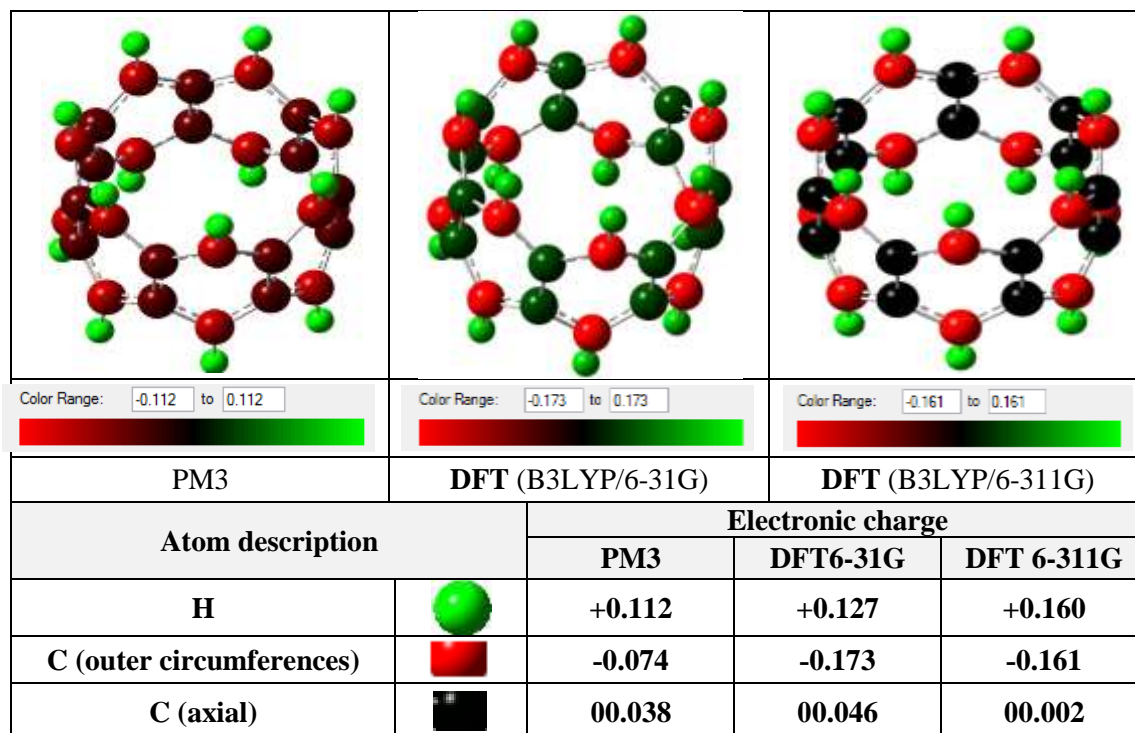


Figure 4- Mulliken distribution of charge density at the atoms of [7]cyclacene (linear) monoring molecule as calculated by using (PM3, DFT (B3LYP/6-31G and DFT (B3LYP/6-311G) methods.

Conclusion

The important of symmetry is giving as the following:

- Ideas about symmetry are of great important in connection with both theoretical and experimental studies of molecular structures.
- The basic principles of symmetry are applied in quantum mechanics, spectroscopy, and structural determination.
- When symmetry is present, certain calculations are simplified, if symmetry is taken into account.
- Aspects of symmetry also determine whether a molecule can be optically active or whether it may have a dipole moment.
- Modern treatments of rotation, vibration, and electronic spectroscopy of molecules, all make extensive use of group theory.

The important of the character table (table of eigen values) is for:

- Determining the symmetry species of the total degrees of freedom(transition, rotation, and vibration).
- Identify the active and inactive modes of vibration in the IR and Raman spectra.
- Identify the polarized and non-polarized modes of vibration in the Raman spectra.
- Determining the in-plane and out of plane modes of vibration of the molecule.
- Determining of many physical properties related to compounds and molecules and simplified the determination of the lengths, angles and electronic charge at atoms of the molecules.
- The construction character table of the D_{7h} point group in this study, which is not found in the literature, and their symmetry species are not included in the Gaussian program could be used for extracting and classifying the symmetry species for the total degrees of freedom. (degrees of transition movements, degrees of the rotation movements, and degrees of modes of vibration with the number of $(3N-6)$ for the monoring molecule (zigzag nanotube molecule)).
- The complete physical image of D_{7h} nanotube could be described from the calculated bond lengths and angles, energy values and the distribution of the charges after obtaining the optimization geometric shape according to the method of calculations of quantum mechanics DFT using the Gaussian 09 program.

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