Comparison study of CC and CH vibration frequencies and eelectronic properties for mono, Di, Tri, and tetra-rings layer of arm chair (SWCNTs)

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Abstract

Semi-empirical methods were applied for calculating the vibration frequencies and IR absorption intensities for normal coordinates of the {mono ($C_{56}H_{28}$), di ($C_{84}H_{28}$), tri ($C_{112}H_{28}$) and tetra ($C_{140}H_{28}$)} -rings layer for (7,7) armchair single wall carbon nanotube at their equilibrium geometries which were all found to have D_7d symmetry point group.
Assignment of the modes of vibration (3N-6) was done depending on the pictures of their modes by applying (Gaussian 03) program. Comparison of the vibration frequencies of (mono, di, tri and tetra) rings layer which are active in IR, and inactive in Ramman spectra. For C-H stretching vibrations, the results showed that vibration frequencies value increased with increased of length nano tube (rings layer SWCNT).

The results include the relation for axial bonds, which are the vertical C-C bonds (annular bonds) in the rings and for circumferential bonds which are the outer ring bonds. Also include the assignment of puckering, breathing and clock-anticlockwise bending vibrations. They allow a comparative view of the charge density at the carbon atom too.

Key words
SWCNT single wall carbon nano tube,
G03 aprogram for calculation,
γ: Out of plane of the molecule,
δ: In- plane of the molecule.

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دراسة مقارنة ترددات الاهتزاز لاواصر CC, CH والخواص االكترونية (لاحادي وثنائي وثلاثي ورباعي) الطبقات الحلقية لانابيب ارم جير (لانابيب النانوكاربون أحادية الطبقة).

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الخلاصة

تم تطبيق طرائق الحسابات شبه التجريبية لحساب ترددات الاهتزاز وشدد امتصاص الاشعة تحت الحمراء ,لجميع الاحداثيات الداخلية لجزيئات) احادي($C_{56}H_{28}$) وثنائي($C_{84}H_{28}$) وثلاثي($C_{112}H_{28}$) ورباعي($C_{140}H_{28}$)الطبقات الحلقية لانابيب من نوع arm chair 7,7 لانابيب النانو كاربون على وفق الشكل الهندسي المتوازن والتي وجد امتلاكها للتماثل (D_{7d}) لها لمجموعة النقطة.اعتمد حساب الانماط الاهتزازية وبعددها ((3N–6))ومناقشتها تماثليا و تأصريا على وفق الشكل الهندسي التوازني لها باستعمال برنامج كاوس 2003. وتم مقارنة ترددات الانماط الاهتزازية لهذه الجزيئات الفعالة في طيف الأشعة تحت الحمراءIR والغير فعاله في طيف الرامان ، بالنسبة لترددات مط الاصرة C-H وجد ان قيم ترددات الأنماط الاهتزازية تعتمد على، طول الانبوب الاحادي الطبقة (عدد الطبقات الحلقية) للجزيئات. النتائج تضمنت العلاقة بين اطوال الاواصر C-Caxial المتجه على طول المحور السيني كذلك اطوال اواصر C-C المتجه على طول محيط انبوب النانوكاربون أحادي الطبقة C-Cc. الطبقة كما تم وبدقة تعيين جميع ألانماط الاهتزازية العائدة للحركات الانبعاجية و التنفسية والانحنائية باتجاه وعكس اتجاه عقرب الساعة، و التي تعود اليها التشوهات الحاصلة من جراء الاهتزاز، وتم حساب ودراسة توزيع الكثافة الالكترونية على ذرات الكاربون لهذه الجزيئات ايضا.

Introduction

Carbon nanotubes have been intensively studied due to their importance as building block in nanotechnology. The special geometry and unique properties of carbon nanotube offer great potential applications, including nanoelectronic devices, energy storage, gas sensing, chemical probe, electron transport, and biosensors, field emission display, etc. Such devices operate typically on the changes of electrical response characteristics of the nanowire active component with the application of an externally applied mechanical stress or the adsorption of chemical or bio-molecule.

The study of vibration of CNTs is for successful applications in nanotechnology. Specifically, some vibration modes of CNTs, e.g., radial breathing mode [1-4], beam-like bending mode, [5-6] and longitudinal mode [7], offers valuable probes for the molecular structures and the elastic properties of CNTs. On the other hand, CNTs consisting of straight concentric layers with circular cross-section could lose their structural symmetry due to the vibration in axial, circumferential and radial directions [8,9]. This could result in a sudden change in their physical properties (e.g., the electrical properties [10] and in turn, significantly affect their performance in nanostructures. Thus, similar to the buckling behaviour [11] the vibration of CNTs turns out to be a major topic of great interest in nanomechanics, considerable efforts [12] have been devoted to capturing the fundamental vibration behaviours of CNTs by using experimental techniques [1-2,6-7] and multi-scale modelling tools [3-4,8-9,13-15].Recently, the interest of the mechanics of CNTs has been transferred from their fundamental behaviours to the effect of internal and external factors on the elastic properties [16-18], buckling [19-22,23] of CNTs. However no comparison study could be found in the literature for a normal coordinate analysis of the simplest type of nanotube i.e. the (mono, di, tri and tetra) rings-layer CNTs.

Methods of calculation

Both G03 program by PM3 method [24], and Mopac 2000 program by PM3 method, Computational Packages have been employed throughout this study to compute the geometrical Parameters (bond lengths and bond angles) and the energetic properties [25] were applied throughout the present work.

Results and Discussion

To study the vibration motions of such molecules, one has to define its geometric parameters, and has to distinguish between the axial CC (C-Caxial) bonds and circumferential CC (C-Cc) bonds, Fig.1 shows the two types of bonds in an armchair CNT [26].

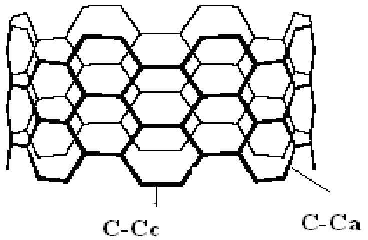


Fig.1: Structure of armchair CNT, indicating the two types of C-C bonds; C-Caxial (C-Ca) and C-Ccircumferential (C-Cc).

Various quantum mechanical studies were done for the physical properties of the nanotubes [27-31]. Structure deformation is expected to change their thermal and electronic properties too. Basic vibrations of SWCNTs were measured and assigned as breathing, puckering and clock-anti-clockwise deformation modes [32]. They are considered as finger print vibrations for the carbon nanotubes (CNTs) [33]. The active vibrations causes a change in its geometry structure Fig.2, The calculation gives different geometry were done to study the impact of the puckering distortion on the electronic properties of CNTs [34-36]. For a normal mode of vibration to be infrared active, there must be a change in the dipole moment of the molecule during the course of vibration. During the vibration motion of a molecule, a regular fluctuation in the dipole moment occurs, and a field is established which can interact with the electrical field associated with radiation. For the absorption of infrared radiation, a molecule must undergo a net change in its dipole moment as a result of its vibrational or rotational motions [37].

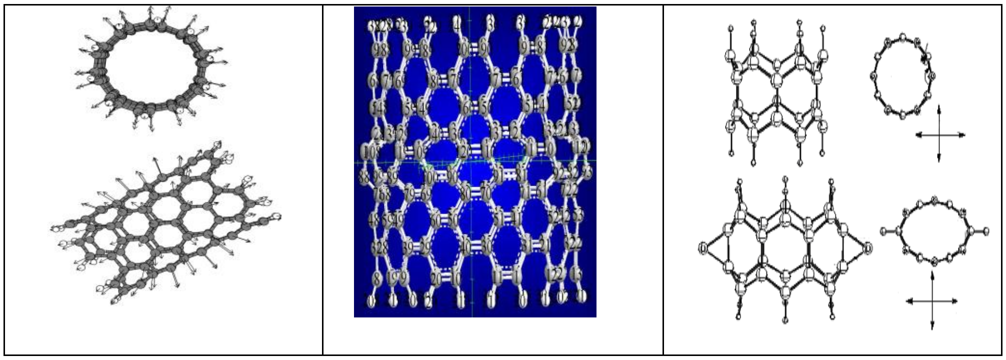
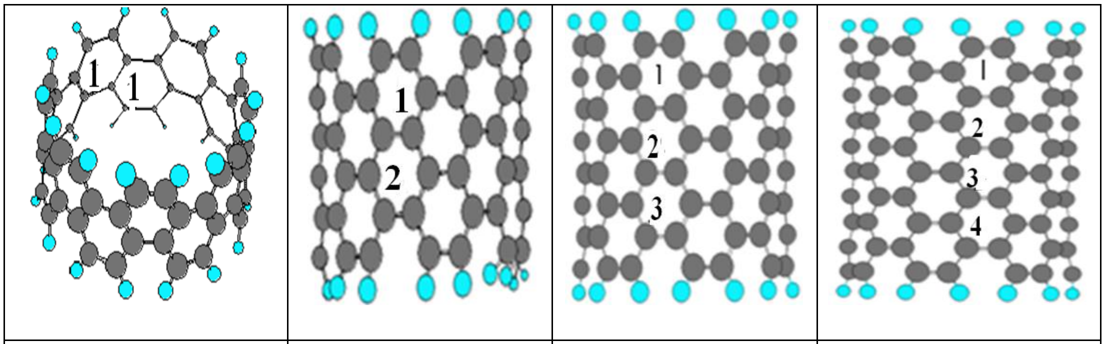


Fig.2: Structure deformation of a SWCNT as caused by its vibration motion.

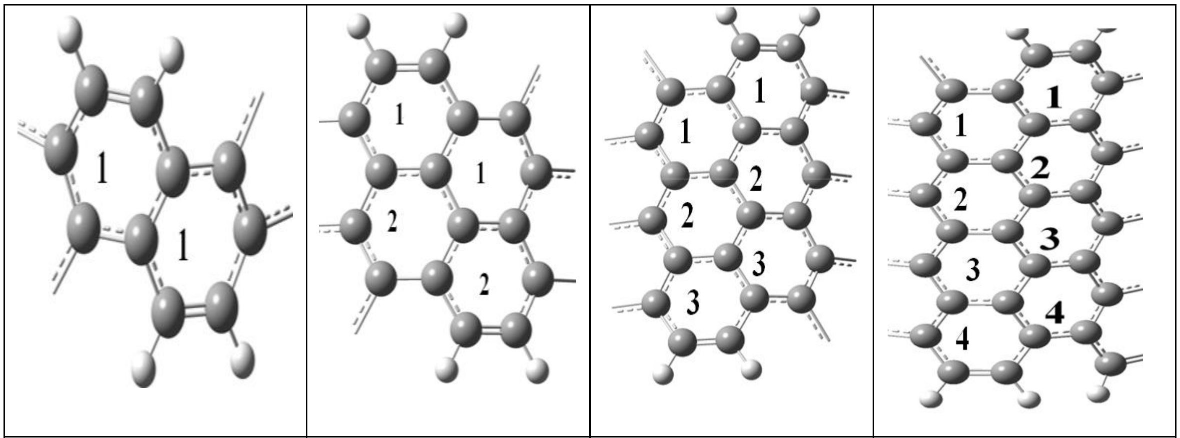
The four classifications of carbon nanotubes (mono, di, tri and tetra)-rings layer, determined by the different of the numbers of rings and the length of CNT, can also be described as single-walled nanotubes (SWNT), resembling by rolling a graphene sheet into a cylinder mathematically structures are uniquely defined by specifying the coordinates of the smallest folding vector (n,n), (armchair) molecule is composed of annulated number of member aromatic rings molecules. The (mono, di, tri and tetra)-rings layer SWCNTs are composed of annulated six member aromatic rings. Their (PM3) calculated equilibrium geometry shows D_7d symmetry [13-14], Fig. 3.

Due to their symmetry (D_{7d}) [38], Fig.4 and Table1, shows a repetitive sections of bonds. Table2 shows comparison of their calculated geometric parameters.



Mono-rings layer **SWCNT** (D_{7d})	**Di-rings layer** **SWCNT** (D_{7d})	**Tri-rings layer** **SWCNT** (D_{7d})	**Tetra-rings layer** **SWCNT** (D_{7d})

Fig.3: Equilibrium geometry for (mono, di, tri and tetra)-rings layer for (7,7) armchair single wall carbon nanotube (SWCNT) by using Mopac2000 program.



Mono-rings layer (D_{7d}) **Di-rings layer** (D_{7d}) **Tri-rings layer** (D_{7d}) **Tetra-rings layer** (D_{7d})

Fig.4: Repetitive sections of bonds and angles for (mono, di, tri and tetra) rings layer of (7,7) armchair SWCNT at their equilibrium geometries according to their point group (D_{7d}).

Table1: PM3 calculated bond distances of (mono, di, tri and tetra) rings layer for (7,7) Arm Chair SWCNT.

Arm Chair (SWCNT)	**Diameter (Å)**	**CNT Length (Å)**	**Bond length (Å)**						
			=C…Ca	**—C…Ca**	**…C…Ca**	**C=Cc**	**C…Cc**	**C—Cc**	**C—H**
Mono-ring layer D_{7d}	**10.049**	**5.526**	**1.4302**	**--------**	**1.4005**	**1.3604**	**1.4351**	**--------**	**1.0997**
Di-rings layer D_{7d}	**10.047**	**7.974**	**1.4092**	**1.4065**	**1.4411**	**1.3802**	**1.4137**	**1.4521**	**1.0995**
Tri-rings layer D_{7d}	**10.103**	**10.444**	**1.4363**	**--------**	**1.4083 1.4224 1.4409**	**1.3583**	**1.4342 1.3975 1.4221**	**--------**	**1.0991**
Tetra-rings layer D_{7d}	**10.041**	**12.901**	**1.4246**	**--------**	**1.4031 1.4346 1.4301 1.4044**	**1.3670**	**1.4276 1.4292 1.3974 1.4395**	**--------**	**1.0996**

C-Ca: axial bond. ***C-Cc: circumferential bond***

Noting that the C-Ca bonds in the angular SWCNTs are conjugated double bonds for all of different rings layer, but it may be connect to (CC double or single or conjugated double bond). The C-Cc bonds are double or conjugated double bond for (mono, tri and tetra)-rings layer SWCNT, and double or conjugated double bond or single bond for di-rings layer SWCNT.

The C=Cc bond decrease with increasing odd number or even numbers of rings layer. For odd rings layer mono and tri, (C-H) and (C-Cc) bonds are longer in mono from that in tri, the reverse had noticed for even-rings layer di and tetra-rings layer.

Also note that (…C…Ca), increase in length from outer to centre in tri-rings layer, and decrease in length from outer to centre in tetra-rings layer. Fig.4, Table 1.

Table 2 shows some physical properties of calculated (mono, di, tri and tetra)-rings layer for (7,7) armchair SWCNT at their equilibrium geometry.

Table 2: Some physical properties of the calculated (mono, di, tri and tetra) rings layer for (7,7) armchair SWCNT at their equilibrium geometry by using Mopac2000 program.

Arm Chair (SWCNT)	M. Wt. g/ mol	ΔH_f kcal/mol,(kJ)	(debye)μ	HOMO (eV)	LUMO (eV)	ΔE (eV) LUMO-HOMO
Mono-ring layer $C_{56}H_{28}$	700.837	300.346 1256.648	0.000	-8.054	-1.213	6.841
Di-rings layer $C_{84}H_{28}$	1037.145	440.174 1841.689	0.000	-7.301	-2.206	5.095
Tri-rings layer $C_{112}H_{28}$	1373.453	601.062 2514.846	0.000	-7.008	-2.664	4.344
Tetra- rings layer $C_{140}H_{28}$	1709.761	721.486 3018.699	0.000	-7.403	-2.437	4.066

ΔH_f =heat of formation, HOMO=Highest Occupied molecular orbital, LUMO=Lowest Unoccupied molecular orbital, ΔE= The difference in energy levles.

ΔH_f, increase with increasing number of odd and even rings layer, ΔE (LUMO-HOMO) decrease with increasing number of rings layer that prove their electrical conductivity increased with increasing number of rings layer . Dipole moment μ is zero for all, because they all have center of inversion symmetry element. same relation noticed for vibrations modes (IR active).

Vibration frequencies assignment of Mono-rings layer ($C_{56}H_{28}$) armchair SWCNT

The di-rings layer SWCNT posses 246 fundamental vibrations (3N-6). Inspection of its irreducible representation, as defined by the symmetry (D_7d) character table, results in the following modes of vibration;

Γvibration = Γtotal - (Γrotation + Γtranslation) = 3N - 6 = 246

$\Gamma vibration=18E_3u+18E_3g+18E_2g+18E_2u+17E_1u+17E_1g+9A_1u+8A_2g+9A_1g+8A_2u= 246$

There are 42 vibration modes (IR active) ($17E_1u$, and $8A_2u$). Their assignments are as follows:

CH stretching vibration

These are 28 in number, the displacement vectors of which are located at the H atoms. Their frequency values range from (3005.2-3029.4 cm^{-1}) (IR active), Inspecting the values in Table 3.

Ring (CCC) stretching vibration

Their displacement vectors are not located at definite C atoms as could be seen from the atomic displacement vectors. Their calculated vibration frequencies (IR active) as modes range from (1347.6-1809.5cm^{-1}), Inspecting the values in Table 3.

In-plane CH bending vibration (δCH)

There are as few as the C-H bonds. Their displacement vectors are mainly located at the corresponding H atoms. Their calculated vibration frequencies (IR active) as modes range from (237.5-1105,6 cm^{-1}),. Inspecting the values in Table 3.

In-plane (CCC) bending vibration (δCCC)

Their calculated vibration frequencies (IR active) as modes range from (326.4-1011.7 cm^{-1}), Inspecting the values in Table 3.

Out of plane CH bending vibration (γCH)

Their calculated vibration frequencies (IR active) as modes range from (572.8-1215.4cm^{-1}), Inspecting the values in Table3.

Out of plane ring bending vibrations (γCCC)

The modes include puckering deformations, as well as breathing vibrations of the whole ring. Their calculated vibration frequencies (IR-active) as modes range from (572.8-1215.4 cm^{-1}), Inspecting the values in Table3.

Table 3: Vibration frequencies and IR absorption intensities for (mono-rings layer ($C_{56}H_{28}$) molecule as calculated applying G03 program.

EU	Symmetry & description	PM3 Freq. cm^{-1}	Intensity km/mol
ν_{237}	**CH str.**	**3029.383**	**28.714**
ν_{227}	**CH str.**	**3005.239**	**107.300**
ν_{215}	**C=C str**	**1809.491**	**15.036**
ν_{191}	**ring)CC$_{str.}$((elongation)**	**1625.087**	**0.0384**
ν_{187}	**C--C str**	**1593.311**	**12.2663**
ν_{179}	**C=C str**	**1526.865**	**17.4909**
ν_{153}	**γCH(wag.)**	**1197.14**	**16.559**
ν_{136}	**δCH(siccer.)**	**1105.650**	**0.4390**
ν_{125}	**δCH(rock))+δring (δCCC)**	**1011.752**	**0.2571**
ν_{103}	**γCH (wagg.)+ γring (γCCC)**	**890.496**	**18.575**
ν_{94}	**γCH (wagg.)+ γring (γCCC)**	**852.991**	**93.477**
ν_{86}	**δCH(rock)**	**812.674**	**137.946**
ν_{74}	**γCH (wagg)+ γring (γCCC)**	**702.001**	**1.791**
ν_{60}	**γCH (wagg)+ γring (γCCC)**	**572.863**	**13.074**
ν_{34}	**δCH(rock)**	**388.437**	**15.734**
ν_{28}	**δCH(rock)+δring (δCCC)**	**326.432**	**11.190**
ν_{21}	**δCH(rock)**	**237.476**	**10.236**
A_2u			
ν_{231}	**CH str.**	**3010.232**	**358.860**
ν_{191}	**C=C str**	**1695.497**	**8.1662**
ν_{165}	**C=C str**	**1347.570**	**7.2816**
ν_{156}	**γCH (wagg)+ γring (γCCC)**	**1215.372**	**48.906**
ν_{132}	**δCH(siccer.)**	**1077.490**	**0.6641**
ν_{88}	**δCH(rock))+δring (δCCC)**	**814.134**	**0.590**
ν_{51}	**δCH(rock))+δring (δCCC)**	**516.299**	**7.919**

Vibration frequencies assignment of di-rings layer ($C_{84}H_{28}$) armchair SWCNT

The di-rings layer SWCNT posses 433 fundamental vibrations (3N-6). Inspection of its irreducible representation, as defined by the symmetry (D_7d) character table, results in the following modes of vibration;

$\Gamma vibration=\Gamma total- (\Gamma rotation + \Gamma translation) = 3N - 6 = 330$

$\Gamma vibration=24E_3u+24E_3g+24E_2g+24E_2u+23 E_1u+23 E_1g+12A_1u+11A_2g+12A_1g+11A_2u =330$

There are 59 vibration modes (IR active) ($24E_2u$, and$11A_2u$). Their assignments are as follows:

CH stretching vibration

These are 28 in number, the displacement vectors of which are located at the H atoms. Their frequency values as modes range from (3004.4- 3029.3 cm^{-1}) (IR active), Inspecting the values in Table 4.

Ring (CCC) stretching vibration

Their displacement vectors are not located at definite C atoms as could be seen from the atomic displacement vectors. Their calculated vibration frequencies (IR active) as modes range from (1242.7-1786.93cm^{-1}),. Inspecting the values in Table 4.

In-plane CH bending vibration (δCH)

There are as few as the C-H bonds. Their displacement vectors are mainly located at the corresponding H atoms. Their calculated vibration frequencies (IR active) as modes range from (161.6 -1001.6 cm^{-1}), Inspecting the values in Table 4.

In-plane (CCC) bending vibration (δCCC)

symmetric modes range from (149.6-914.9 cm^{-1}), Inspecting the values in Table4.

Out of plane CH bending vibration (γCH)

Their calculated vibration frequencies (IR active) as modes range from (348.6-1284.0 cm^{-1}), inspecting the values in table 4.

Out of plane ring bending vibrations (γCCC)

The modes include puckering deformations, as well as breathing vibrations of the whole ring. Their calculated vibration frequencies (IR-active) as modes range from (321.1-1284.0 cm^{-1}), Inspecting the values in Table4.

Vibration frequencies assignment of tri-rings layer ($C_{1١٢}H_{28}$) armchair

The tri-rings layer SWCNT posses 414 fundamental vibrations (3N-6). Inspection of its irreducible representation, as defined by the symmetry character table, results in the following modes of vibration;

Γvibration = Γtotal - (Γrotation + Γtranslation) = 3N - 6 = 414

$\Gamma vibration=30E_3u+30E_3g+30E_2g+30E_2u+29E_1u+29E_1g+15A_1u+14A_2g+15A_1g+14A_2u = 414$

There are 72 vibration modes (IR active) ($29E_1u$, and $14A_2u$). Their assignments are as follows:

CH stretching vibration

These are 28 in number, the displacement vectors of which are located at the H atoms. Their frequency values as modes range from (3008.1- 3032.1 cm^{-1}) (IR active), Inspecting the values in Table 5.

Ring (CCC) stretching vibration

Their displacement vectors are not located at definite C atoms as could be seen from the atomic displacement vectors. Their calculated vibration frequencies (IR active) as modes range from (1416.9- 1796.6 cm^{-1}), Inspecting the values in Table 5.

In-plane CH bending vibration (δCH)

There are as few as the C-H bonds. Their displacement vectors are mainly located at the corresponding H atoms. Their calculated vibration frequencies (IR active) as modes range from (138.7- 792.1 cm^{-1}), Inspecting the values in Table 5.

In-plane bending (CCC) vibration (δCCC)

Their calculated vibration frequencies (IR active) as modes range from (650.3- 1116.8 cm^{-1}), Inspecting the values in Table 5.

Out of plane CH bending vibration (γCH)

Their calculated vibration frequencies (IR active) as modes range from (278.4- 1364.1 cm^{-1}), Inspecting the values in Table 5.

Out of plane ring bending vibration (γCCC)

The modes include puckering deformations, as well as breathing vibrations of the whole ring. Their calculated vibration frequencies (IR active) as modes range from (278.4-1364.1cm^{-1}),. Inspecting the values in Table5.

Table 4: Vibration frequencies and IR absorption intensities for (di-rings layer ($C_{84}H_{28}$) molecule as calculated applying G03 program by PM3 method.

EU	Symmetry & description	PM3 Freq. cm^{-1}	Intensity km/mol
ν_{321}	CH str.	3029.32	5.157
ν_{313}	CH str.	3004.43	87.929
ν_{290}	C=C str	1786.93	29.090
ν_{286}	ring (CC$_{str.}$)	1765.19	0.033
ν_{259}	C- C str	1624.74	1.608
ν_{251}	C- C str	1590.6	14.307
ν_{238}	C=C str	1478.47	22.973
ν_{230}	C- C str	1434.80	25.709
ν_{213}	γCH(twiss.)+γring (γCCC)	1284.01	21.413
ν_{193}	γCH (wag.)	1135.610	1.084
ν_{178}	γCH(siccer.)	1058.010	3.844
ν_{169}	δCH (rock.)	1001.142	11.930
ν_{153}	γring (γCCC)+γCH(twiss.)	948.942	0.5129
ν_{150}	δCH+δring (δCCC)(siccer)	914.984	30.582
ν_{129}	δCH(rock.)	819.102	207.138
ν_{99}	γring (γCCC)+γCH(twiss.)	672.731	0.0734
ν_{87}	γCH (wagg)+ γring (γCCC)	630.422	0.199
ν_{80}	γring (γCCC)+γCH(twiss.)	582.769	2.0624
ν_{74}	γCH (wagg)+ γring (γCCC)	530.382	47.086
ν_{63}	γring (γCCC)+γCH (wag.)	480.462	0.0103
ν_{41}	γCH(twiss.)+ γring (γCCC)	348.624	0.348
ν_{35}	γring (γCCC)breath.	321.064	4.169
ν_{15}	δCH (rock.)	161.639	8.1066
A_2u			
ν_{315}	CH str.	3008.51	484.441
ν_{279}	ring)CCstr.((elong.)	1746.01	4.6279
ν_{248}	C=C str	1569.93	5.1196
ν_{237}	C- C str	1469.77	56.657
ν_{207}	ring)CCstr.((elong.)	1242.74	0.0583
ν_{180}	γCH(twist..)	1064.96	9.1125
ν_{155}	γCH(twist.)+γring (γCCC)	955.296	5.856
ν_{123}	δCH(rock.)	797.23	1.8236
ν_{86}	γCH (wagg)+ γring (γCCC)	611.612	4.1519
ν_{45}	δCH+δring (δCCC) breath.	358.916	1.4007
ν_{10}	δCH+δring (δCCC)	149.602	0 .376

Table 5: Vibration frequencies and IR absorption intensities for (di-rings layer ($C_{112}H_{28}$) molecule as calculated applying G03 program by PM3 method.

EU	Symmetry & description	PM3 Freq. cm^{-1}	Intensity km/mol
ν_{405}	**CH str.**	**3032.11**	**6.8021**
ν_{397}	**CH str.**	**3008.1**	**142.728**
ν_{377}	**C- C str**	**1796.58**	**10.2513**
ν_{371}	**C- C str**	**1784.38**	**0.0041**
ν_{349}	**C=C str**	**1710.91**	**0.626**
ν_{328}	**C- C str**	**1624.18**	**0.348**
ν_{312}	**C=C str**	**1574.96**	**14.8256**
ν_{301}	**ring ($CCC_{str.}$)**	**1545.87**	**15.710**
ν_{292}	**ring ($CCC_{str.}$)**	**1466.53**	**5.0778**
ν_{281}	**ring ($CCC_{str.}$)**	**1416.97**	**0.5857**
ν_{278}	**γCH(wagg.)+ γring (γCCC)**	**1364.08**	**1.2167**
ν_{247}	**γCH(wagg.)+ γring (γCCC)**	**1155.24**	**11.7072**
ν_{234}	**γCH(wagg.)+ γring (γCCC)**	**1080.82**	**0.3068**
ν_{221}	**γCH(twiss.)**	**1036.62**	**3.7063**
ν_{214}	**γCH(twiss.)**	**998.785**	**0.5345**
ν_{197}	**γCH(twiss.)+ γring (γCCC)**	**937.036**	**11.6353**
ν_{188}	**γCH(twist.)+ γring (γCCC)**	**899.016**	**15.649**
ν_{166}	**γCH(wagg.)+ γring (γCCC)**	**824.343**	**32.543**
ν_{160}	**γCH(wagg.)+ γring (γCCC)**	**806.363**	**130.246**
ν_{144}	**γCH(wagg.)+ γring (γCCC)**	**747.612**	**2.318**
ν_{109}	**γCH(wagg.)+ γring (γCCC)**	**623.098**	**45.345**
ν_{107}	**γCH(twiss.)+ γring (γCCC)**	**611.811**	**0.1942**
ν_{93}	**γring (γCCC)+γCH(twiss.)**	**540.388**	**1.5285**
ν_{87}	**γCH(twiss.)+ γring (γCCC)**	**505.551**	**0.3273**
ν_{65}	**γCH(wagg.)+ γring (γCCC)**	**395.983**	**13.2551**
ν_{57}	**γCH(twiss.)+ γring (γCCC)**	**361.336**	**2.526**
ν_{40}	**γCH(twiss.)+ γring (γCCC)**	**318.444**	**6.3217**
ν_{38}	**γring (γCCC)**	**306.600**	**0.0033**
ν_{11}	**δCH(rock.)**	**144.079**	**9.707**
A_2u			
ν_{399}	**CH str.**	**3013.16**	**497.47**
ν_{363}	**C- C str**	**1766.76**	**9.276**
ν_{345}	**C=C str**	**1690.55**	**4.9801**
ν_{318}	**ring ($CCC_{str.}$)**	**1588.24**	**0.5889**
ν_{299}	**γring (γCCC)**	**1531.39**	**0.4049**
ν_{263}	**γCH(twist.)+ γring (γCCC)**	**1267.74**	**91.423**
ν_{238}	**δring (δCCC)**	**1116.81**	**1.2855**
ν_{220}	**γCH(twist.)**	**1028.42**	**0.2526**
ν_{155}	**δCH+δring (δCCC)**	**792.111**	**3.3319**
ν_{151}	**δCH+δring (δCCC)**	**771.932**	**8.8077**
ν_{123}	**δCH(rock.)+δring (δCCC)**	**650.264**	**0.4184**
ν_{70}	**γCH(wagg.)+ γring (γCCC)**	**428.731**	**4.944**
ν_{35}	**γCH(wagg.)+ γring (γCCC)**	**278.406**	**0.7373**
ν_{10}	**δCH(rock.)**	**138.721**	**0.2038**

Vibration frequencies assignment of tetra-rings layer ($C_{140}H_{28}$) armchair SWCNT.

The tetra-rings layer posses 498 fundamental vibrations (3N-6). Inspection of its irreducible representation, as defined by the symmetry character table, results in the following modes of vibration;

$\Gamma vibration = \Gamma_{total} - (\Gamma rotation + \Gamma translation) = 3N - 6 = 498$

$\Gamma vibration=36E_3u+36E_3g+36E_2g+36E_2u+35E_1u+35E_1g+18A_1u+17A_2g+18A_1g+17A_2u = 498$

These are 87 IR active ($35E_1u$, and $17A_2u$). Their assignments are as follow:

Relative to the σ_h reflection the vibration modes are classified as symmetric and antisymmetric modes.

CH stretching vibration

These are 28 in number, the displacement vectors of which are located at the H atoms. Their calculated vibration frequencies (IR active) *as* modes range from (3004.3-3029.0 cm^{-1}), Inspecting the values in Table6.

Ring (CCC) stretching vibration

Their displacement vectors are not located at definite C atoms as could be seen from the atomic displacement vectors. Their calculated vibration frequencies (IR active) as modes range from (1409.13-1796.6 cm^{-1}), Inspecting the values in Table 6.

In-plane CH bending vibration (δCH)

There are as few as the C-H bonds. Their displacement vectors are mainly located at the corresponding H atoms. Their calculated vibration frequencies (IR active) as modes range from (149.7- 1067.7 cm^{-1}), Inspecting the values in Table 6.

In-plane (CCC) bending vibration (δCCC)

Their calculated vibration frequencies (IR active) as modes range from (149.7- 1343.7 cm^{-1}), Inspecting the values in Table 6.

Out of plane CH bending vibration (γCH)

Their calculated vibration frequencies (IR active) as modes range from (270.1- 1288.6 cm^{-1}), Inspecting the values in Table 6.

Out of plane ring bending vibration (γCCC)

The modes include puckering deformations, as well as breathing vibrations of the whole ring. Their calculated vibration frequencies (IR active) as modes range from (256.3-1363.9 cm^{-1}), Inspecting the values in Table6.

Table 6, includes the calculated frequencies as calculated applying semi-empirical methods (PM3) by Gaussian03 program and IR absorption intensities of the vibration modes. Commonly known, the vibrations with (intensity= 0.0) are forbidden (IR inactive, Ramman active), those with (intensity≠ 0.0) are allowed (IR active, Ramman inactive).

Fig. 5 shows the vibration pictures for some modes of the (7,7) CNT (Armchair), as calculated applying semi-empirical methods (PM3) by Gaussian 03 program.

The whole relations

νCH_{str}.(tri-rings layer) >νCH_{str}.(mono-rings layer) > $\nu CH_{str.}$ (di-rings layer)> $\nu CH_{str.}$ (tetra-rings layer)

νCC_{str}.(mono-rings layer) > ν CC_{str}.(tri=tetra-rings SWCNT) > ν CC_{str} (di-rings layer)

νδring (tetra-rings layer) >νδring.(tri-rings layer) >νδring (mono-rings layer) > νδring(di- rings layer)

νγring(tri-rings layer) > νγring(tri-rings layer) >νγring(di-rings layer) >νγring(mono-rings layer)

νδCH(mono-rings layer) >νδCH(tetra-rings layer) >νδCH(di-rings layer) >νδCH(tri-rings layer) νγ CH(tri-rings layer) >νγ CH(tetra-rings layer) >νγ CH(di-rings layer) >νγ CH(mono-rings layer)

The results include the relation for odd ring number in length.

νCH_{str}.(tri-rings layer) >νCH_{str}.(mono-rings layer)

νCC_{str}.(mono-rings layer) > ν CC_{str}.(tri=tetra-rings)

νδring.(tri-rings layer) >νδring (mono-rings layer)

νδCH(mono-rings layer) >νδCH(tri-rings layer)

νγring(tri-rings layer) > νγring(mono-rings layer)

νγ CH(tri-rings layer) >νγ CH(mono-rings layer)

The results include the relation for even ring number in length.

νCH_{str}.(di-rings layer) ≈νCH_{str}.(terta-rings layer)

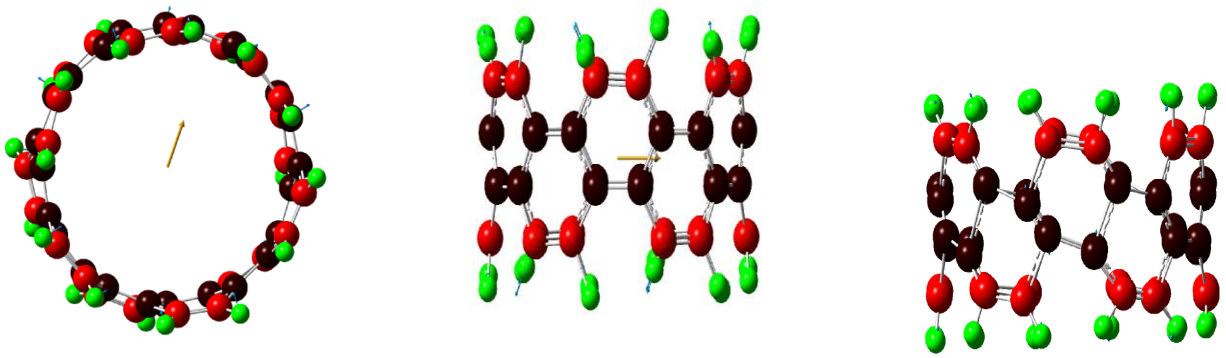
νCC_{str}.(tetra -rings layer) > ν CC_{str}.(di--rings)

νδring.(terta -rings layer) >νδring (di -rings layer)

νδCH(terta -rings layer) >νδCH(di -rings layer)

νγring(terta -rings layer) > νγring(di -rings layer)

Finally, the calculated vibration frequencies (IR-active) show that vibration frequency values of (C-C stretching), (γring, νδring.) Vibrations frequency shows higher frequency values with increased numbers of rings layer in length lead to many more electronic and mechanical applications.



asym. (γCCC) (puck.) **asym. CH str.** **(sym. ring)C--C str.**

Fig.5: The graphical pictures of some vibration modes for CNT (armchair) as calculated applying G03 program.

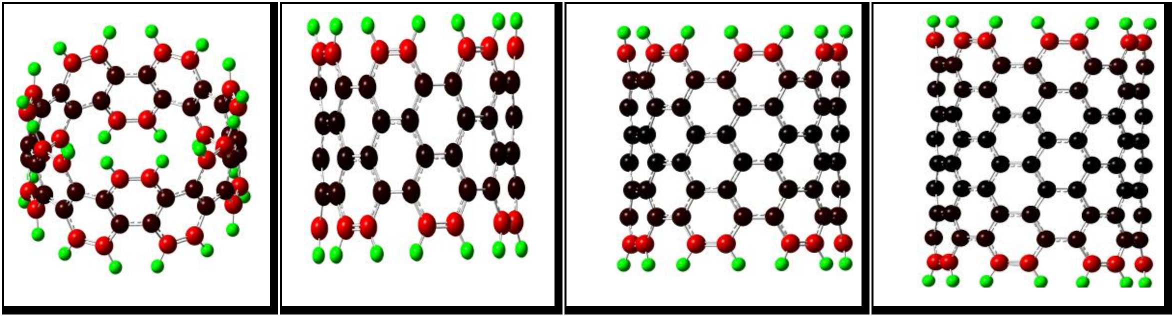
Table 6: Vibration frequencies and IR absorption intensities for (tetra-rings layer ($C_{140}H_{28}$) molecule as calculated applying G03 program.

EU	Symmetry & description	PM3 Freq. cm^{-1}	Intensity km/mol
ν_{489}	CH str.	3029.03	9.0755
ν_{481}	CH str.	3004.26	117.43
ν_{461}	C-C str	1796.56	4.349
ν_{457}	C=C str	1793.22	14.884
ν_{435}	C=C str	1722.35	2.539
ν_{414}	C=C str	1675.17	0.278
ν_{403}	C-C str	1643.15	1.444
ν_{399}	ring ($CCC_{str.}$)	1602.76	0.0197
ν_{369}	ring ($CCC_{str.}$)	1556.18	0.4601
ν_{363}	C- C str	1536.56	8.336
ν_{352}	ring ($CCC_{str.}$)	1498.85	17.8001
ν_{334}	ring ($CCC_{str.}$)	1409.13	30.762
ν_{321}	δring (δCCC)	1343.71	0.2808
ν_{313}	γCH(wagg.)+ γring (γCCC)	1288.64	6.322
ν_{295}	γCH(wagg.)	1152.63	5.5834
ν_{274}	δCH(siccer.)	1067.71	1.0663
ν_{260}	δCH(siccer.)	1004.26	0.076
ν_{247}	γring (γCCC)+ γCH	964.564	1.2371
ν_{241}	γCH(twiss.)+ γring (γCCC)	945.735	0.0122
ν_{227}	γCH(twiss.)+γring (γCCC)	896.6	5.1302
ν_{216}	δCH+δring (δCCC)	858.66	22.623
ν_{194}	δCH(rock)	812.82	125.337
ν_{153}	γCH(twiss.)+ γring (γCCC)	674.771	1.1662
ν_{150}	δCH+δring (δCCC)	664.392	11.594
ν_{143}	δCH(rock.)+ +δring (δCCC)	653.804	7.2941
ν_{124}	γCH(wagg.)+ γring (γCCC)	602.856	3.0915
ν_{99}	γCH(twiss.)+ γring (γCCC)	492.552	22.087
ν_{95}	γCH(twiss.)+ γring (γCCC)	481.314	1.5762
ν_{82}	γCH(twiss.)+ γring (γCCC)	436.045	4.3508
ν_{61}	γCH(twiss.)+ γring (γCCC)	357.166	2.9102
ν_{59}	γCH(twiss.)+ γring (γCCC)	346.147	1.0289
ν_{44}	γring (γCCC)+ γCH(wagg.)	284.641	0.935
ν_{38}	γCH(wagg.)+ γring (γCCC)	270.122	5.758
ν_{13}	δCH(rock.)+δring (δCCC)	149.751	6.048
A_2u			
ν_{483}	CH str.	3008.892	616.385
ν_{442}	C=C str	1765.63	14.298
ν_{409}	C=C str	1654.39	3.1335
ν_{387}	ring ($CCC_{str.}$) elonga.	1600.18	4.349
ν_{367}	ring ($CCC_{str.}$) elonga.	1542.98	2.304
ν_{348}	ring ($CCC_{str.}$)elonga.	1480.57	0.2087
ν_{329}	γring (γCCC)	1363.96	100.904
ν_{303}	ring ($CCC_{str.}$)	1193.15	5.645
ν_{284}	γCH(twist.)	1114.75	20.534
ν_{260}	γCH(twist.)	1028.51	1.906
ν_{188}	δCH(rock)	801.216	4.297
ν_{147}	γring (γCCC)+ γCH(breath.)	660.794	0.366
ν_{138}	γring (γCCC)+ γCH(breath.)	642.957	2.8819
ν_{109}	δCH(rock)+δring (δCCC)	518.928	10.4807
ν_{67}	δCH(rock.)+δring (δCCC)	376.334	1.735
ν_{35}	γring (γCCC)(breath.)	256.287	0.4318
ν_{15}	δCH(rock.)+δring (δCCC)	152.02	0.7306

Table 7: Calculated Vibration frequencies of (mono, di, tri and tetra) rings layer for (7,7) armchair SWCNT applying G03 program by PM3 method.

Arm Chair (SWCNT)	**C-H$_{str.}$**	**C- Ca$_{str}$**	**C=Cc$_{str.}$**	**C--Cc$_{str}$**
Mono-rings layer **$C_{56}H_{28}$**	**3029.38** **Eu**	**1625.08** **Eu**	**1809.50** **Eu**	**1593.30** **Eu**
Di-rings layer **$C_{48}H_{28}$**	**3029.38** **Eu**	**1765.19** **Eu**	**1786.90** **Eu**	**1634.17** **Eu**
Tri-rings layer **$C_{112}H_{28}$**	**3032.11** **Eu**	**1545.80** **Eu**	**1710.90** **Bu**	**1796.50** **Eu**
Tetra-rings layer **$C_{140}H_{28}$**	**3029.11** **Eu**	**1602.70** **Eu**	**1793.22** **Eu**	**1796.50** **Eu**

Finally, the calculations show that, similar to the carbon nanotubes [39-40], the charge densities are mainly concentrated at the circumferential carbon and hydrogen atoms of mono and multi-rings layer SWCNT, parallel with their physical properties for electrical conductivity. The axial carbon atoms have diminishing charges from outer to centre. The H atoms are positively charged, the C atoms are of the negative charge, Fig. 6.



Mono-rings layer D_{7d}		**Di- rings layer D_{7d}**		**Tri-rings layer D_{7d}**		**Tetra-rings layer D_{7d}**	
C—H 0.112	🟩	**C—H 0.112**	🟩	**C—H 0.112**	🟩	**C—H 0.113**	🟩
C=C -0.091	🟥	**C=C -0.090**	🟥	**C=C -0.088**	🟥	**C=C -0.088**	🟥
C---C -0.022	■	**C—C -0.014**	🟫	**C---C -0.016**	🟫	**C—C -0.015**	🟫
		C---C -0.008	🟧	**C---C -0.007**	🟧	**C---C -0.007**	🟧
				C---C -0.002	■	**C---C -0.002**	■
						C---C -0.001	⬛

Fig.6: Distribution of charge density at the atoms for (mono, di, tri and tetra) rings layer of (7,7) armchair SWCNT as calculated applying G03 program.

Note. All calculations were done applying the G03 program of Pople et al. [24].

Conclusions

Quantum mechanics semi-empirical (PM3) calculations were carried out with Gaussian 03 program, for investigated the result In order to calculate the vibration frequencies modes that active in infrared. Comparison of the Vibration modes which were active in IR for the three molecules ($C_{56}H_{28}$,$C_{84}H_{28}$,$C_{112}H_{28}$,$C_{140}H_{28}$).

Vibrational motion of atoms decreases the electrical conductivity of nanotubes and limits the performance of nanotransistors and other electronic devices based on them. Similarly, the stiffness of a nanotube and its capability for transporting heat is reduced with increasing defect density[41,42]. They allow a comparative view of the charge density at the carbon atom too. The calculations show that, the charge densities are mainly concentrated at the hydrogen atoms (positively charged) and at the outer circumferential carbon atoms (negatively charge). The axial carbon atoms and the circumferential carbon atoms have diminishing charges from outer to the centre of the CNTs. They can have metallic properties (armchair, some zigzag) depending on their structure. CNTs are much better conductors of electricity than copper nanowires because there is less scatter of electrons. Nanotubes are exceptional ballistic conductors, which can be used in a variety of nanodevices that can operateat room temperature. Nanotubes possess extraordinary mechanical properties and are among the strongest materials known.

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