ISSN: 0067-2904

Comparison of Physical Properties, Energetic, Vibration Frequencies and Normal Coordinates, for Construction Units of Fullerene C_{60} Using Quantum Mechanical Calculations

Rehab Majed Kubba*, Khalida Aubead Samawi
Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

PM3 semiempirical method and Density Functional Theory (DFT) calculations of the type (B3LYP) and a Gaussian basis set (6-311G) were carried out for fullerene C_{60} molecule with its construction units (5radialene, 1,2,3-trimethylene indan, and corannulene), to evaluate the geometrical structure (bond lengths, symmetry, and energetic such as heat of formation ΔH^0_f, total energy $E_{tot.}$, dipole moment μ, E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap $\Delta E_{HOMO-LUMO}$), the distribution of electron density and vibration frequencies, all at their equilibrium geometries. Assignment of the vibrations modes was done according to the movement of the atoms as a result of DFT calculation using Gaussian program view. Comparison was done for the distribution of electron density with the expense of vibration frequencies and for the relationship of all the physical and electronic properties of fullerene C_{60} with its construction units.

Keywords: Fullerene molecule, physical properties, energetic, vibrations frequencies.

مقارنة الخواص الفيزياوية والطاقية وترددات الاهتزاز والاحداثيات المتعامدة لوحدات بنية الفلرين C_{60} بأستخدام حسابات ميكانيك الكم

رحاب ماجد كبة*، خالدة عبيد سماوي
قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم استخدام حسابات ميكانيك الكم التقريبية PM3 والعائدة لنظرية دوال الكثافة DFT الأساسية لعناصر قاعدة 6-311G وباسلوب B3LYP وباستخدام برنامج Gaussian-09 في حساب الشكل الهندسي التوازني لجزيئة الفلرين مع وحدات بناءها (5radialene, 1,2,3-trimethylene indan, corannulene) وذلك بغرض حساب أطوال التأصر والتماثل وبعض الصفات الطاقية والفيزياوية كحرارة التكوين القياسية ΔH^0_f والطاقة الكلية E_{tot} وعزم ثنائي القطب μ وطاقة اعلى مدار محجوز بالالكترونات E_{HOMO}، وطاقة اوطأ مدار غير محجوز بالالكترونات E_{LUMO}، والفرق الطافي بينهما $\Delta E_{HOMO-LUMO}$، وتوزيع الكثافة الالكترونية مع حساب وتصنيف ترددات الاهتزاز تكافؤيا وتماثليا لجزيئة الفلرين وفق نظرية المجموعة ودراسة علاقة كل ذلك بالخواص الفيزيائية والالكترونية لهذه الجزيئة مع وحدات بنائها.

---

*Email: Rehab_ mmr_kb@yahoo.com

Introduction

Fullerene C_{60} is one of the earliest man-made nano-structure and its discovery [1] started the revolution of nanotechnology, marked by key discoveries such as carbon nanotube and graphene [2]. Extensive experimental [3-10] and theoretical studies [11-14] have been conducted on different types of fullerenes to develop further understanding of these cage-like structures containing carbon atoms.

Fullerenes have attracted considerable interest as an electron acceptor and undergo many addition reactions. There are two main objectives concerning organic functionalization of C_{60}: one is focused on modification of some of their properties for easier handling, and the other on a combination of the fullerene properties with those of other materials. The beauty and the unprecedented spherical architecture of these molecular cages immediately attracted the attention of many scientists [15-16]. In a very fast development buckminsterfullerene C_{60}, became one of the most intensively investigated molecules. The fascinating physical and chemical properties of buckminsterfullerene such as the discovery of the superconductivity of alkali metal doped C_{60}, and the possibility of chemical functionalization of the fullerene core have made C_{60} to arguably the most interesting single molecule of the past years. The vibrational spectra of icosahedral fullerene C_{60} have attracted a considerable attention and have been extensively used as a probe of intra and intermolecular interactions [17].

There are a number of available theoretical approaches of C_{60} and C_{70} vibration calculation belong to quantum mechanical method, which can mainly be classified as the Icosahedral symmetry analysis and have been attempted to explain the pattern of the vibration modes and variability of the natural frequencies, assuming the fullerenes as thin spherical elastic shells (Harter and Weeks [18], Weeks and Harter [19]), force field model (Wu et al. [20], Cyvin et al. [21], Jishi et al. [22]), Quantum mechanical Consistent Force Field Method for Pi-Electron Systems (QCFF/ PI) (Negri et al. [23]), Austin Model 1 (AM1) (Slanina et al. [24]), density functional theory (Adams et al. [25]; Schettino et al. [26], Sun and Kertesz [27], and Schettino et al. [28].

In the present work, Gaussian 09 computational packages have been employed to compute the geometrical structure (bond lengths) for fullerene with its construction units (5radialene, 1,2,3-trimethylene indan, corannulene), as well as the energetic (heat of formation ΔH^0_f, highest occupied molecular orbital energy E_{HOMO}, lowest unoccupied molecular orbital energy E_{LUMO}, the energy gap $\Delta E_{HOMO-LUMO}$) and physical properties such as dipole moment μ, electronic charge density,----etc. The obtained equilibrium geometry was applied for the calculation of all 3N-6 vibration frequencies and analysis the normal coordinates **at which the literature do not assign or analyze them**. The comparison was done for the distribution of the electron density with the expense of vibration frequencies, physical and electronic properties for the calculated molecules.

Computational Details

All the quantum mechanical calculations were performed with complete geometry optimizations using Gaussian-09 software package [29]. Geometry optimization was carried out by PM3 semiempirical method and Density Functional Theory (DFT) using Becke′s three-parameter functional and the correlation functional of Lee, Yang and Parr (B3LYP) with a 6-311 level of the theory [30,31]. In order to make computation less cumbersome, solvent and charge effects were neglected. This is because when being compared, they are subjected to identical conditions and the overall effect will be the same and virtually cancelled out.

Results and Discussion

Figure-1 shows the structure of fullerene C_{60} molecule with its construction units (5radialene, 1,2,3-trimethylene indan, and corannulene) drawn by using the Mopac (Ultra Chem. Draw 2011), and their equilibrium geometries with their symmetry of (D_{5h}), (C_{2v}), (C_{5v}), and (I_h) calculated using PM3 and DFT (B3LYP/ 6-311G) level methods.

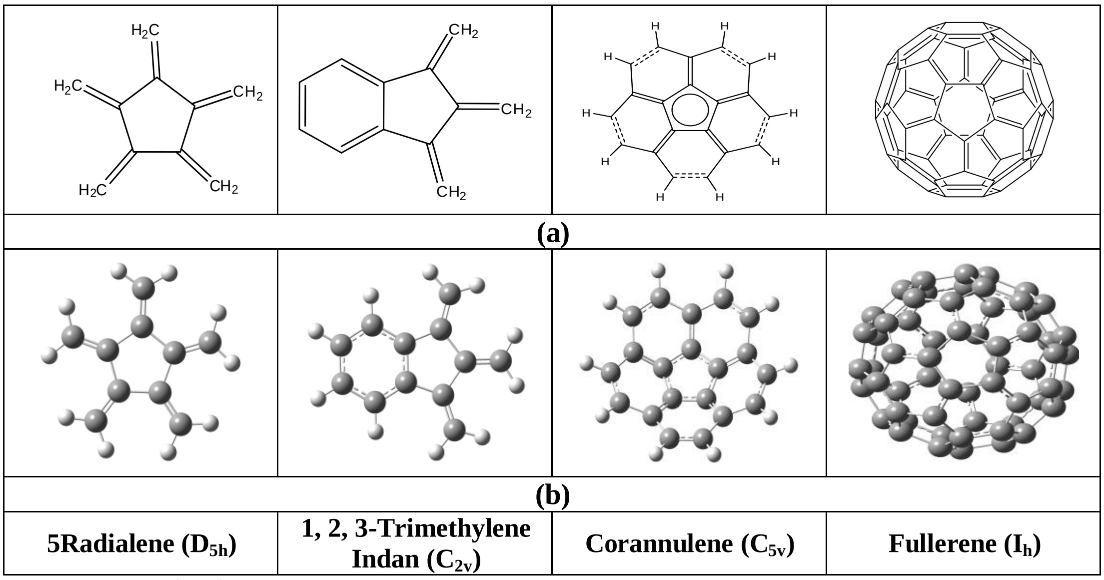
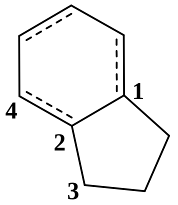


Figure 1- Structure for fullerene molecule and its construction units; **(a)** Drawing by Chem Draw Ultra 11 program. **(b)** Equilibrium geometries, as calculated by DFT (6-311G/ B3LYP) level.

The most common fullerene C_{60} consists of 60 carbon atoms arranged on a sphere of $7.1A^0$ diameter. The atoms form twenty hexagons and twelve pentagons, there is two type of C-C bonds at the pentagon-hexagon and hexagon-hexagon border equal to d_{C-C} $1.460A^0$ and $d_{C=C}$ $1.400A^0$ respectively [32], where the two types of bonds are often considered as single and double ones. The geometrical parameters (bond lengths, bond angles, the heat of formation and the energetic properties are shown in Table-1.

Table 1- PM3 and DFT (6-311G/ B3LYP) calculated geometric structures of fullerene molecule.

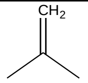
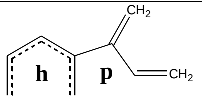
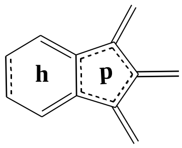
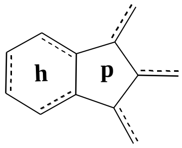


Description of bond lengths & angles	Bond lengths (Å) & angles (deg)		
	PM3	DFT (6-311G/ B3LYP)	[32]
(C1-C2)p	1.457	1.458	1.460
(C2=C4)h	1.384	1.394	1.400
< C1C2C3	107.999	108.00	-------
<C1C2C4	119.999	120.000	-------
m.wt. (g/mol.)	720.660		
Point group	I_h		I_h
ΔH_f (kcal/mol) ΔH_f (kJ/ mol)	812.154 3398.053	--------	-------
E_{total} (eV)	--------	-62453.27	-------
Ionization potential (eV)	9.468	-------	-------
E_{HOMO} (eV)	-9.468	-6.624	-------
E_{LUMO} (eV)	-2.868	-3.749	-------
$\Delta E_{HOMO-LUMO}$ (eV)	6.600	2.875	-------
Dipole moment (Debye)	0.000	0.000	0.000

The correlation of bond lengths

1. The C=CH$_2$ bond length was found to increase slightly (1.341, 1.342**Å**) with increasing the size of the construction units 5r, and 1,2,3-trimethylene. (C=C **h**) for hexagon ring of corannulene is longer (1.385**Å**) due to the decrease in the bond order of this bond.
2. The (C-C **p)** bond length for pentagon ring decreases with increasing of the size of the construction units 5r, 1,2,3-trimethylene and fullerene (1.493,1.479**,**1.458**Å**) respectively, may be due to the transition from a tense planar geometrical 5r to a more stable and highly symmetrical shape molecule Fullerene C$_{60}$. The length of (C-C **h**) bond for hexagon ring of corannulene (1.450**Å**) is nearly to (C-C **p)** bond length of Fullerene due to its bowel structure, Table-2.
3. The length of the conjugated double bond (C$\overline{\cdots\cdots}$C **h**) in hexagon ring decreases for 1,2,3-trimethylene, fullerene and corannulene (1.397,1.394**,**1.391**Å**) respectively. The largest one was (1.450**Å**) which belongs to the conjugated bond (C$\overline{\cdots\cdots}$C **p**) of the pentagon ring (the centre ring for corannulene molecule), Table-2.
4. The length of the C-H bond increased slightly with increasing the size of the molecules 1,2,3-trimethylene and corannulene.

Table 2- DFT calculated bond distances for the fullerene C$_{60}$ and its construction units.

Molecule	**Bond length (Å)**					**Cross section of molecule**
	C=C	**C-C**	**C$\overline{\cdots\cdots}$C**	**CH$_2$**	**C—H**	
5Radialene (D$_{5h}$)	C=CH$_2$ 1.341	**C-C p** 1.493	------	1.081	------	
1,2,3-Trimethylene Indan (C$_{2v}$)	C=CH$_2$ 1.342	1.479 **p**	1.397 **h**	1.082	1.082	
Corannulene (C$_{5v}$)	**C=C h** 1.385	C-C **h** 1.450	C$\overline{\cdots\cdots}$C **h** 1.391 C$\overline{\cdots\cdots}$C **p** 1.419	------	1.083	
Fullerene 60 (I$_h$)	-------	C-C **p** 1.458	C$\overline{\cdots\cdots}$C **h** 1.394	------	------	

p.; pentagon ring, h.; hexagon ring

The correlation of physical properties

1. The total energy decreased with increasing the size of the fullerene construction units, (increasing instability) from the smallest unit 5radialene (-10572.410 eV) to the largest one fullerene molecule (-62453.27 eV) Table-3.
2. The HOMO energy (E$_{HOMO}$) is often associated to the electron donating ability of the molecule; therefore, corannulene and Fullerene were found to have the higher values of E$_{HOMO}$ (-6.280, -6.623) respectively, in otherward have a higher tendency to donate electrons to appropriate acceptor of low empty molecular orbital energy. Conversely, the LUMO energy (E$_{LUMO}$) indicates the electron-accepting ability of the molecule, so the lowest value (-3.748 eV for fullerene) the higher the capability of accepting electrons.

   The gap energy between the Frontier orbital ($\Delta E_{HOMO-LUMO}$) is another important factor in describing the molecular activity, so when the gap energy decreased, the conducting efficiency is improved [33]. Table 3 shows that fullerene C$_{60}$ possess the lowest value of energy gap (2.875 eV), so it has the highest ability for electrical conductivity, which in agreement with the research of Brus [34].
3. The dipole moment (μ in Debye unit) results from the non-uniform distribution of charges on the various atoms in the molecule, and depends on the geometric structure and symmetry of the molecule. Table 3 shows that μ was found to be zero for the higher symmetry (5r (D$_{5h}$) [35,36], fullerene molecules (I$_h$)), and possess greater value than zero for the lower symmetry molecules (1,2,3, trimethylene indan (C$_{2v}$) [37] and corannulene (C$_{2v}$) [37,38]).

Table 3- DFT (6-311G/ B3LYP) physical properties. for the calculated fullerene C_{60} molecule and its construction units.

Molecule	**m. wt. (g/ mol)**	**ΔH^0_f (kcal/mol)**	**μ (debye)**	**$E_{tot.}$ (eV)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE (eV) HOMO - LUMO**
5Radialene (D_{5h})	130.00	80.875	0.000	-10572.41	-9.088	-0.381	8.707
1,2,3-Trimethylene Indan (C_{2v})	154.00	75.974	0.302	-12655.84	-8.000	-0.323	7.677
Corannulene (C_{5v})	250.00	139.41	2.326	-20902.04	-6.280	-1.836	5.444
Fullerene 60 (I_h)	720.66	811.022	0.000	-62453.27	-6.623	-3.748	2.875

The calculated of charge densities

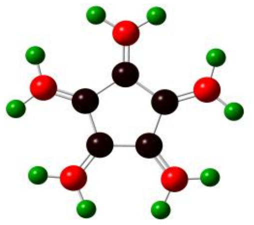
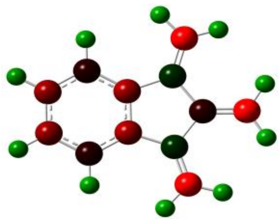
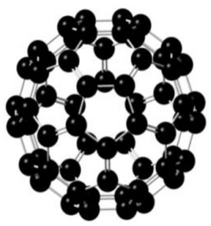
- For 5radialene, as it was studied previously [35,36], the positive charge density concentrated at the hydrogen atoms (σ -H) with (0.161) value. The negative charge density concentrated at the methylene carbon atoms (σ $=CH_2$) with (-0.294) value, and diminished at pentagon carbon atoms (-0.028) in meaning (σ=C > σ—C), contradict the assumption of sp hybridization at the pentagon ring atoms, which should possess higher electron affinities than expected. Two factors might explain these results, Figure-2.

1. For the external methylene carbon atoms a partial shift of electrons exists from the neighbored H atoms to C, as might be viewed considering the calculated electron densities at the H atoms.
2. The delocalization of the ring electrons, causing a partial distribution of the electrons in the bond regions besides the localization at the C atoms.

- For 1,2,3-trimethylene indan, it is shown that the positive charge densities also concentrated at hydrogen atoms (0.162 H_α, 0.147 H_β of hexagon ring and 0.158 for hydrogen of ($=CH_2$) group**).** For carbon atoms charge densities are higher at methylene carbon atom of mid ($=CH_2$) group than that at side in methylene carbon group (σ$=CH_{2\,\mathbf{mid}}$ (-0.298) > σ $=CH_{2\,\text{side in}}$ (-0.288)). The charge of hexagon-pentagon carbons is (-0.172), and for β position carbons (-0.157). The positive charges are concentrated at the hydrogen atoms mainly, and slightly at the carbon atoms attached to methylene group ($C=CH_{2\,\text{side in}}$) which has a positive charge density of (0.045) value, Figure-2.

- For corannulene molecule, the calculations of Mulliken electronic charges population analysis by DFT (B3LYP/6-311G) method illustrated, that the carbon atoms are diminishing charges from center to outer (σ C⎓C $_{\text{pentagon}}$ (-0.155) > σ C⎓C $_{\text{hexagon}}$ (-0.140)). The H atoms are positively charged. The carbon atoms are of the negative charge, except carbon atoms located at the edge between two hexagon rings (0.133), Figure-2.

- For fullerene molecule, according to the highly symmetrical shape (I_h) with no hydrogen atoms, the charge density on every carbon atom is zero (σC⎓C hexagon= σC⎓C pentagon). For this reason, fullerenes in chemistry play a role of functional groups carriers. They readily form adducts as well as charge transfer complexes. Fullerene also proved to be a strong acceptor of electrons in the presence of many organic donors. This property does not result as much from the low energy of LUMO of the neutral fullerene that may accept a charge from the donor but rather fullerene geometrical structure allowing distribution of the acquired charge over large volume thus diminishing electrostatic interaction at the donor site.

											
5Radialene (D_{5h})			**1,2,3-Trimethylene Indan (C_{2v})**			**Corannulene (C_{5v})**			**Fullerene (I_h)**		
Electronic charge density (e)(-0.294-0.294)			**Electronic charge density (e) (-0.298-(0.298)**			**Electronic charge density(e)(-0.155-0.155)**			**Electronic charge density(e) (0.000)**		
-H	**0.161**	🟩	**$-H_\alpha$ (h.)**	**0.162**	🟩	**$-H_h$**	**0.151**	🟩	**$-C_h$**	**0.000**	⬛
=C	**-0.294**	🟥	**$-H_\beta$ (h.)**	**0.147**	🟩	**$=C_h$**	**0.133**	🟩	**$-C_p$**	**0.000**	⬛
$-C_p$	**-0.028**	⬛	**-H (CH_2)**	**0.158**	🟩	**$-C_h$**	**-0.140**	🟥			
			-C (p.)	**0.045**	🟩	**$-C_p$**	**-0.155**	🟥			
			$-C_\alpha$ (h.)	**-0.044**	⬛		**0.151**				
			-C (p.)	**-0.050**	⬛		**0.133**	**0.13**			
			$-C_\beta$ (h.)	**-0.157**	🟥						
			-C (p-h.)	**-0.172**	🟥						
			$=CH_2$ side in	**-0.288**	🟥						
			$=CH_2$ mid	**-0.298**	🟥						

p.; pentagon ring, h.; hexagon ring, α; α position in hexagon ring, β; β position in hexagon ring., mid: middle position. The color change from, red (higher electronic density) to black (zero electronic density)

Figure 2- Distribution of electronic charge density of the calculated molecules by using DFT (6-311G/ B3LYP) level method.

Vibration frequencies and IR absorption intensities of fullerene

The most striking property of the fullerene C_{60} molecule is its high symmetry. There are 120 symmetry operations, like rotations around an axis or reflections in a plane, which map the molecule onto itself. This makes fullerene C_{60} molecule with its largest number of symmetry operations, the most symmetric molecule. Fullerene molecule possesses 174 fundamental vibrations. Inspection of its irreducible representations, as defined by the symmetry character table, (which agrees with the calculation done by Schettino et al. [39], without taking into account the assignment of the valance of the vibration modes). The results of the calculation for this work show the following modes of vibration;

$\Gamma_{vibration} = \Gamma_{total} - (\Gamma_{rotation} + \Gamma_{translation}) = 3N–6 = 180–6 = 174 = 2A_g + 9T_{1g} + 12T_{2g} + 24G_g + 40H_g + A_u + 12T_{1u} + 15T_{2u} + 24G_u + 35H_u$.

The 3N-6 modes of vibration calculated in this research are 174, 42 of which are Raman active ($2A_g$ (polarized)+ $40H_g$ (depolarized), and IR active ($12T_{1u}$)). The rests are both IR and Raman inactive.

The valance assignments of the modes are as follows:

- νRing (C=C) stretching vibrations.

The calculated C=C stretching vibration frequencies range from (1251-1576cm^{-1}), showing the following correlation:

$\nu_{sym.}$ (C=C str.) (1576 cm^{-1}) (H_g) > $\nu_{asym.}$ (C=C str.) (1567cm^{-1}) (H_u).

The highest intensity is 1.732 km/mole due to $\nu_{13\text{-}15}$(1433cm^{-1}) (T_{1u}).

- νRing (C-C) stretching vibrations

The C-C vibration modes, located at C atoms of the ring, as can be seen from the atomic displacement vectors. Their frequencies are lower than those of the C=C vibration modes.

According to the calculated results, the range of these frequencies is (1040-1340 cm^{-1}).

The highest intensity is 0.653 km/mole due to $\nu_{16\text{-}18}$ (1180cm^{-1}) (T_{1u}).

- δRing in-plane bending vibrations (δCCC)

The deformation (δCCC) vibrations are smaller values. According to their assignment, they fall in the range (614-1142cm^{-1}). These models include the expected clock and breathing and puckering vibration motions.

- γRing out of plane vibrations (γCCC)

The ring out of plane vibrations (γCCC), show frequencies values range (267-831cm^{-1}).

The highest intensity is 0.953 km/mole due to ν_{21-23} (526cm^{-1}) (T_{1u}).

The correlations of vibration frequencies

The correlation was done for the most important calculated vibration frequencies, showing the following relations:

1. The vibration frequencies of C=C stretching were found to decrease (decrease in the force constant) with increasing the size of the molecule, Table-4, indicating that the increase in elasticity, is in agreement with the correlation of the C=C bond lengths, Table-2.
2. The vibration frequencies of the in-plane ring deformation (δring), were found to increase with increasing the size of the molecule (increased from 5radialene, 1,2,3-trimethylene indan, corannulene, to fullerene) Table-4. This means that fullerene molecule shows a better stiffness and electrical conductance among its construction units (the electrical conductivity properties increase with increasing δring [37].
3. The vibration frequencies of the out of plane ring deformation γring (puckering) of 5radialene, 1,2,3-trimethylene indan, to corannulene, were found to decrease with increasing size of the molecule, Table-4. This also indicates that fullerene C_{60} molecule has better electrical conductance among its construction units (the electrical conductivity properties increase with decreasing γring [37].

Table 4- Vibrational frequencies and IR absorption intensities for fullerene molecule

Symmetry and Description		PM3		Exptl. [26]	DFT This work	Calcd. [26]
		Freq. cm^{-1}	Intensity km/mol	Freq. cm^{-1}		
A_g						
ν_1	Ring C=C sym. str.	1506	0.000	1470	1470	1474
ν_2	γring (puckering)	623	0.000	496	495	487
A_U						
ν_3	δring (δCCC)	978	0.000	------	1078	946
T_{1g}						
ν_4	Ring str.(C-C str.) (p.)	1440	0.000	1369	1290	1276
ν_7	δring (δCCC)	866	0.000	970	904	823
ν_{10}	γring (γCCC) (puck.)	613	0.000	------	565	562
T_{1U}						
ν_{13}	Ring C=C sym. str.	1469	1.732	1428	1433	1431
ν_{16}	Ring str.(C-C str.)	1377	0.653	1183	1180	1189
ν_{19}	γring (breathing)	733	0.527	577	577	577
ν_{21}	γring (puckering)	558	0.953	527	526	528
T_{2g}						
ν_{24}	Ring str.(CCC str.)	1518	0.000	1360	1340	1344
ν_{27}	γring (puckering) (p.)	913	0.000	870	831	789
ν_{30}	δring (δCCC) (p.)	817	0.000	------	668	724
ν_{33}	δring (δCCC) (p.)	586	0.000	560	614	555
T_{2U}						
ν_{36}	Ring C=C sym. str.	1528	0.000	------	1524	1507
ν_{39}	δring (δCCC) (h.)	1337	0.000	------	1142	1177
ν_{42}	δring (δCCC) (p.)	1159	0.000	------	955	958
ν_{45}	γring (puckering)	763	0.000	680	716	709
ν_{48}	γring (puckering)	355	0.000	355	340	337

H_g						
ν_{53}	Ring C=C sym. str.	1560	0.000	1575	1576	1585
ν_{58}	Ring C=C sym. str.	1436	0.000	1428	1427	1426
ν_{63}	Ring C=C sym. str.	1236	0.000	1250	1251	1251
ν_{68}	δring (δCCC) (p.) (breathing) + δring (h.)	1291	0.000	1099	1101	1104
ν_{73}	δ ring (breathing)	941	0.000	774	775	772
ν_{78}	γring (puckering)	758	0.000	710	711	705
ν_{83}	γring (γCCC) (puck.)	440	0.000	437	431	429
ν_{88}	γring (γCCC) (puck.)	266	0.000	273	267	261
H_U						
ν_{93}	Ring C=C asym. str.	1548	0.000	1555	1567	1576
ν_{98}	Ring C=C asym. str.	1501	0.000	------	1343	1343
ν_{103}	Ringstr. (C-C asym. str.)	1379	0.000	------	1214	1219
ν_{108}	δring (δCCC)	816	0.000	------	737	729
ν_{113}	δring (δCCC) (p. & h.)	701	0.000	------	694	665
ν_{118}	γring (puckering)	547	0.000	560	535	531
ν_{123}	δring (δCCC)	407	0.000	355	403	400
G_g						
ν_{128}	Ring C=C sym. str.	1488	0.000	------	1497	1507
ν_{132}	Ring str.(C-C str.)	1445	0.000	1360	1348	1308
ν_{136}	Ring C-C sym. str.	1246	0.000	1065	1040	1072
ν_{142}	δring (δCCC)	850	0.000	------	758	741
ν_{146}	δring (δCCC) (h.)	593	0.000	------	592	565
ν_{150}	γring (puckering)	488	0.000	------	485	480
G_u						
ν_{154}	Ring C=C asym. str. (p.)	1656	0.000	1440	1429	1434
ν_{158}	Ring str.(C-C $_{\text{asym.}}$ str.)p.	1476	0.000	1310	1315	1307
ν_{162}	δring(δCCC)(breath.) h.	1125	0.000	1065	970	962
ν_{166}	γring (puck.) (p. & h.)	909	0.000	------	797	751
ν_{170}	γring (γCCC) (puck.)	783	0.000	760	707	738
ν_{174}	γring (puckering)	356	0.000	403	354	351

p.; pentagon ring, h.; hexagon ring, γ; out of plane bending vibration., δ; in-plane bending vibration. The scaling factor for C=C str. 0.86. in PM3 calculations.

Figure-3 shows the IR spectrum of fullerene molecule. Figure-4 shows the graphical pictures of some vibration modes of fullerene molecule as calculated applying the DFT method.

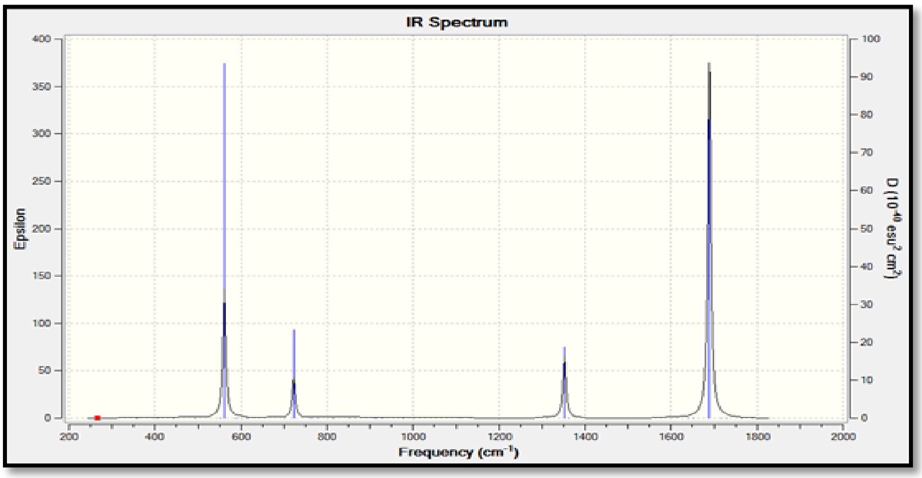


Figure 3- IR spectrum of fullerene molecule as calculated applying the DFT method**.**

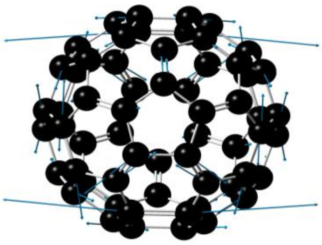
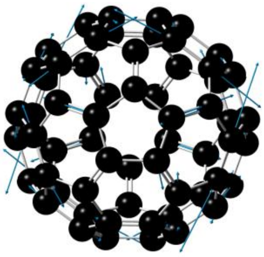
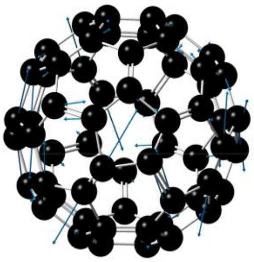
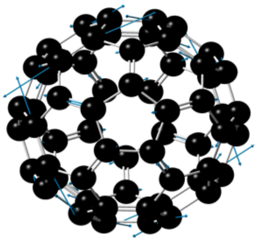
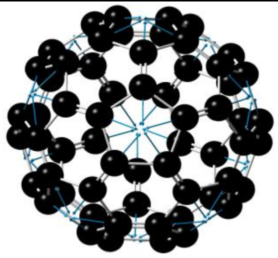
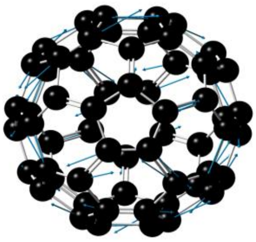
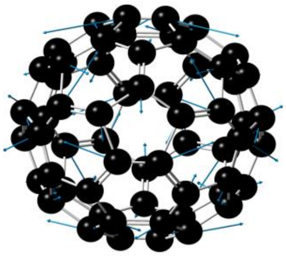
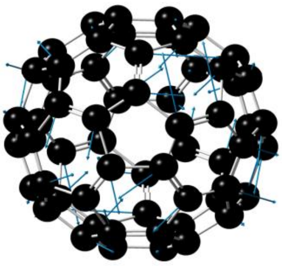
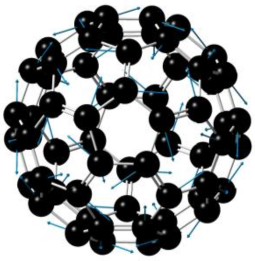
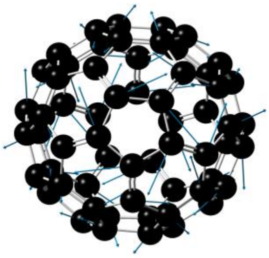
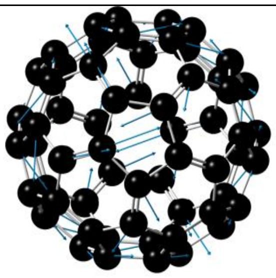
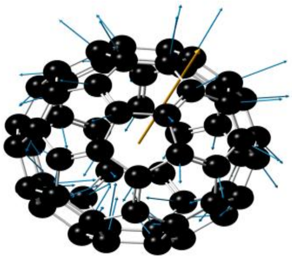
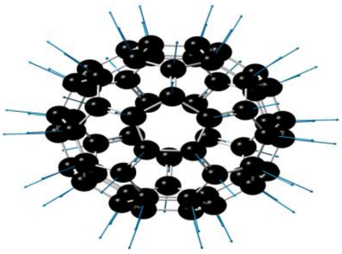
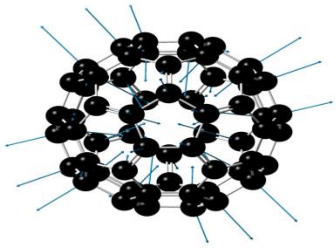
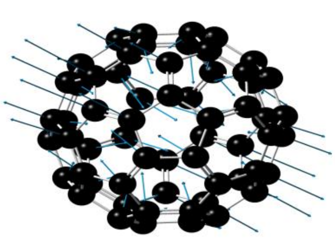
		
ν_{53}, 1576 cm^{-1} **Ring C=C sym. str.**	**ν_{1}, 1470 cm^{-1}** **Ring C=C sym. str.**	**ν_{93}, 1567 cm^{-1}** **Ring C=C asym. str.**
		
ν_{36}, 1524 cm^{-1} **Ring C=C sym. str.**	**ν_{128}, 1497 cm^{-1}** **Ring C=C sym. str.**	**ν_{58}, 1427 cm^{-1}** **Ring C=C sym. str.**
		
ν_{4}, 1290 cm^{-1} **Ring C-C sym. str.**	**ν_{136}, 1040 cm^{-1}** **Ring C-C sym. str.**	**ν_{3}, 1078 cm^{-1}** **δring (δCCC)**
		
ν_{7}, 904 cm^{-1} **δring (δCCC)**	**ν_{142}, 758 cm^{-1}** **δring (δCCC)**	**ν_{170}, 707 cm^{-1}** **γring (γCCC) (puck.)**
		
ν_{10}, 565 cm^{-1} **γring (γCCC) (puck.)**	**ν_{83}, 431 cm^{-1}** **γring (γCCC) (puck.)**	**ν_{88}, 267 cm^{-1}** **γring (γCCC) (puck.)**

Figure 4- Graphical pictures of some vibration modes for fullerene molecule as calculated applying the DFT method.

Table 5- Some important vibrational frequencies for construction units of fullerene C_{60} molecule calculated according to DFT method.

Molecule	**C-H**	**=CH$_2$**	**C⎓ C**	**C⎓ C$_h$**	**C⎓ C$_P$**	**δring δCCC**	**δCH sciss.**	**γCH wagg.**	**γCH twist.**	**γring puck.**
5Radialene (D_{5h})	------	3022 A_1'	1685 A_1'	------	1268 E_2'	631 A_1'	1486 E_1'	938 E_2''	738 E_1''	805 E_2''
1,2,3-Trimethylene indan (C_{2v})	3068 A_1	3017 A_1	1683 A_1	1616 A_1	1274 A_1	844 A_1	1465 A_1	948 B_1	662 A_2	770 B_1
Corannulene (C_{5v})	3051 A_1	------	1659 A_1	1466 A_1	1486 E_1	872 E_1	1276 A_1	876 A_1	993 E_1	603 A_1
Fullerene 60 (I_h)	------	------	1470 A_g	------	1290 T_{1g}	904 T_{1g}	------	------	------	495 A_g

p.; pentagon ring, h.; hexagon ring.

Conclusions

The geometry equilibration was applied for the calculation of all 3N−6 vibration frequencies of fullerene, and for the analysis of their normal coordinates. The calculated frequencies of the molecules were close to the available experimental frequencies and those of the calculations done by others. Both valance and symmetry assignments of the frequencies allow useful comparison between modes of the same valance nature for the fullerene and the construction units. The results are expected to be of major importance in discussing the bond strengths and reactivity of the species at different sites of the molecule.

- The bond length of the conjugated (C⎓C), increased with increasing the bulk of the molecule from 1,2,3-trimethylene indan (planar) to corannulene (bowl) molecule due to the increase in the aromatic and elastic properties of the geometric structures.
- Compared with the frequencies of fullerene construction units, fullerene possesses the lowest symmetrical C⎓C stretching and lowest γring (puckering) bending vibration. On the other hand, has the highest in-plane (δring) ring bending deformation, especially breathing vibration which decreases the resistance toward electrical conductivity properties.
- Fullerene was found to have the highest E_{HOMO}, lowest E_{LUMO} and smallest $\Delta E_{LUMO\text{-}HOMO}$ among the unit's constructions, explaining the highest electronic conductivity properties.

References

1. Kroto, H., Heath, J., Obrien, S., Curl, R. and Smalley, R. **1985**. C_{60} Buckminsterfullerene. *Nature*, 318, pp: 162-163.; b- Hirsch A. **2006**. Functionalization of fullerenes and carbon nanotubes. *Physica Status Solidi (B) Basic Research*, 243, pp: 3209-3212.
2. Novoselov, K., Geim, A., Morozov, S. Jiang, D., Zhang, Y., Dubonos, S., Grigorieva, I. and Firsov, A. **2004**. Electric field effect in atomically thin carbon films. *Science*, 306(5696), pp: 666-669.
3. Dennis, T., Hare, J.P., Kroto, H.W., Taylor, R., Walton, D.R., and Hendra, P.J. **1991**. The vibrational Raman spectra of C_{60} and C_{70}. *Spectrochimica Acta, Part A, Molecular Spectroscopy*, 47(9), pp: 1289-1292. b- Sathish, M. and Miyazawa, K. **2012**. Synthesis and characterization of fullerene nanowhiskers by liquid-liquid interfacial precipitation: influence of C_{60} solubility. *Molecules, 17,* pp: 3858-3865.
4. Lynch, K., Tanke, C., Menzel, F., Brockner, W., Scharff, P. and Stumpp, E. **1995.** FT-Raman spectroscopic studies of C_{60} and C_{70} subsequent to chromatographic separation including solvent effects. *J. Phys. Chem*., 99, pp: 7985-7992.
5. Meilunas, R., Chang, R.P.H., Liu, S., Jensen, M. and Kappes, M.M. **1991.** Infrared and Raman spectra of C_{60} and C_{70} solid films at room temperature. *J. Appl. Phys*., 70, pp: 5128-5130.
6. Bethune, D.S., Meijer, G., Tang, W.C., Rosen, H.J., Golden, W.G., Seki, H. Brown, C.A. and de Vries, M.S. **1991**. Vibrational Raman and infrared spectra of chromatographically separated C_{60} and C_{70} Fullerene clusters. *Chem. Phys. Lett.*, 179, pp: 181-186.
7. Eisler, H.J., Gilb, S., Hennrich, F.H. and Kappes, M.M. **2000**. Low frequency Raman active vibrations in fullerenes. 2. quadrupolar modes. *J. Phys. Chem.*, 104 A, pp: 1769-1773.

8. Kuzmany, H., Pfeiffer, R., Hulman, M., Kramberger, C. and Philos, T. **2004**. Raman spectroscopy of fullerenes and fullerene–nanotube composites. Philosophical transactions. *Series A, Math. Phys. Eng. Sci.*, 362(824), pp: 2375-2406.

9. Adhikari, S. and Chowdhury, R. **2011**. Vibration spectra of fullerene family. *Physics Letters,* 375A(22), pp: 2166–2170. b- Ferguson, A.J.; Blackburn, J.L. and Kopidakis, N. **2013**. Fullerenes and carbon nanotubes as acceptor materials in organic photovoltaics. *Mater. Lett., 90,* pp:115–125.

10. Iijima, S. **1991**. Helical microtubules of graphitic carbon. *Nature,* 354 (6348), pp: 56–58.

11. Stanton, R.E. and Newton, M.D. **1988**. Normal vibrational modes of buckminsterfullerene. *J. Phys. Chem.*, 92(8), pp: 2141-2145.

12. Malolepsza, E., Witek, H.A. and Irle, S. **2007**. Comparison of geometric, electronic, and vibrational properties for isomers of small fullerenes C_{20}-C_{36}. *J. Phys. Chem.*, 111A, pp: 6649-6657.

13. Jing, D. and Pan, Z. **2009**. Molecular vibrational modes of C_{60} and C_{70} via finite element method. *Europ. J. Mech. A. Solids*, 28, pp: 948-954.

14. Chadderton, L. **1993.** Axisymmetric vibrational modes of fullerene C_{60}. *J. Phys. Chem. Solids*, 54, pp: 1027-1033.

15. Zhou, Z. **2013**. Liposome formulation of fullerene-based molecular diagnostic and therapeutic agents. *Pharmaceutics*, *5*, pp: 525-541.

16. Liu, T. and Troisi, A. **2013.** What makes fullerene acceptors special as electron acceptors in organic solar cells and how to replace them. *Adv. Mater.*, 25, pp: 1038-1040.

17. Bourgoin, J.P., Loiseau, A. and Nierengarten, J.F. **2007**. Fullerenes and carbon nanotubes. *Nanoscience: Nanotechnologies and Nanophysics*, pp: 279-323.

18. Harter,W.G. and Weeks, D.E. **1989**. Rotation-vibration spectra of icosahedral molecules. Icosahedral symmetry analysis and fine structure. *J. Chem. Phys*., 90 (9), pp: 4727–4743.

19. Weeks, D.E. and Harter,W.G. **1989.** Rotation-vibration spectra of icosahedral molecules. II. Icosahedral symmetry, vibrational eigen frequencies, and normal modes of Buckminsterfullerene. *J. Chem. Phys.*, 90 (9), pp: 4744–4771.

20. Wu, Z.C., Jelski, D.A. and George, T.F. **1987.** Vibrational motions of Buckminsterfullerene. *Chem. Phys. Lett*., 137, pp: 291–294.

21. Cyvin, S.J., Brendsdal, E., Cyvin, B.N. and Brunvoll, J. **1988**. Molecular vibrations of footballene. *Chem. Phys.Lett.*,143 (4), pp: 377–380.

22. Jishi, R.A., Mirie, R.M. and Dresselhaus, M.S. **1992**. Force-constant model for the vibrational modes in C_{60}. *Physical Review,* 45 B, pp: 13685-13689.

23. Negri, F., Orlandi, G. and Zerbertto, F. **1988.** Quantum-chemical investigation of Franck-Condon and Jahn-Teller activity in the electronic spectra of Buckminsterfullerene. *Chem. Phys. Lett.*, 144, pp: 31-37.

24. Slanina, Z., Rudzin´ ski, J.M., Togasi, M. and Osawa, E. **1989**. Quantum-chemically supported vibrational analysis of giant molecules: the C_{60} and C_{70} clusters. *J. Mol. Struc. (Theochem),* 202, pp: 169–176.

25. Adams, G.B., Page, J.B., Sankey, O.F., Sinha, K., Menendez, J. and Huffman, D.R. **1991**. First-principles quantum molecular-dynamics study of the vibrations of icosahedral C_{60}. *Phys. Rev.*, 44B(8), pp: 4052-4055.

26. Schettino, V., Pagliai, M., Ciabini, L. and Ianni, G. **2001**. The vibrational spectrum of fullerene C_{60}. *J. Phys.Chem.*, A 105, pp:11192–11196.

27. Sun, G.Y. and Kertesz, M. **2002**. Vibrational Raman spectra of C_{70}, studied by density functional theory. *J. Phys. Chem*., A106 (26), pp:6381–6386.

28. Schettino, V., Pagliai, M., and Cardini, G. **2002**. The infrared and Raman spectra of fullerene C_{70}. DFT calculations and correlation with C_{60}. *J. Phys. Chem., A*106, pp:1815–1823.

29. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A. D., Raghavachari, K., Foresman, J.B., Ortiz,J. V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C. and Pople, J.A. **2009.** Gaussian 09, Revision E.01. *Gaussian, Inc., Wallingford CT*

30. Becke, A.D. **1993**. Density-functional thermochemistry. III. The role of exact exchange. *Chem. Phys.*, 98, pp: 5648-5652.
31. Lee, C., Yang, W. and Parr, R.G. **1988**. Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev.*, 41B, pp: 785-789.
32. Cataldo, F. **2009**. Fullerenes Nanotubes and carbon nanostructures. *J. Art*icle/ *Scientific*, 17, pp: 79-84. b- Husen1, A. and Siddiqi, K.S. **2014**. Fullerenes nanotubes and carbon nanostructures. *Journal of Nanobiotechnology*, 12(16), pp: 2-10.
33. Kubba, R.M. and Abood, F.K. **2015**. DFT, PM3, AM1, and MINDO/3 quantum mechanical calculations for some INHC Cs symmetry schiff bases as corrosion inhibitors for mild steel. *Iraqi Journal of Science*, 56(1C), pp: 602-621.
34. Brus, L.B. **1986**. Electronic wave functions in semiconductor clusters. *Feature Article. J. Chem. Phys.*, 90, pp: 2555-2560.
35. Kubba, R.M. and Samawi, K.A. **2013**. Studying of frequencies, normal modes of vibration and electronic charge densities of 5radialene molecule. *Iraqi J. Science*, 54(4), pp: 753-760.
36. Shanshal, M. and Kubba, R.M. **2006**. Bonding, electron densities and vibration frequencies of [3]-, [4]-, [5]- and [6] radialenes; a B3LYP density functional study. *Z. Naturforsch*, 61a, pp: 95–98.
37. Samawi, K.A. **2014**. Comparison study of physical properties and energies for construction units of fullerene molecule and for (ZigZag) SWCNTs using quantum mechanical methods. Ph.D. Thesis. Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.
38. Kubba, R.M., AL-Dolaimie, M.A. and Shanshal, M. **2011**. Studying the vibration frequencies of corannulene and it's positive and negative radical ions using quantum mechanical calculations. *Anbar, J. of pure science*, 5(2), pp: 32-48.