Theoretical Study of Vibration Frequencies of Fullerene Molecule (C_{60}) by Using Density Function Theory (DFT)

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ABSTRACT

Fullerene molecule C_{60} was studied optimize structure, harmonic vibration frequencies, infrared active vibration modes and some physical values in the gaseous state theoretically by using Density function Theory (DFT), from view animations of the mode displacement patterns, the infrared active vibration modes can be classified theoretically to; Twisting vibration for (=C-C=C-) group at 510.0 cm^{-1}, Wagging vibration for (=C-C=C-) group at 579.8 cm^{-1}, Stretching vibration for (C-C) bond in 1165.6 cm^{-1} and Stretching vibration for (C=C) bond at 1464.7 cm^{-1}. These results were compared with other calculation data and experimental measurements. Two from these modes are in good agreement with experimental measurement while the two are nearly approach.

دراسة ترددات أهتزاز جزيئة الفللرين ((Fullerene (C_{60})نظرياً بأستخدام نظرية دوال الكثافة

الخلاصة

دُرسَ الشكل الأمثل وترددات الأهتزاز التوافقية الفعالة في طيف الأشعة تحت الحمراء وبعض القيم الفيزياوية لجزيئة الفللرين (fullerene C_{60}) في الحالة الغازيةنظرياً بواسطة أستخدام نظرية دوال الكثافة (Density function Theory (DFT)). وتصنيف تلك الأنماط الفعالة في طيف الأشعة تحت الحمراء عن طريق رؤية الصور المتحركة لها ومقارنة هذه النتائج مع نتائج أخرى نظرية وعملية إذ أظهرت جزيئة الفللرين أربعة أنماط فعالة في طيف الأشعة تحت الحمراء وهي: نمط أهتزاز ألتوائي عند (510.0 cm^{-1}) لمجموعة (=C-C=C-)؛ ونمط أهتزاز أرتجاجي عند (579.8 cm^{-1}) لمجموعة (=C-C=C-)؛ ونمط أهتزاز مطّ ي عند (1165.6 cm^{-1})ناتج عن مطّ الآصرة (C-C)؛ ونمط أهتزاز مطّ ي عند (1464.7 cm^{-1})ناتج عن مطّ الآصرة (C=C). أثنان من الأنماط كانت مطابقة مع القيم العملية، والأثنان الأخرى كانت قريبة منها.

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INTRODUCTION

The first fullerene to be discovered, and the family's namesake, buckminsterfullerene (C_{60}), was prepared in 1985. The name was an homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion."[1] Fullerenes have since been found to occur in nature.[2] The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology. Buckminsterfullerene (C_{60}) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome. Since buckminsterfullerenes have a shape similar to that sort of dome, the name was thought appropriate.

Since the discovery of fullerenes in 1985, structural variations on fullerenes have evolved well beyond the individual clusters themselves. Examples include:[3]

- buckyball clusters: smallest member is C_{20} (unsaturated version of dodecahedrane) and the most common is C_{60};
- nanotubes: hollow tubes of very small dimensions, having single or multiple walls; potential applications in electronics industry;
- megatubes: larger in diameter than nanotubes and prepared with walls of different thickness; potentially used for the transport of a variety of molecules of different sizes;[4]
- polymers: chain, two-dimensional and three-dimensional polymers are formed under high-pressure high-temperature conditions;
- nano"onions": spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants;[5]
- linked "ball-and-chain" dimers: two buckyballs linked by a carbon chain;[6]
- fullerene rings.[7]

Buckminsterfullerene is the smallest fullerene molecule in which no two pentagons share an edge (which can be destabilizing, as in pentalene). It is also the most common in terms of natural occurrence, as it can often be found in soot. The structure of C_{60} is a truncated (T = 3) icosahedron, which resembles an association football ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge. The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm). The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm. The C_{60} molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms.[8]

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THE CALCULATION METHOD

Gaussian 03, Revision C.01 [9] used for calculation the ground-state geometry optimized to a local minimum without any symmetry restrictions using basis set 3-21G [10,11]. The becke three-parameter hybrid (B3) [12,13] exchange functional in combination with the Lee-Yang-Parr (LYP) [14] correction functional (B3LYP) was used for all geometry optimizitions, harmonic vibration frequency and studied the active vibration frequncy in infra red, the job of time the central processing unit (cpu): 30 days & 10 hours for geometry optimizations calculation and job of time the central processing unit (cpu): 5 days & 19 hours for harmonic vibration frequency calculation.

RESULTS AND DISCUSSION

The optimized structure for fullerene molecule C_{60} is shown in figure(1). Displayed in Table (1). Results of geometry optimization calculations, it has high stability because the big potential energy (-1426656.63 KCal.Mol^{-1}), this molecule is an asymmetric top, it has no symmetry at all symmetry element is the identity, E. Such molecule belongs to the C_1 point group, and it is nonpolar because the dipole moment is very low (0.0002 Debye).The fullerene C_{60} molecule has (3N-6)=174 harmonic vibration modes, gust four vibrations modes are triple degenerates are active in the IR absorption spectrum is shown in figure(2)., two modes are single degenerates are Raman-active, eight modes are quintuple degenerates are Raman-active, and 120 modes are no active in IR or Raman. The results had compared with other calculation (Giannozzi and Baroni [15], Adams et al. [16] and experimental measurments [17] in table 2. From view animation of the mode displacement patterns, the infrared active vibration modes can be classified theoretically to:

1- Twisting vibration for (=C-C=C-) group at 510.0 cm^{-1}.
2- Wagging vibration for (=C-C=C-) group at 579.8 cm^{-1}.
3- Stretching vibration for (C-C) bond at 1165.6 cm^{-1}.
4- Stretching vibration for (C=C) bond at 1464.7 cm^{-1}.

In solid state physics, a band gap, also called an energy gap, is an energy range in a solid where no electron states can exist, the gap energy generally refers to the energy difference (in electron volts) between the Low Unoccupied Molecular Orbital (LUMO) and the High Occupied Molecular Orbital (HOMO) in insulators and semiconductors figure 3. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material. So the band gap is a major factor determining the electrical conductivity of a solid. Substances with large gaps energies are generally insulators, those with smaller gaps energies are semiconductors, while conductors either have very small gaps energies or none. In this research have been studied molecule Fillerene in gas phase isolates of this account is that energy gap is an approximation and is equal to value (3.008 eV), and indicates that the molecule in gas phase is insulator for electrical conductivity.

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CONCLUSIONS

We have carried out quantum chemistry calculations using the DFT method to study geometry optimization of fullerene C_{60} molecule, harmonic vibration frequencies, infrared active vibration modes theoretically, the results of fullerene C_{60} molecule are in good agreement with experimental measurement, two from four modes of theoretical active infrared vibration in IR are in good agreement with experimental measurement while the two are nearly approach.

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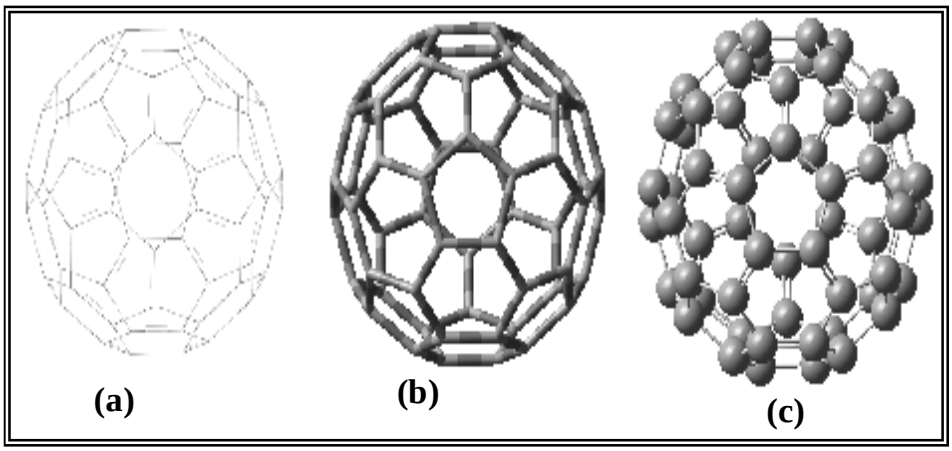

Figure (1). The optimized structure for fullerene molecule C_{60}: display format (a) Wire frame, (b) Tube, (c) Ball and bond type.

Table (1). Some physical values are calculated of fullerene C_{60} molecule.

Subject	Value
Potential energy	-2273.52196 a.u. (-1426656.63 KCal.Mol^{-1})
E_{HOMO}	-0.24004 a.u.
E_{LUMO}	-0.12950 a.u.
$\lambda_{Max.}$	412.16 nm
Gap energy	3.008 eV
Zero-point energy	231.112 KCal.Mol^{-1}
Thermal energy	244.506 KCal.Mol^{-1}
Heat capacity (C_v)	118.314 Cal.Mol^{-1}
Entropy	137.991 Cal.Mol^{-1}
Point group	C_1
Dipole moment	0.0002 Debye

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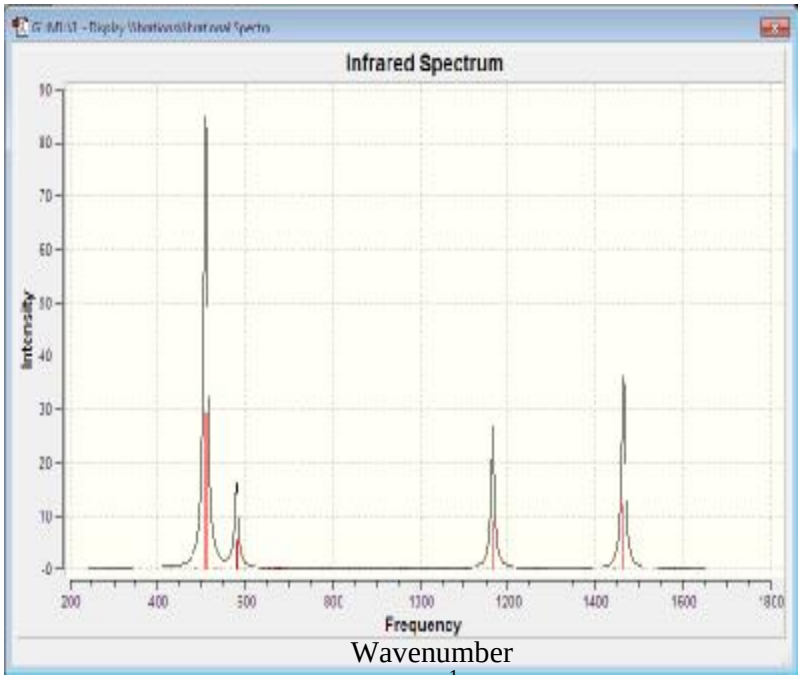

Figure (2). Infrared absorption spectrum for fullerene molecule C_{60}.

Table (2). Comparison of calculated vibration frequencies (cm^{-1}) are active in the IR absorption for fullerene C_{60} molecule with experimental measurement.

Mode	This work	Theoretical calculation		Experimental
		Giannozzi and Baroni [15]	*Adams et al.* [16]	
T1u	510.0	527	522	525
T1u	579.8	586	570	577
T1u	1165.6	1218	1227	1190
T1u	1464.7	1462	1560	1464

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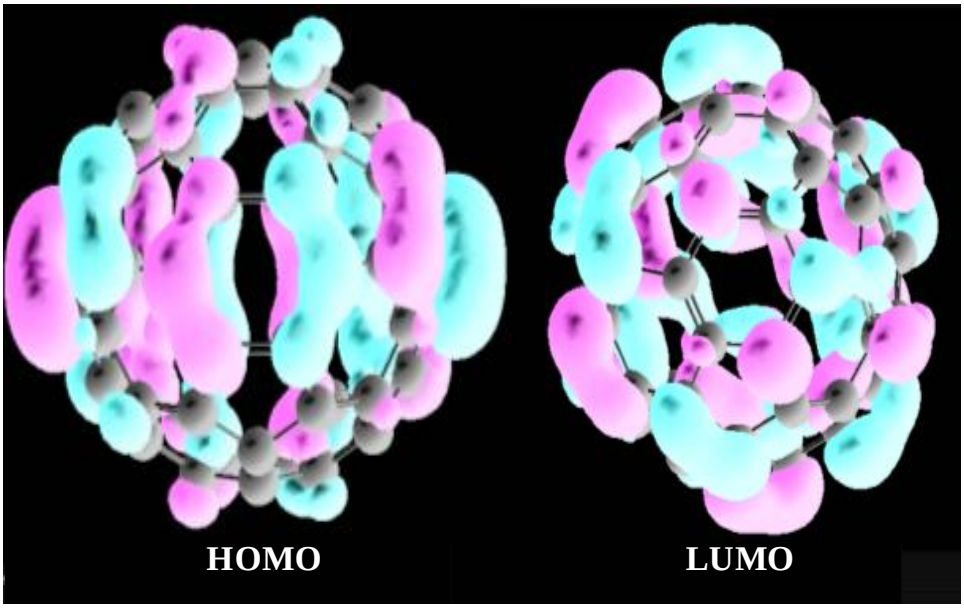

Figure (3). the distribution of electron density of High Occupied Molecular Orbital (HOMO) and Low Unoccupied Molecular Orbital (LUMO) for Fullerene molecule C_{60}.

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