Molecular Dynamics and Vibrational Analysis of Pentacene: RHF and DFT Study

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Abstract

The molecular dynamics of Pentacene molecule and its vibrational behavior is studied using the Gaussian software at the Restricted Hartree Fock and Density Functional Theory levels of computation. Two medium size basis sets, 6-31G and 6-31G* are used. The dipole moments, thermal energies and band gap computations for the molecule are obtained. The Infra Red (IR) and Raman vibrational frequencies are vividly examined and the most intense IR and Raman frequencies identified. The computed band gap at DFT level of theory for both basis sets is much in agreement with the experimental value.

Keywords: Pentacene, Hartree-fork, DFT, bond-angle, bondlength, Raman, frequencies

1. INTRODUCTION

The concept of individual molecules functioning as active devices has been around for decades. The active device size has continuously decreased during the century, starting with meter sized vacuum valve tubes of the early 1930's and 1940's, through millimeter sized transistors in 1960's to micrometer sized integrated circuits in 1970's and 1980's. Thus the molecular scale devices represent the logical evolution to nanoscale devices expected towards the end of this century and the beginning of the next(Abdulsattar, 2012) .

Current scientific literature has numerous reports of single molecules carrying out a wide variety of electrical, magnetic, optical and mechanical functions. A molecule functioning as electronic components, switches, wires, shuttles, brakes, motors and several more devices has been demonstrated. Molecules in solution, in the adsorbed state on surfaces or in the solid state such as crystal and thin films, could function as molecular scale devices (Abszabo and Ostlunnd, 2000).

Organic semiconductors are materials with semiconducting properties these include Polycyclic aromatic hydrocarbons such as anthracene, rubrene and pentacene. Among many organic semiconductors, pentacene has been reported to be the most promising applicant, because of its high hole mobility up to 5.5cm^2/Vs that exceed amorphous Silicon (*Abc Levine, 1991)*.. Pentacene is a linear acene consisting of five benzene rings with molecular formula $C_{22}H_{14}$, molar mass 278.36 g/mol, density 1.3 g/cm^3 and melting point of > 300 °C; sublimes at 372 °C which behaves   as a p-type semiconductor. These kind of materials are important in electrical applications as their band gap is controlled by selecting the number of aromatic rings that is the more rings, the smaller the band gap (Becke, 1993).

Nowadays, the molecular modelization techniques offer a competitive alternative for the interpretation of experimental data arising from industrial interest and applications (*Abc Levine, 1991*; Becke, 1993) This is done principally by obtaining approximate solutions of Schrodinger equation of the molecule. Several types of functions have been proposed. The two more commonly used are the Slater-type functions (STF), introduced by Slater (Perdew and Wang, 1992) in 1930, and the Gaussian-type functions (GTF) proposed by Boys (Lee, Yang. and Parr, 1988) in 1950. The former functions represent mainly features of the radial part of an atomic orbital. The problem in using these functions comes from the difficulty in calculating the integrals. Boys showed that by taking GTF, complete systems of functions can be constructed which is appropriate to any molecule and the necessary integrals can be evaluated explicitly. The usefulness of GTF as basis functions for large-scale molecular calculations was put forward by Huzinaga (Parr and Yang, 1989) in 1965. He concluded that even if the number of GTF needed in the analytical Hartree-Fock expansion calculation would be larger than if STF were used, the number of GTF would not be prohibitively large. Consequently, most molecular calculations are done using CGTF (Contracted Gaussian-Type Functions)(Frisch *et al.,* 2004).

There are major classes of electronic structure methods used in GTF, semi empirical method, ab initio method and Density Functional Theory (DFT) Method. The former deals with parameters derived from experimental data to simplify computations; while the other methods use no experimental data for their computation. Instead, their computations are based solely on the laws of quantum mechanics using values of a small number of constants such as speed of light ,the mass and charge of element, its nuclei and Planck's constant (Andrews and Demidov 1999). Furthermore, ab initio method provides high quality quantitative prediction for a broad range of systems compared to semi empirical methods and is capable of handling any type of atom. Restricted Hatree Fock (RHF) is an example of this method. The Density Functional Theory (DFT) method is similar to ab initio method but provides more accurate results due to the fact that it includes the effect of electron correlation that accounts for the instantaneous interactions of pairs of electrons with opposite spin.

(Baumann and Fayer, 1986). In this article we use RHF and DFT methods to compute the dipole moments, quadrupole moments, band gap and vibrational frequencies of the pentacene molecule.

2. METHODOLOGY

The Gaussian software is used in this study. Mainly, the Gaussian program is characterized by using different basis sets. This is the mathematical representation of the molecular orbital within the molecules and can be interpreted as restricting each electron to a particular region of space. This implies that larger basis sets impose fewer constraints on electrons and more accurately approximate exact molecular orbitals.

The optimized structure of the molecule is obtained and the molecular dynamics of the molecule obtained. The molecular structures and geometries of the organic semiconductor material, pentacene is completely optimized using ab- initio quantum mechanical calculations at the Restricted Hartree-Fock (RHF) level of theory without using the basis sets 6-31G and 6-31G*. The structures are refined further using Density Functional Theory which is a cost effective method for inclusion of electron correlations with the three-parameter density functional generally known as Becke3LYP (B3LYP) (Becke, 1993; Lee, Yang and Parr, 1988; Parr and Yang, 1989)

using the same basis sets. At the first step, geometry optimizations are carried out then, the Infra Red (IR) and Raman frequencies are calculated using the Hessian which is the matrix of second derivatives of the energy with respect to geometry.

The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are computed. Also, total energies, dipole and quadrupole moments are computed. A detailed analysis of the IR and Raman active vibrational frequencies is carried out to determine the most intense frequencies and their descriptions. All computations in this work were modelled in gas phase.

3. RESULTS AND DISCUSION

3.1 Dipole Moments

The dipole moment of a molecule is the first derivative of the energy with respect to an applied electric field. It is a measure of the asymmetry in the molecular charge distribution and is given as a vector in three dimensions. For Hartree-Fock calculations, this is equivalent to the expectation values of X, Y and Z, which are the quantities reported in the output. The computed dipole moments (in Debye) for pentacene at RHF and DFT levels of theory using 6-31G and 6-31G* basis sets is given in Table 1.

Table 1: Dipole moments (in Debye) in gas phase

RHF/6-31G	RHF/6-31G*	B3LYP/6-31G	B3LYP/6-31G*
Gas	Gas	Gas	Gas
X = -0.0001	-0.2226	0.0002	0.0000
Y = 0.0000	0.2745	0.0000	0.0000
Z = 0.0000	0.1060	-0.0002	0.0001
Tot= 0.0001	0.3690	0.0002	0.0001

In other words, the dipole moment of the molecule gives the strength of the polarity of the molecule. As seen from Table 1, the predicted total dipole moment of pentacene is almost zero at RHF/6-31G, B3LYP/6-31G and B3LYP/6-31G* level. Though the RHF/6-31G* values are slightly higher, it can be predicted that the molecule is not polar and the charge distribution is fairly symmetrical.

3.2 Quadrupole Moments

The quadrupole moments of a molecule provide a second order approximation of the total electron distribution within the molecule; providing at least an approximate idea of its shape. One of the components being significantly larger than the others would represent an elongation of the sphere along that axis. If present, the off-axis components represent trans-axial distortion (stretching or compressing of the ellipsoid). The quadrupole moments for pentacene molecule at different levels of theory are shown in Table 2.

Table 2: Quadrupole moments (in Debye) in gas phase.

RHF/6-31G	RHF/6-31G*	B3LYP/6-31G	B3LYP/6-31G*
Gas	Gas	Gas	Gas
XX = -108.6428 YY= -110.2306 ZZ= -138.8677 XY= 0.0000 XZ= 0.0004 YZ= 0.0000	XX= -106.9830 YY= -110.6382 ZZ= -132.9868 XY= 0.8483 XZ= 1.1152 YZ= -0.0592	XX= -108.0591 YY= -110.1880 ZZ= -134.2709 XY= -0.0002 XZ= -0.0014 YZ= 0.0000	XX= -107.1009 YY= -109.7363 ZZ= -132.9972 XY= 0.0000 XZ= -0.0006 YZ= 0.0000

At all levels of theory, the molecule is predicted to be slightly elongated along the ZZ axis, with RHF/6-31G predicting the highest elongation. The total electron distribution in order of magnitude beginning with the least is XX, YY, ZZ and the off-axis components are very small, showing that trans-axial distortions are minimal.

3.3 Thermal Energies

In RHF and DFT computations using Gaussian software, the frequency calculations include thermochemical analysis of the molecular system. By default, this analysis is carried out at 298.15 K and 1 atmosphere of pressure, using the principal isotope of each element type in the molecular system. Predicted total, electronic, translational, rotational and vibrational energies in kcal/mol for pentacene in gas phase are listed in Table 3. The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy is observed as the tumbling motion of a molecule as a result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring.

Table 3: Predicted thermal energies (in kcal/mol) in gas for pentecene molecule

Energy	RHF/6-31G	RHF/6-31G*	B3LYP/6-31G	B3LYP/6-31G*
Total energy	187.624	188.521	189.782	193.217
Electronic	0.000	0.000	0.000	0.000
Translational	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889
Vibrational	185.846	186.743	188.005	191.439

From Table 3, it is seen that the predicted total energy for the molecule is slightly higher when electron correlation at DFT/B3LYP level of theory is considered. Also, the 6-31G* basis set gives slightly higher values compared to 6-31G at all levels of theory. Basically, the bulk thermal energy of the molecule is contributed mostly by the vibrational energies of the atoms in the molecule while the electronic energy is very minimal and approximated to zero at all levels of theory.
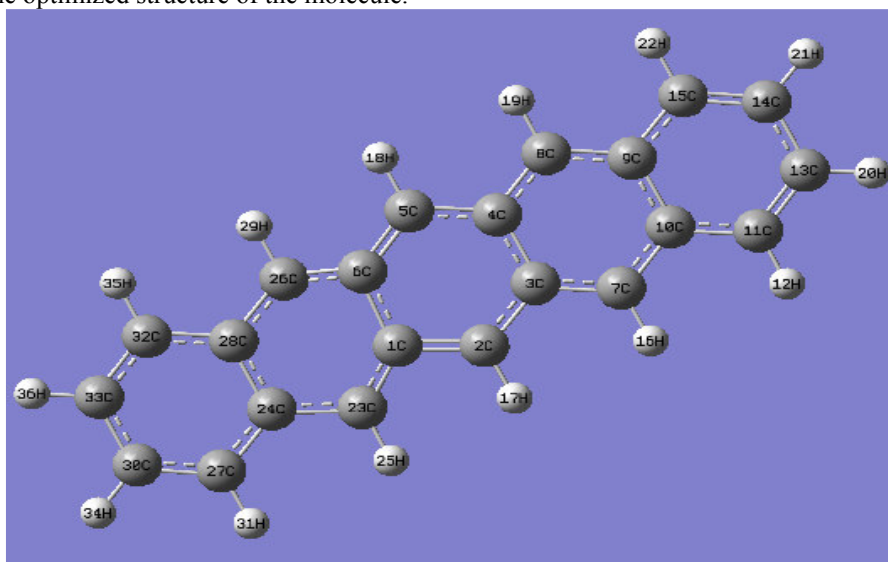Fig.1 shows the optimized structure of the molecule.

Fig.1: Optimized Structure of Pentacene

3.4 Energy Band Gap

The difference between the energies of the Highest Occupied Molecular Orbital (HUMO) and the Lowest Unoccupied Molecular Orbital (LUMO) energy levels in a polymer is its band gap (Eg) .

$$E_{bg} = E_{LUMO} - E_{HOMO} \qquad (1)$$

The computed band gap energy for pentacene at different levels of theory using 6-31G and 6-31G* is shown in Table 4.

Table 4: Energy band gap

	RHF/6-31G	RHF/6-31G*	B3LYP/6-31G	B3LYP/6-31G*	Experimental
E_{bg} (a.u)	0.04952	0.06741	0.08214	0.08125	
E_{bg} (eV)	1.3475	1.834	2.2352	2.2109	2.1 [12]

The band gap energies are less than 3eV at all levels of theory for all basis sets. This indicates that the molecule is a very good semi-conductor material. Inclusion of electron correlation increases the values of the band gap and approaches the experimental value. Thus, DFT calculations are more in agreement with the experimental value than the RHF values.

3.5 Vibrational Frequency Analysis

In general, a molecule with N atoms has 3N – 6 normal modes of vibration, but a linear molecule has 3N – 5 such modes, as rotation about its molecular axis cannot be observed. Pentacene molecule with molecular formula $C_{22}H_{14}$ has a total of 36 atoms and thus N=36; giving 3(36)-6 = 102 possible number of vibrational modes for each IR and Raman frequencies. A vibrational motion for a molecule is when the bonds between atoms within a molecule move. The vibrational coordinate of a normal vibration is a combination of changes in the positions of atoms in the molecule. When the vibration is excited the coordinate changes sinusoidally with a frequency ν, the frequency of the vibration. Some of the vibrations observed and their descriptions are:

Stretching: A change in the length of a bond, such as C-H or C-C. Symmetric stretching is when the two attached atoms move away and toward the central atom at the same time. Anti-symmetric stretching is when the two attached atoms do not move away and toward the central atom at the same time.

Bending: A change in the angle between two bonds, such as the HCH angle in a methylene group.

Rocking: A change in angle between a group of atoms, such as a methylene group and the rest of the molecule. This motion is like a pendulum on a clock going back and forth only here an atom is the pendulum and there are two instead of one.

Wagging: A change in angle between the plane of a group of atoms, such as a methylene group and a plane through the rest of the molecule. It can be visualized as follows: If a person holds up their hand in front of them and puts there two fingers in a "V" sign and bend there wrist toward and away from them. Here the tips of the fingers are the attached atoms and the wrist is the central atom.

Twisting: A change in the angle between the planes of two groups of atoms, such as a change in the angle between the two methylene groups. This motion is like a person is walking on a treadmill where their waist is the central atom and their feet are the two attached atoms.

Scissoring: Just like the name says scissoring is when the two atoms move away and toward each other.

A vibration is said to be out-of-plane if there is a change in the angle between any one of the C-H bonds and the plane defined by the remaining atoms of the molecule. In a rocking, wagging or twisting, the bond lengths within the groups involved do not change but the angles do. Rocking is distinguished from wagging by the fact that the atoms in the group stay in the same plane.

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared (IR) spectrum can be used as a fingerprint for identification by the comparison of the spectrum from an 'unknown' with previously recorded reference spectra. The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. The vibrational frequency is usually expressed in cm^{-1}. Another important form of vibrational spectroscopy is Raman spectroscopy, which is complementary to infrared spectroscopy. The selection rules for Raman spectroscopy are different to those for infrared spectroscopy, and in this case a net change in bond polarizability must be observed for a transition to be Raman active [ ].

Approximate descriptions of the most intense vibrational frequencies for pentacene in gas phase at RHF and B3LYP levels with 6-31G and 6-31G* basis sets are presented in Tables 5 to 12.

Table 5: Some IR intense vibrational frequencies and their approximate description for pentecene molecule at RHF/6-31G level of theory

S/N	Freq. IR in Gas	Approximate Descriptions
1	1095.3	C-H Stretching except C15,C11, C32, C27, H22,H12,H35,H31
2	3387.68	C-H Ant Symmetric Stretching at the edge of molecule
3	848.931	C-H All Stretching
4	3372.92	C-H symmetric Stretching at the edge of the molecule
5	525.764	C-H symmetric Stretching of the rings except the central ring
6	3353.14	C-H symmetric Stretching of the rings
7	1864.53	Rings distortion and C-H wagging except of the central one
8	1241.9	C-H wagging and C-C stretching
9	774.178	C-H Ant Symmetric Stretching of the rings
10	963.419	C-H Rocking at the middle rings

Table 6: Some Raman intense vibrational frequencies and their approximate description for pentecene molecule at RHF/6-31G level of theory

S/N	Freq.Raman in Gas	Approximate Descriptions
1	1529.08	C-C symmetric Stretching of the rings
2	1827.17	C-C symmetric Stretching of the rings and hydrogen rocking
3	1595.6	C-C symmetric Stretching of the rings and C-H rocking
4	1326.22	Rings breathing and C-H wagging
5	3387.98	C-H Ant symmetric Stretching of the rings at the edge
6	1743.08	Rings distortions
7	3372.88	C-H symmetric Stretching of the rings at the edge
8	1347.69	C-C symmetric Stretching of the rings and rocking
9	829.756	C-H symmetric Stretching of the rings and wagging out of plane
10	3347.29	C-H Ant symmetric Stretching and rings bending except the central

Table 7: Some IR intense vibrational frequencies and their approximate description for pentecene molecule at B3LYP/6-31G level of theory

S/N	Freq. IR in Gas	Approximate Descriptions
1	3222.48	C-H symmetric Stretching at the edge of the rings
2	3207.49	C-H Ant symmetric Stretching except the central ring
3	3186.02	C-H Ant symmetric Stretching
4	1244.83	C-H symmetric Stretching of the rings in plane
5	40.0814	Rings breathings
6	488.778	C-H Stretching and rings bending
7	951.114	C-H symmetric Stretching and rings breathing
8	1341.75	C-H Ant symmetric Stretching of the rings out of plane
9	1389.79	C-C symmetric Stretching of the rings and C-H bending
10	656.972	Rings breathings

Table 8: Some Raman intense vibrational frequencies and their approximate description for pentecene molecule at B3LYP/6-31G level of theory

S/N	Freq.Raman in Gas	Approximate Descriptions
1	1434.01	C-C Ant symmetric Stretching of the rings
2	3222.75	C-H symmetric Stretching at the edge of the rings
3	1656.96	Distortion of the middle rings
4	1244.17	C-C symmetric Stretching of the rings
5	3192.36	C-H Ant symmetric Stretching of the rings
6	3207.46	C-H Ant symmetric Stretching at the edge of the rings
7	772.161	Rings breathings
8	524.985	Twisting of the rings
9	772.311	C-H stretching
10	1244.83	C-C Ant symmetric Stretching of the rings and C-H bending

Table 9: Some IR intense vibrational frequencies and their approximate description for pentecene molecule at RHF/6-31G* level of theory

S/N	Freq. IR in Gas	Approximate Descriptions
1	3387.35	C-H symmetric Stretching at the edge of the molecule
2	1039.03	C-H All Stretching
3	3375.07	C-H Ant symmetric Stretching at the edge of the molecule
4	1866.14	Rings distortions C-H wagging except the central ring
5	1230.01	C-H wagging and C-C stretching
6	3350.76	C-H Ant symmetric Stretching of the rings
7	1499.03	C-C symmetric Stretching of the rings and C-H rocking

Table10: Some Raman intense vibrational frequencies and their approximate description for pentecene molecule at RHF/6-31G* level of theory

S/N	Freq.Raman in Gas	Approximate Descriptions
1	1516.79	C-C Ant symmetric Stretching of the rings
2	1819.93	C-C Ant symmetric Stretching of the rings and hydrogen rocking
3	1301.14	Rings breathing and C-H wagging
4	3363.64	C-H symmetric Stretching the rings
5	1732.82	C-C A symmetric Stretching of the rings
6	547.174	Rings twisting
7	3352.12	C-H symmetric Stretching of the rings except the central ring
8	484.651	Rings twisting
9	3352.24	C-H Ant symmetric Stretching of the rings

Table 11: Some IR intense vibrational frequencies and their approximate description for pentecene molecule at B3LYP/6-31G* level of theory

S/N	Freq. IR in Gas	Approximate Descriptions
1	3209.33	C-H symmetric Stretching at the edge of the rings
2	917.433	C-H Stretching
3	3197.02	C-H symmetric Stretching of the rings except the central ring
4	3179.6	C-H symmetric Stretching of the rings
5	1690.27	C-C Ant symmetric Stretching of the rings
6	3177.64	C-H Ant symmetric Stretching of the rings
7	3183.25	C-H symmetric Stretching of the rings
8	639.527	Rings breathings

Table 12: Some Raman intense vibrational frequencies and their approximate description for pentecene molecule at B3LYP/6-31G* level of theory

S/N	Freq.Raman in Gas	Approximate Descriptions
1	1426.38	C-C Ant symmetric Stretching of the rings
2	3209.56	C-H symmetric Stretching of the rings except the central ring
3	1648.78	Distortion of the middle rings
4	1572.1	C-H symmetric Stretching of the rings
5	3196.98	C-H Ant symmetric Stretching at the edge of the rings
6	765.385	Rings breathings
7	3180.31	C-H Ant symmetric Stretching of the rings
8	452.248	Twisting of the rings
9	724.917	Twisting of the rings and stretching

In this work, Gaussian software was used to predict the vibrational spectra of the three molecules in their ground states. These frequency calculations are valid only at stationary points on the potential energy surface, thus our computations were preformed on the optimized structures of the molecules. Raw frequency calculations computed at the Hartree-Fock level contain known systematic errors due to the neglect of electron correlation, resulting to overestimates of about 10-12%. Therefore, it is usual to scale frequencies predicted at the HF level by an empirical factor of 0.8929. Use of this factor has been demonstrated to produce very good agreement with experiment for a wide range of systems. Our values in this study must be expected to deviate even a bit more from experiment because of the choice of a medium-sized basis sets (6-31G and 6-31G*)-around 15%. For B3LYP/6-31G a scale factor of 0.9613 is used [11]. The IR and Raman Spectra for the
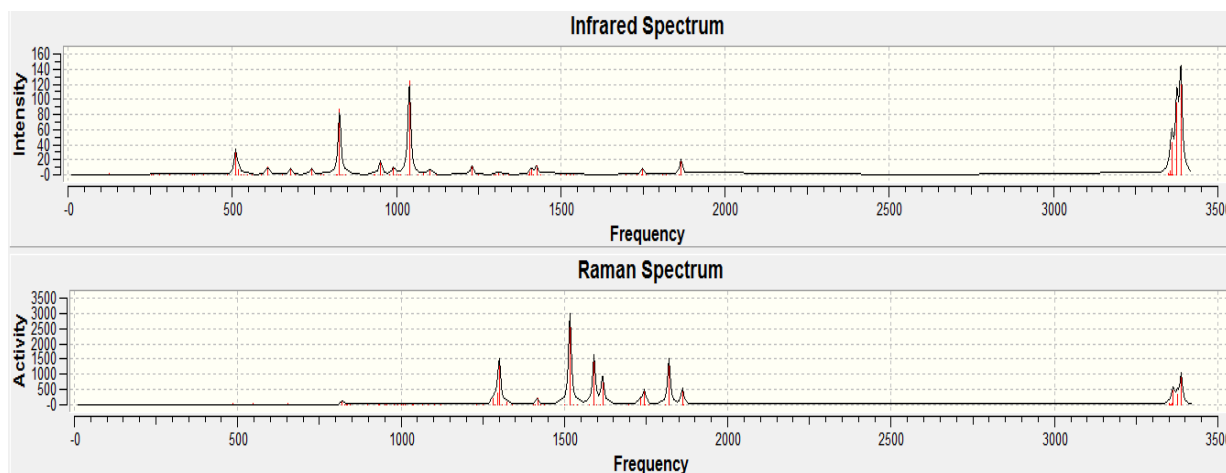
molecule are shown in Fig. 1 to 4.
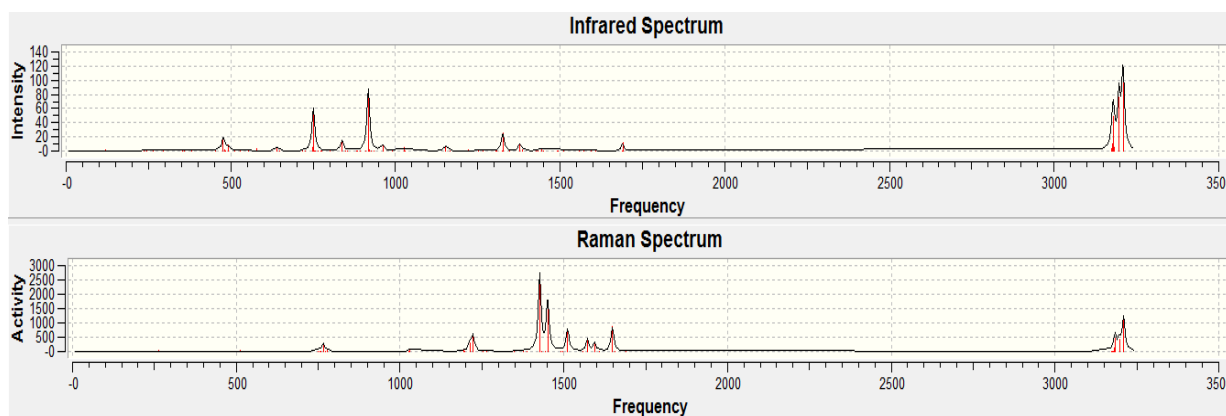

Fig. 1: IR and Raman Spectra at RHF/6-31G*
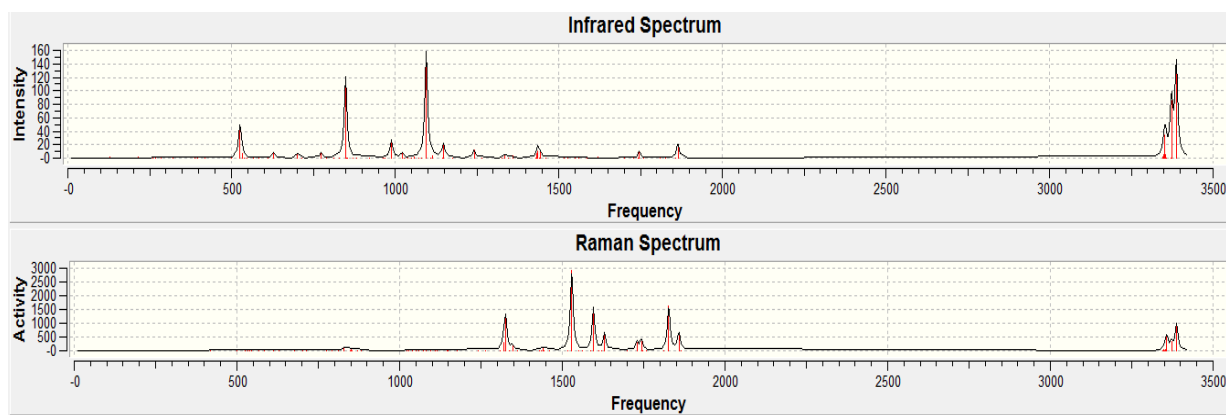

Fig. 2: IR and Raman Spectra at DFT/6-31G*

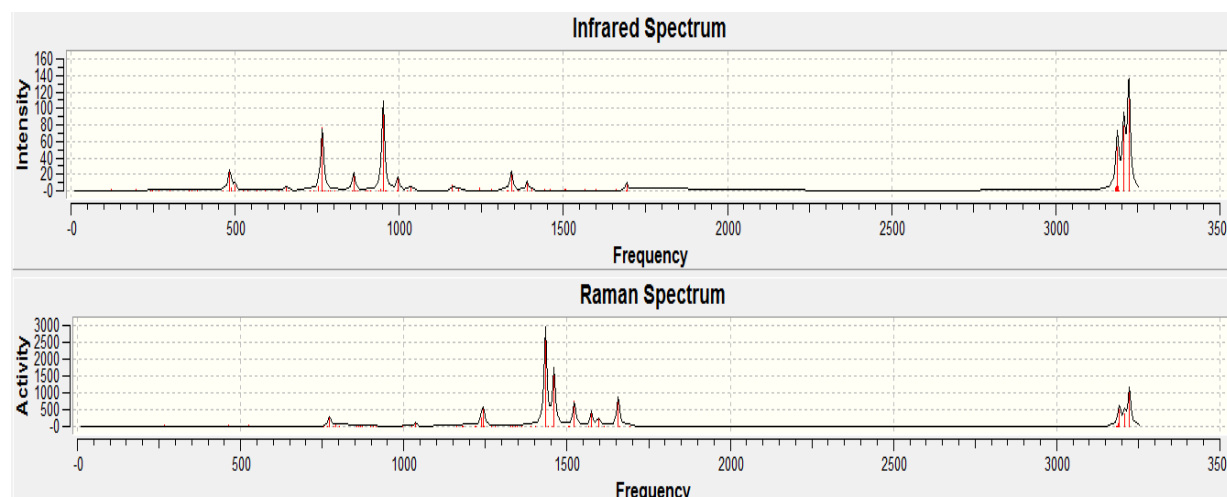**Fig. 3: IR and Raman Spectra at RHF/6-31G**

Fig. 4: IR and Raman Spectra at DFT/6-31G

4. CONCLUSION

In conclusion, RHF and DFT were used to appreciate the molecular dynamics and vibrational behavior of the semi conductor material Pentacene. The DFT results obtained for the band gap are much in agreement with experimental findings. The two basis sets used in the work give almost the same predictions for the dipole moments, thermal energies and vibrational frequencies.

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