DETERMINATION OF THE ELECTRONIC STRUCTURE, CHARGE-TRANSFER, AND OPTICAL PROPERTIES OF NEUTRAL, ANIONIC, AND CATIONIC PERFLUOROPENTACENE

ABSTRACT

Perfluoropentacene ($C_{22}F_{14}$) is an n-type organic semiconductor made by fluorination of p-type semiconductor Pentacene and can find applications in molecular thin film devices. In this work, a theoretical study of Perfluoropentacene was carried out based on density functional theory (DFT) and time dependent (TD-DFT) as implemented in Gaussian 09 package using B3LYP/6-31++G (d, p) and B3LYP/6-31+G(d) basis sets. The electronic, charge transfer, Linear and nonlinear optical properties of the molecule were calculated and reported for the neutral, anionic, and cationic forms of the molecule. The results show that the cationic state of the molecule has the strongest bond length at R(28,32) using the basis sets b3lyp 6-311++G (d,p) and the weakest bond length was found at R(4,6) in the ionic state with 6-31+G (d) basis set.The energy gap obtained for the neutral molecule using 6-31+G (d) and 6-311++G (d,p) basis sets are 2.00eV, 1.99eV respectively. The results show a strong agreement with a previously related work that reported the energy gap as 2.02eV thus indicating high stability of the molecule. Perfluoropentacene has the highest value of chemical hardness of 1.3929eV in its anionic state (Beta MO), so is considered to be harder and more stable than the neutral and cationic. The findings also revealed that with toluene as solvent, the strongest absorption was found at wavelength of 738.38 nm, highest oscillator strength of 0.0599 and the lowest excitation energy of 1.6791eV. The calculated results of polarizability, first and second hyperpolarizability confirm that this molecule is a good non-linear optical material. On the whole the molecule could be a good material for optoelectronic applications.

Keywords:, DFT, energy gap, optimization, andperfluoropentacene

1.0 INTRODUCTION

Over the past three decades, organic semiconductors have garnered significant interest from both academic and industrial research communities due to their simpler production processes compared to traditional inorganic technology (Lukeš *et al.*, 2018). These materials, composed primarily of pi-bonded molecules or polymers with carbon, hydrogen, and occasionally heteroatoms like nitrogen, sulfur, and oxygen, exhibit typical semiconductor properties (Gidado *et al*., 2017). They can form molecular crystals or amorphous thin films, which are used in various organic devices such as organic thin-film semiconductors (Hasan, 2013). Generally, organic semiconductors act as insulators but become conductive when charges are injected from appropriate electrodes, doped, or photoexcited. They are categorized into two main types: low-molecular-weight materials and polymers, and can further be classified based on the type of charge carriers into p-type (holes), n-type (electrons), or ambipolar (both electrons and holes) (Lukeš *et al.*, 2018).

According to Sakamoto *et al.*, (2004), perfluorination of p-type organic materials is an effective method for producing n-type semiconductors. This is because the introduction of highly electronegative fluorine atoms lowers the highest occupied molecular orbital (HOMO) levels, enhancing electron injection. Additionally, fluorination minimally alters the molecular structure due to fluorine's relatively small atomic size. Perfluorinated Pentacene ($C_{22}F_{14}$) has been recognized as a potentially complementary alternative to Pentacene (Jacobs et al., 2007). Consequently, efficient n-type interfaces need to be developed to enable the fabrication of complementary integrated circuits (Toyoda et al., 2011). The primary distinction between Perfluoropentacene and Pentacene lies in their semiconductor type: Perfluoropentacene is an n-type semiconductor. Despite this difference, both Pentacene and Perfluoropentacene exhibit herringbone packing in the bulk, though they have distinct lattice parameters and angles (Darancet & Smerdon, 2020).

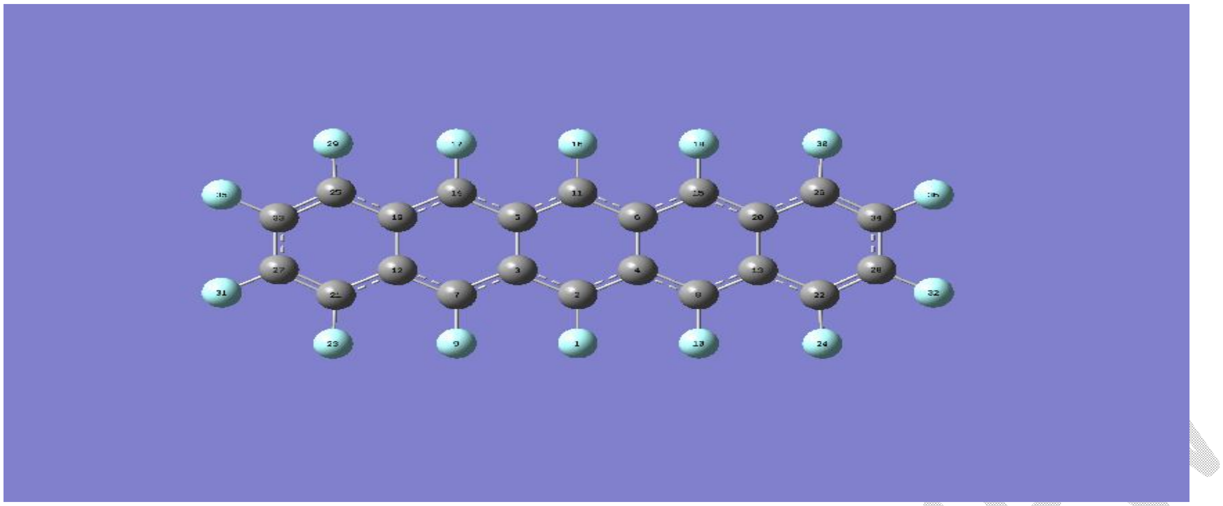
Several studies were reported on perfluoropentacene and related molecules. Density functional theory (DFT) calculations were carried out to estimate the reorganization energies of perfluoropentacene (PF-Pentacene), perfluorosexithiophene (PF-6T), and their non-fluorinated parent compounds, examining the impact of fluorine substitution. The electron affinity (EA) and ionization potential (IP) of these compounds were also reported and analyzed.Results showed that fluorine has effect on the electronic properties of these molecules (Fujii et al., 2009).

Additionally, an experiment using high-resolution electron energy loss spectroscopy (HREELS) and Raman spectroscopy investigated the vibrational properties of perfluoropentacene (PFP) thin films on highly oriented pyrolytic graphite (HOPG) substrates. The results revealed slight increase in vibrational energies with thicker films and lower temperatures. Polarization-dependent Raman spectra showed depolarization ratios greater than 1 for all Ag vibrational modes, indicating molecular distortion in the multilayer films. These results suggest strong intermolecular interactions in PFP multilayer films (Fujii et al., 2009). Density-functional theory with semi-empirical dispersion correction was used to study how varying the number of fluorine (F) atoms affects the atomic and electronic structures of fluorinated pentacene (C22FnH14-n) on Cu(111) surfaces. The fluorination on carrier injection efficiency at organic/metal interfaces was examined. Results showed that fewer F atoms decreased the electron affinity of isolated molecules, making them less reactive. However, in adsorbed systems, fewer F atoms led to strong hybridization with substrate states while maintaining n-type energy alignment, reducing the carrier injection barrier. It was proposed that C22FnH14-n (n ≤ 8) should be used with Cu electrodes for efficient electron injection (Toyoda et al., 2011). Another study examined the growth of perfluoropentacene (PFP) and pentacene (PEN) ultrathin films on Ag (111) using low-temperature scanning tunneling microscopy to understand how perfluorination influences packing structures. The findings revealed distinct morphological differences between the two molecules' monolayers. PFP exhibited a single closely packed arrangement with periodic dislocation lines, while PEN displayed two co-existing arrangements within the first monolayer. Both monolayers were commensurate with the underlying substrate, with the molecules' long axes aligned along the silver surface. The differences in arrangement were attributed to the variations in the peripheral atoms of PFP and PEN【Effect Of, 2005】. Another work involved the fabrication of n-channel OTFTs using different gate insulators, specifically polyimide (PI) and SiO_2, with perfluoropentacene as the semiconductor layer. The instability of the transistor characteristics was examined under various environments, including air, vacuum, and oxygen. The study showed that both types of transistors exhibited a notable increase in mobility when measured in a vacuum (Ueki *et al.,* 2010).

First-principles density functional theory calculations using the projected augmented wave (PAW) method were performed to investigate the structural and electronic properties of the perfluoropentacene (PFP)/Al(100) interface. The results indicated that the adsorption of the PFP molecule on the Al(100) surface was physisorption. The change in the work function of the Al(100) surface upon PFP adsorption was calculated. Additionally, electronic properties such as the density of states (DOS), partial density of states (PDOS), Mulliken population analysis, and Schottky barrier height (SBH) were examined for the stable adsorption geometry. The study revealed that charge transfer occurred from the aluminum surface to the PFP molecule, suggesting that the PFP/Al(100) interface is favorable for electron transport (Saranya *et al.*, 2014).

Perfluoropentacene has emerged as a promising organic semiconductor material with significant potential in optoelectronic applications. However, several research gaps and unanswered questions persist regarding its optical, electronic, and non-linear optical properties particularly in anionic and cationic states. These properties are crucial in determining the performance of perfluoropentacene in optoelectronic devices. This work aims to address these gaps by employing density functional theory.

Picture 1 shows the molecular structure.



Picture 1: molecular structure of perfluoropentacene molecule

2.0 THEORETICAL BACKGROUND

2.1 Density FunctionalTheory (DFT)

Density functional theory (DFT) is a quantum-mechanical simulation method used to compute a wide variety of properties for nearly any atomic system, including molecules, crystals, surfaces, and even electronic devices when combined with non-equilibrium Green's function (NEGF). It belongs to the family of first-principles (*ab initio*) methods. Density Functional Theory (DFT) is a computational method that derives properties of the molecules based on a determination of their electron density(Maigari *et al.*, 2022). It is so named due to its ability to predict material properties for unknown system without any experimental input. Hybrid DFT functional are popular for predicting reasonably accurate ground and excited state energies of many conjugated systems(Lukeš *et al.*, 2018). The main advantage of Density Functional Theory is to determine reasonable vibrational frequencies, geometries, photo-physical, nonlinear optical (NLO) properties which are much superior to the conventional methods(Abbas *et al.*, 2019). Density functional theory (DFT) was proposed by Hohenberg and Kohn as a method to determine the electronic structure of a system at ground state with a theory stating that all ground-state properties for many-particle systems are functional of the electron density(Ismail *etal.*, 2019). In 1965, Kohn and Sham (KS) reformulated the problem in a more familiar form and opened the way to the practical application of DFT.

The Kohn and sham (KS) theorem states that the ground state electron density uniquely determines the electronic wave function and hence all ground state properties of an electronic system(Maigari *et al.*, 2022).That is

$$\rho(r) = \Psi^2(r) \tag{1}$$

$$E = E_{in} + E_{en} + \frac{1}{2}\int \rho(r)dr \int \frac{\rho(r)}{r_e - r_i} dr + E_{xc} \quad (2)$$

The theorem says that: the energy of an electron distribution functional reaches a minimum in correspondence to the actual ground-state electron density.
But $\Psi' \neq \Psi$

$$E(n) = \Psi'\Psi' > \{\psi_o H \psi_o\} \quad (3)$$

Where $\rho(r)$ is the ground state electron density, E_{XC} is the exchange correlation energy, $\psi(r)$ is the wave function of an electron and E(n) is the ground state of energy functional

2.2 Geometry Optimization

Geometrical optimization is a procedure that attempts to find the configuration of minimum energy of the molecule. This will also calculate the wave function and the energy at the starting geometry and then proceed to search a new geometry of a lower energy. The procedure will have to be repeated until the lowest energy geometry is obtained(Muhammad *et al.*, 2021).

2.3 GlobalQuantities: - Chemical potential, chemical hardness-softness, electronegativity and electrophilicity index which are global reactivity descriptors are useful quantities in predicting and understanding global chemical reactivity trends. The ionization potential (IP) and electron affinity (EA) are expressed in terms of the highest occupied molecular orbital (HOMO)and the lowest unoccupied molecular orbital (LUMO).(Muhammad *et al.*, 2021)

The ionization potential (IP) and electron affinities (EA) can be computed by using Koopmans's as;

$$IP = -E_{HOMO} \quad (4)$$

$$EA = -E_{LUMO} \quad (5)$$

The energy gap E_g can be obtained from the relation;

$$E_g = E_{LUMO} - E_{HOMO} \approx IP - EA \quad (6)$$

The chemical hardness (η) could be expressed in terms of IP and EA as;

$$\eta = (E_{LUMO} - E_{HOMO})/2 \approx (IP - EA)/2 \quad (7)$$

And softness is given by;

$$S = \frac{1}{\eta} \quad (8)$$

The chemical potential is given;

$$\mu = -\left(\frac{IP+EA}{2}\right) \quad (9)$$

The electronegativity is given by;

$X = \frac{IP+EA}{2}$ (10)

The electrophilictity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilictity index (ω) is expressed as;(Muhammad *et al.*, 2021)

$$\omega = \frac{\mu^2}{2\eta} \qquad (11)$$

2.4 Non-linear Optical Properties: -The NLO properties in molecules originate from the interactions between the electrons in a molecule and the electric field. These are the basis of many components of materials research, optical sensing and optical communication system. To gain an insight into the study of non-linear optical properties (NLO) of Perfluoropentacene molecule; the dipole moment (μ), polarizability (α), and hyperpolarizability (β and γ) are defined as follows:

For molecular systems, dipole moment can be obtained from;

$\mu_{tot} = [\mu^2{}_x + \mu^2{}_y + \mu^2{}_z]^{1/2}$ (12)

whereμ_x, $\mu_y and \mu_z$ are the components of the dipole moment in x, y and z coordinates

Electric dipolepolarizability is given by;

$\propto = \frac{\partial^2{}_E}{\partial F_a \partial F_b}$(13)

where a and b are coordinates of x, y and z.

The mean polarizability is calculated using;

$< \alpha > = \frac{1}{3}(a_{xx} + a_{yy} + a_{zz})$(14)

where a_{xx}, $a_{yy,} a_{zz}$ are known as principal values of polarizability tensor.

The anisotropic polarizability is given;

$\Delta\alpha = 2^{-\frac{1}{2}}\left[(a_{xx} - a_{yy})^2 + (a_{yy} - a_{zz})^2 + (a_{zz} - a_{xx})^2 + 6a^2{}_{xx}\right]^{1/2}$(15)

The first hyperpolarizability is defined as;

$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2}$(16)

The second order hyperpolarizabilityis given by; $\gamma = \frac{1}{5}\left[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\left(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}\right)\right]$(17)

3.0 COMPUTATIONAL PROCEDURE

The molecular structures and geometries of perfluoropentacene molecule were fully optimized with the (6-31++G(d,p) and 6-31+G(d)) basis sets, without imposing any symmetry constraints. During optimization, parameters were allowed to relax completely, and each calculation converged to a geometry that represented a true energy minimum. Geometry optimization refers to the process of finding the molecular configuration with the lowest energy. This involves calculating the wave function and energy at the initial geometry, then iteratively searching for a new, lower energy geometry until the minimum is found. Before optimization, a stability check confirmed the molecule's stability.The optimized geometries served as the basis for subsequent calculations to determine the highest occupied molecular orbital (HOMO), singly occupied molecular orbital (SOMO), and lowest unoccupied molecular orbital (LUMO) values, as well as global chemical index parameters. Nonlinear optical properties, including dipole moment, isotropic polarizability, anisotropic polarizability, and first and second order hyperpolarizability, were also calculated the optimized geometries.Infrared (IR) frequencies were determined by obtaining the Hessian matrix and force constants for all normal modes of the molecule, with the absence of imaginary frequencies confirming molecular stability. Spectral analysis was conducted with IRPal 2.0 software. Excited states were investigated using time-dependent density functional theory (TD-DFT) with the B3LYP functional and the (6-31++G(d,p) basis set, based on ground state optimized geometries in vacuum and various solvents (acetone, water, toluene, methanol and ethanol).All computations were performed using the Gaussian 09W software package (Sakthi *et al.*, 2017).

4.0 RESULTS AND DISCUSSIONS

4.1 Optimized bond Lengths and bond angles of Perfluoropentacene Molecule for Neutral, Anionic and Cationic

Tables 1, 2, and 3 list the optimized bond lengths and bond angles of some selected results for neutral, anionic and cationicstates. The bond length is the measurable distance between two atoms covalently bonded together measured in angstrom , while the bond angle is the angle between two adjacent bonds of an atom in a molecule measured in degrees(Abdulaziz *et al.*, 2019).The results indicate that the bond length in the cationic state, calculated using the B3LYP 6-311++G(d,p) basis set, is the shortest, measuring 1.3176 Å, compared to the neutral and anionic states. Notably, a shorter bond length corresponds to higher bond energy and a stronger bond(Gidado *et al.*, 2017). The bond angles provide insight into the distribution of orbitals around a central atom in a molecule and contribute to the molecule's shape (Gidado et al., 2017). The lowest bond angle, measured at

117.0578° in the anionic state using the same basis sets, suggests stronger interactions between its substituent atoms compared to those with larger bond angles.

4.2 Frontier Orbitals Energies

Frontier molecular orbitals (FMOs) are essential for assessing the suitability of organic semiconductors, with the energy levels of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals being key parameters for selecting p-type and n-type semiconductors, respectively (Ngoc *et al.,* 2020). The HOMO/SOMO and LUMO for neutral and ionic molecules are presented in Table 4. The energy difference between HOMO and LUMO levels become the energy gap of organic semiconductors(Setsoafia *et al.*, 2022). The HOMO/LUMO energy gap is an important measure of stability, with compounds having smaller HOMO/LUMO energy gap values tending to exhibit higher stability (Srivastava *et al.,* 2014). Additionally, a lower energy band gap facilitates easier electron excitation to the ground state and improves conductivity (Bashir *et al.*, 2023). The energy levels of the HOMO and LUMO in donor and acceptor compounds are critical for photovoltaic devices, as they determine the feasibility of charge transfer between the donor and acceptor (Bourass *et al.,* 2016).

The results in Table 4 indicate that perfluoropentacene in its neutral state has an energy band gap of approximately 2.0005 eV with the 6-31G+(d) basis set and 1.9907 eV with the 6-311++G(d,p) basis set, consistent with the previously reported value of 2.0200 eV (Pichierri, 2006). Additionally, the energy gap for the Beta MO is larger, being 2.7763 eV for the anionic state and 2.5164 eV for the cationic state, compared to the Alpha MO, which has gaps of 2.1173 eV and 1.7886 eV for the anionic and cationic states, respectively, using the 6-31G+(d) basis set. These results suggest that the smaller energy gap for the Alpha MO leads to higher electrical conductivity, as electrons can more easily transition from the HOMO to the LUMO, facilitating charge carrier generation and movement.

4.3 GLOBAL CHEMICAL QUANTITIES

Global chemical quantities (hardness (η), softness (ʃ), chemical potential (μ), electronegativity (χ) and electrophilicity index (ω)) of the molecule perfluoropentacene are presented in Table 5. Chemical hardness is a parameter that characterizes the chemical stability of a molecule. A system with high chemical hardness is considered very stable. Thus, molecules with low chemical hardness are more reactive, polarizable, and less stable. The hardness is also a way to measure the stability of a chemical system in terms of its deformation(Bashir *et al.*, 2023). It is shown in Table 5 that perfluoropentacene has a higher value of chemical hardness of 1.3929eV in its anionic state (Beta MO), so is considered to be harder and more stable than the neutral and cationic molecules.

Table 1: Selected bond lengths(Å)and bond angles(°) for optimized structure of Neutral perfluoropentacene using basis set b3lyp/6-31+g (d) and b3lyp/6-311++g (d,p).

B0ND LENGTH	b3lyp/6-31+g(d) (in Å)	b3lyp/6-311++g(d,p) (in Å)	BOND ANGLE	b3lyp/6-31+g(d)(°)	b3lyp/6-311++g(d,p)(°)
R(1,2)	1.3408	1.3367	A(3,2,4)	123.2775	123.2222
R(3,5)	1.4561	1.4535	A(3,5,14)	118.0512	118.0688
R(7,9)	1.3422	1.3381	A(4,6,15)	118.0467	118.0651
R(12,19)	1.4591	1.4566	A(11,6,15)	123.5948	123.5485
R(19,25)	1.4365	1.4339	A(4,8,13)	123.3848	123.3307
R(21,27)	1.364	1.3599	A(12,21,27)	121.2187	121.1624
R(27,31)	1.3368	1.3323	A(26,34,28)	120.6272	120.6774

Table 2: Selected bond length and bond angle for optimized structure of anionicperfluoropentacene using basis set b3lyp/6-31+g (d) and b3lyp/6-311++g (d,p).

B0ND LENGTH	b3lyp/6-31+g(d) (in Å)	b3lyp/6-311++g(d,p) (in Å)	BOND ANGLE	b3lyp/6-31+g(d)(°)	b3lyp/6-311++g(d,p)(°)
R(4,6)	1.4614	1.4585	A(2,4,8)	124.5496	124.4588
R(5,14)	1.4084	1.4058	A(11,5,14)	124.5464	124.4562
R(8,10)	1.3585	1.3544	A(5,11,6)	124.5024	124.4024
R(12,19)	1.4554	1.4524	A(23,21,27)	117.0729	117.0579
R(13,22)	1.4255	1.423	A(19,25,29)	121.09	121.1799
R(26,30)	1.3522	1.3479	A(29,25,33)	117.0736	117.0586
R(34,36)	1.3512	1.3471	A(30,26,34)	117.0727	117.0578

Table 3: Selected bond length and bond angle for optimized structure of cationic perfluoropentacene using basis set b3lyp/6-31+g (d)and b3lyp/6-311++g (d,p).

B0ND LENGTH	b3lyp/6-31+g(d) (in Å)	b3lyp/6-311++g(d,p) (in Å)	BOND ANGLE	b3lyp/6-31+g(d)(°)	b3lyp/6-311++g(d,p)(°)
R(1,2)	1.3248	1.3195	A(2,3,7)	123.2152	123.109
R(3,5)	1.456	1.453	A(11,6,15)	123.2147	123.1085
R(8,13)	1.4076	1.4048	A(5,11,6)	123.1439	123.0266
R(13,20)	1.4509	1.4478	A(12,21,23)	121.1933	121.2934
R(19,25)	1.4224	1.4199	A(12,21,27)	120.9146	120.8254
R(25,29)	1.3296	1.3245	A(24,22,28)	117.8858	117.8751
R(28,32)	1.3229	1.3176	A(29,25,33)	117.8873	117.8765

Table 4: The Frontier Orbital Energies For both Neutral and Ionic form of perfluoropentacene molecule using b3lyp/6-31+g (d) and b3lyp/6-311++g (d,p) basis sets

Neutral							
Molecule	Basis Set	IP(eV)	EA(eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Energy Gap(eV)	Previous Work(eV)
Perfluoropentacene	6-31+G	5.9551	3.9545	-5.9551	-3.9545	2.0005	2.0200(Pichierri, 2006)
	6-311++G	6.0343	4.0305	-6.0343	-4.0305	1.9907	

Anionic					
Molecule	Basis Set	MO	E_{SOMO} (eV)	E_{LUMO} (eV)	Energy Gap(eV)
perfluoropentacene	6-31+G	Alpha	-1.6098	0.5075	2.1173
		Beta	-2.2688	0.5075	2.7763
	6-311++G	Alpha	-1.6831	0.4528	2.1359
		Beta	-2.3332	0.4528	2.7859

Cationic					
Molecule	Basis Set	MO	E_{SOMO} (eV)	E_{LUMO} (eV)	Energy Gap(eV)
perfluoropentacene	6-31+G	Alpha	-9.4569	-7.6683	1.7886
		Beta	-10.1847	-7.6683	2.5164
	6-311++G	Alpha	-9.5142	-7.7360	1.7782
		Beta	-10.2461	-7.7360	2.5101

Table 5: Global quantities calculated for the optimized structure of perfluoropentacene molecules using basis sets b3lyp/6-31+g (d) and b3lyp/6-311++g (d,p).

	Basis set		η (eV)	∫ (/eV)	**μ** (eV)	X (eV)	ω (eV)
Neutral	6-31+G		1.0002	0.9998	-4.9548	4.9548	12.2730
	6-311++G		0.9954	1.0047	-5.4759	5.4759	15.0611
		MO	η (eV)	∫ (/eV)	**μ** (eV)	X (eV)	ω (eV)
Anionic	6-31+G	Alpha	1.0586	0.9446	-0.5512	0.5512	0.1435
		Beta	1.3881	0.7204	-1.7613	1.7613	8.6124
	6-311++G	Alpha	1.0679	0.9364	-0.6152	0.6152	0.1772
		Beta	1.3929	0.7179	-1.8804	1.8804	1.2692
Cationic	6-31+G	Alpha	0.8943	1.1182	-8.5626	8.5626	40.9911
		Beta	1.2582	0.7948	-8.9245	8.9245	31.6647

	6-311++G	Alpha	0.8891	1.1247	-8.6251	8.6251	41.8359
		Beta	1.2551	0.7968	-8.9911	8.9911	32.2053

4.4 Non-Linear Optical Properties of perfluoropentacene

The non-linear optical (NLO) properties such as the dipole moment, mean polarizabilities, anisotropic polarizabilities, and first-order hyper-polarizabilities of perfluoropentacene in neutral, anionic and cationic states are reported in Table 6. These properties are important in determining the materials' potential applications in the fields of electronics and photonics. Materials exhibiting substantial NLO values are considered significant for electronic applications. From Table 6, it is observed thatin the anionic state, the molecule exhibits greater values of anisotropic polarizability and first-order hyperpolarizability compared to its neutral and cationic states. This implies that the molecule holds greater potential for optoelectronic applications when in its anionic state. The dipole moment is zero for both basis sets in the neutral state. It could suggest that the atoms on either side of the bond have similar or identical electronegativity. This interpretation is based on the concept that a nonpolar bond, where the electronegativity difference between atoms is negligible, typically results in a zero dipole moment.

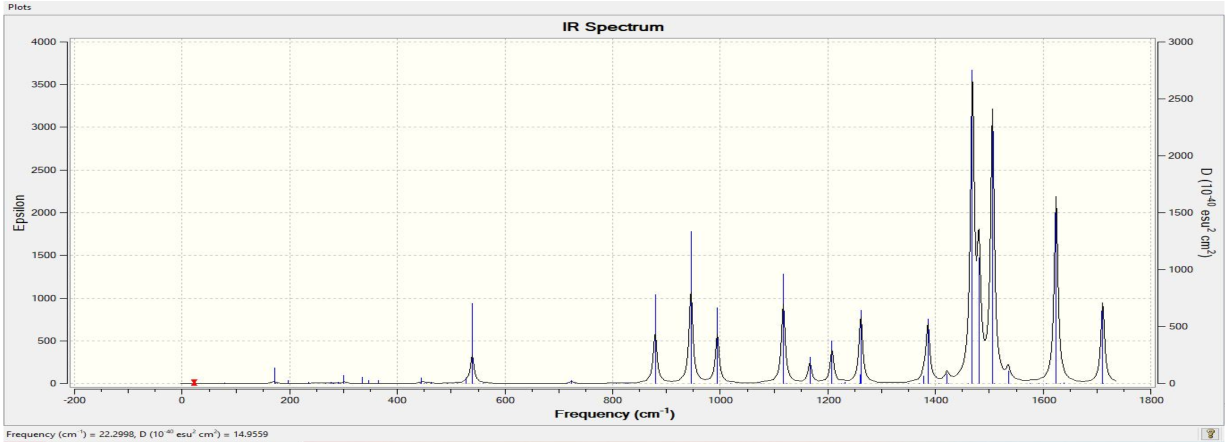
Table 6: Calculated non-linear optical properties of perfluoropentacene molecules for basis set b3lyp/6-31+g (d) and b3lyp/6-311++g (d,p).

	Basis sets	Dipole moment	Mean polarizabity $(<\propto>)(-10^{-23}esu)$	Anisotropic polarizability $(\Delta\alpha)$ in e.s.u	First hyperpolarizability (β) in e.s.u	Second hyperpolarizability (γ) in a.u
Neutral	6-31+G	0.0000	3.0809	5.6328×10^{-23}	3.5621×10^{-36}	-9055.7571
	6-311++G	0.0000	2.0574	6.6546×10^{-23}	9.3451×10^{-36}	-9037.3560
Anion	6-31+G	0.0001	3.7084	8.3391×10^{-23}	4.9146×10^{-35}	10191.0228

	6-311++G	0.0001	3.7114	8.3268×10^{-23}	6.2930×10^{-35}	10164.0915
Cation	6-31+G	0.0000	2.4347	3.1440×10^{-23}	1.3187×10^{-35}	-7954.9803
	6-311++G	0.0001	2.4416	3.1484×10^{-23}	1.2579×10^{-35}	-7943.4905

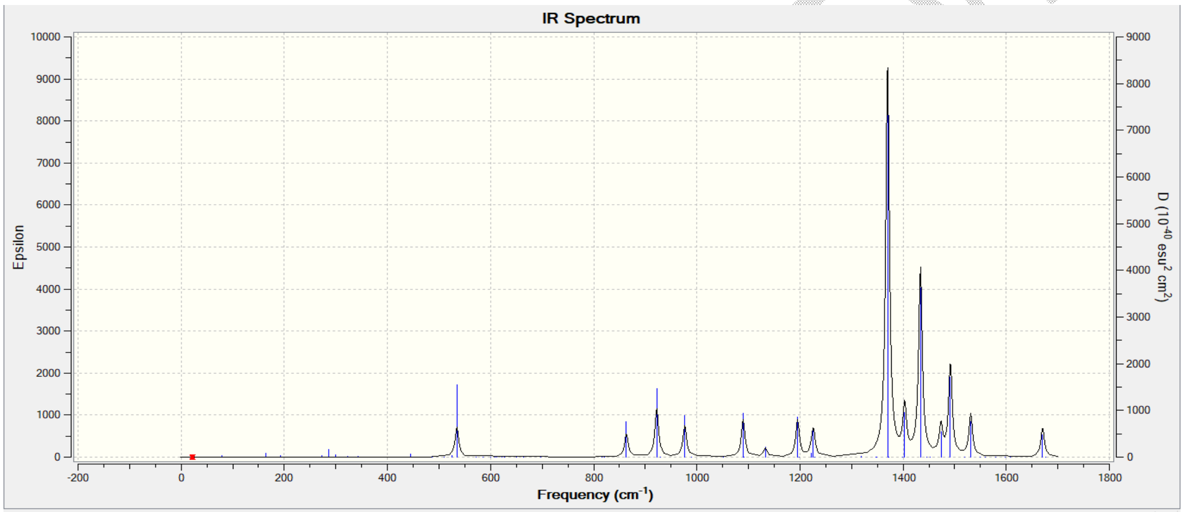
4.5 INFRARED (IR) SPECTRA

Infrared spectroscopy measures the interaction of infrared radiation with matter by absorption, emission, or reflection. When a molecule absorbs infrared radiation, its chemical bond vibrates and may either be stretched, contracted, or bent. Interpreting the most intense frequencies in the infrared (IR) spectra of organic semiconductors involves understanding which molecular vibrations are responsible for the strong absorption peaks. These peaks provide valuable information about the functional groups and bonding environments within the organic semiconductor material. (Maigari et al., 2022). The IR spectra plotted are shown in Figures. 3a,3b and 3c. It was observed that in both neutral and ionic states the molecule has no imaginary frequency which shows that the molecule was stable In neutral, the most intense frequency was found to be 1468.52 cm^{-1} at an intensity of $1013.8394(10^{-40} esu^2 cm^2)$. The second most intense frequency was found to be 1458.01cm^{-1} at an intensity of $1142.8732(10^{-40} esu^2 cm^2)$. In anionic, the most intense frequency was found to be 1369.84cm^{-1} at an intensity of $2766.7945(10^{-40} esu^2 cm^2)$. The second most intense frequency was found to be 1358.96 cm^{-1} at an intensity of $2796.0739(10^{-40} esu^2 cm^2)$. Also In cation, the most intense frequency was found to be 1533.72cm^{-1} at an intensity of $2972.9847(10^{-40} esu^2 cm^2)$. The second most intense frequency was found to be 1522.53 cm^{-1} at an intensity of $2958.2698(10^{-40} esu^2 cm^2)$ .In neutral state, the most intense frequency has a medium C-C stretched mode of vibrations. In anionic state a strong C-F stretched mode of vibration is observed at the most intense frequency while in cationic a medium C=C stretched mode of vibration was recorded.This is expected due to the high electronegativity of fluorine. Strong absorption peaks in the IR spectrum corresponding to C=C stretches. These peaks might be shifted slightly due to the electron-withdrawing effect of the fluorine atoms.



Frequency (cm $^{-1}$) = 22.2998, D (10 $^{-40}$ esu ^{2} cm ^{2}) = 14.9559

Figure 1a: Neutral**perfluoropentacene**(B3LYP/6-31+G (d))



Frequency (cm $^{-1}$) = 22.1679, D (10 $^{-40}$ esu ^{2} cm ^{2}) = 1.00779

Figure 1b: Anionic **perfluoropentacene** (B3LYP/6-31+G (d))

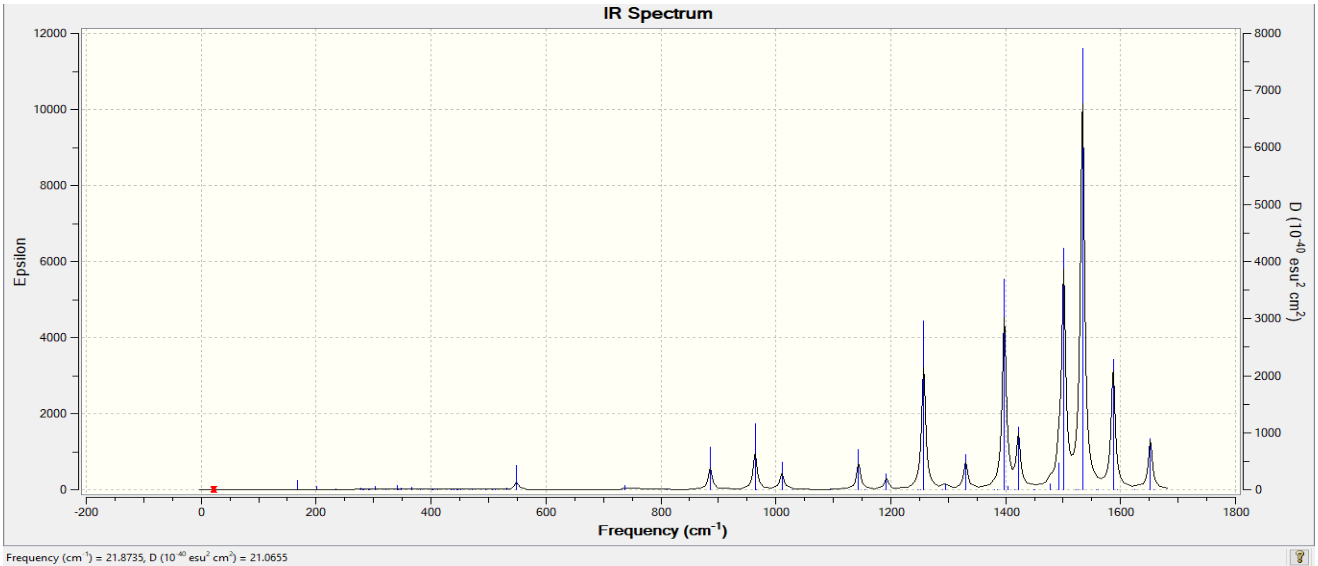


Figure 1c: Cationic **perfluoropentacene** (B3LYP/6-31+G (d))

4.6 UV-Visible Spectrum

The UV-visible (UV-Vis) spectrum in organic semiconductors refers to the absorption of ultraviolet and visible light by the semiconductor material. This absorption can provide valuable information about the electronic structure, energy levels, and optical properties of the organic semiconductor.(Maigari *et al.*, 2022). TD-DFT was employed to calculate the UV-visible spectrum of the optimized geometry at B3LYP 6-311++ G(d,p), displayed as oscillatory strength against excitation energy in Figure 2a-e. The graphs reveal that the molar absorptivity (ε) of the solution varies with solvent. Toluene exhibits the highest impact on the molecule, with an absorptivity range between 35,000 to 40,000, surpassing acetone, methanol, and ethanol (30,000 to 35,000) and water (approximately 30,000). Toluene shows the strongest absorption at a wavelength of 738.38 nm, with the highest oscillator strength of 0.0599 and the lowest excitation energy of 1.6791 eV. Table 7 lists the transition state, wavelength, excitation energy, and oscillation strength for five solvents: Acetone, Water, Toluene, Methanol, and Ethanol. The results indicate that solvent effects lead to an increase in excitation energy and slight fluctuations in oscillator strength. The excitation energy ranges from 1.6791 to 2.9715 eV, while oscillator strength varies from 0.0000 to 0.5130. Water exhibits the highest excitation energy, whereas toluene has the highest oscillator strength. The data also reveal that the lowest excitation energy corresponds to the highest wavelength, demonstrating that excitation energy is inversely proportional to wavelength. These findings imply that the choice of solvent significantly affects the excitation energy and oscillator strength of the molecule, with an inverse relationship between excitation energy and wavelength, which can be crucial for optimizing solvent conditions in spectroscopic applications.

Table 7: Wavelength (nm), excitation energy (eV) and oscillator strength of perfluoropentacene molecules

Solvent	Transition States	Wavelength λ (nm)	Excitation Energies (eV)	Oscillator Strength
Acetone	$S_0 \rightarrow S_1$	729.78	1.6989	0.0562
	$S_0 \rightarrow S_2$	462.02	2.6835	0.0000
	$S_0 \rightarrow S_3$	417.81	2.9675	0.4305
Water	$S_0 \rightarrow S_1$	728.37	1.7022	0.0554
	$S_0 \rightarrow S_2$	461.54	2.6863	0.0000
	$S_0 \rightarrow S_3$	417.24	2.9715	0.4162
Toluene	$S_0 \rightarrow S_1$	738.38	1.6791	0.0599
	$S_0 \rightarrow S_2$	465.23	2.6650	0.0000
	$S_0 \rightarrow S_3$	421.47	2.9417	0.5130
Methanol	$S_0 \rightarrow S_1$	728.62	1.7016	0.0552
	$S_0 \rightarrow S_2$	461.75	2.6851	0.0000
	$S_0 \rightarrow S_3$	417.35	2.9708	0.4165
Ethanol	$S_0 \rightarrow S_1$	729.67	1.6992	0.0563
	$S_0 \rightarrow S_2$	461.93	2.6841	0.0000
	$S_0 \rightarrow S_3$	417.76	2.9678	0.4304

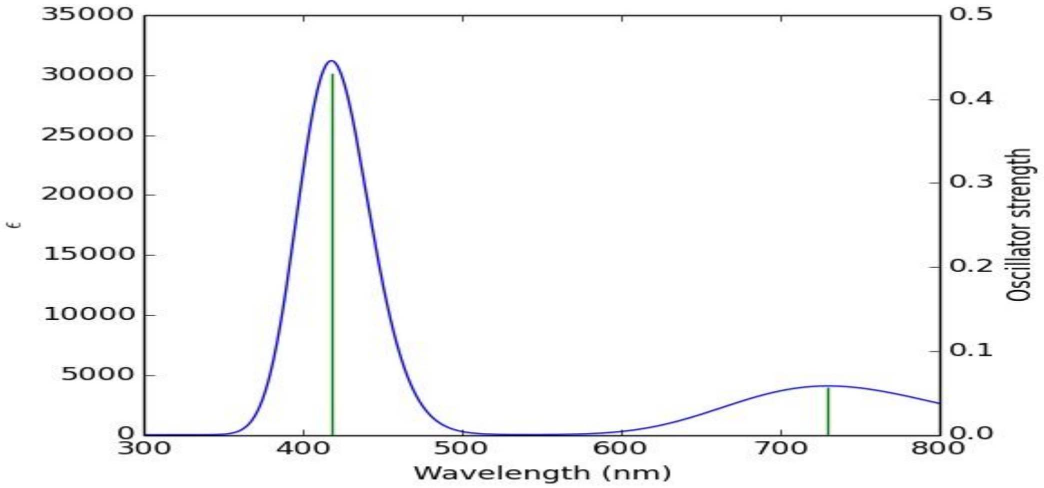


Figure 2a: Acetone

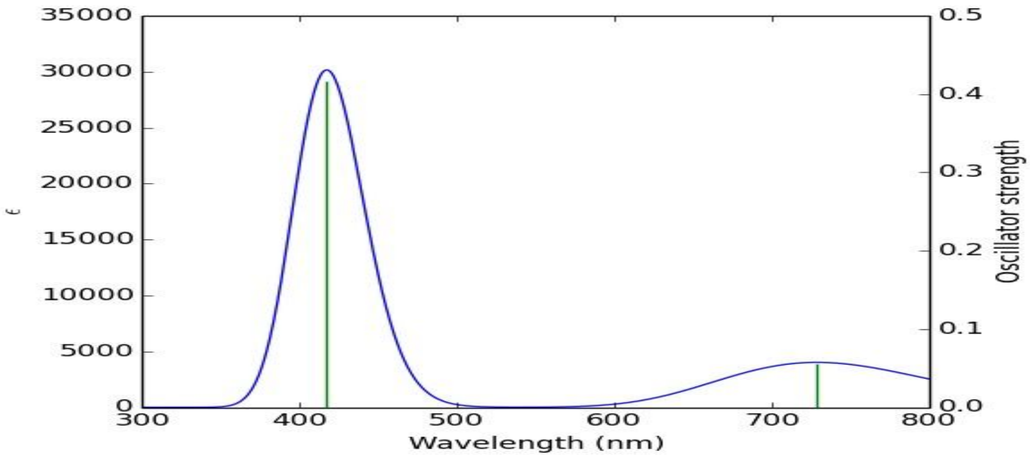


Figure 2b: Water

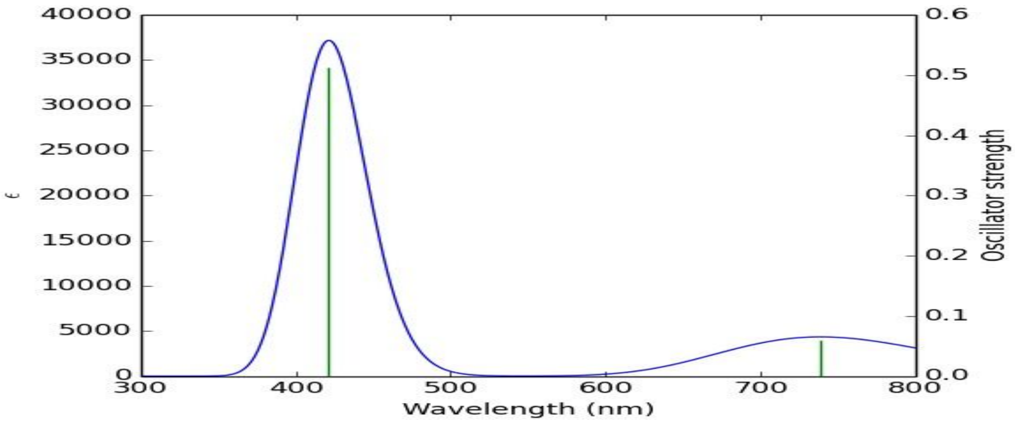


Figure 2c: Toluene

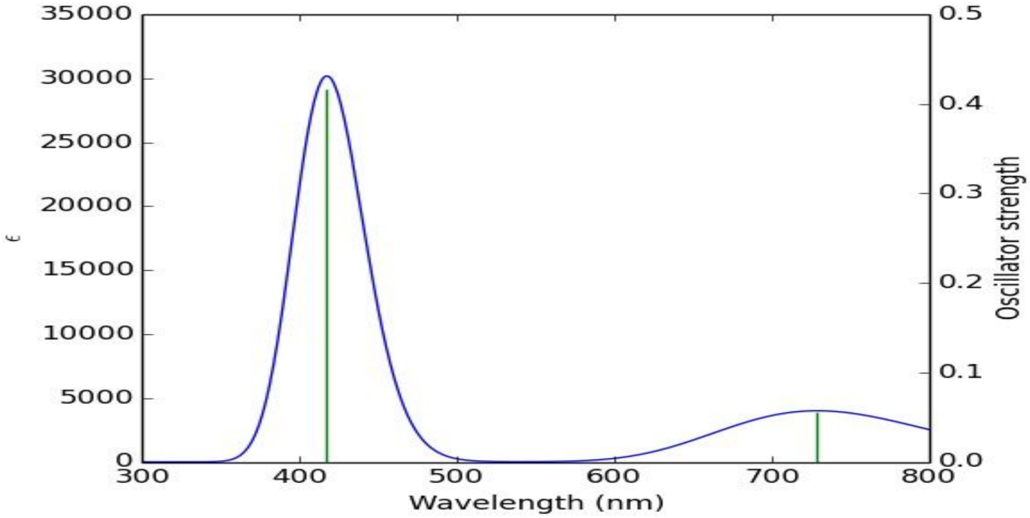


Figure 2d: Methanol

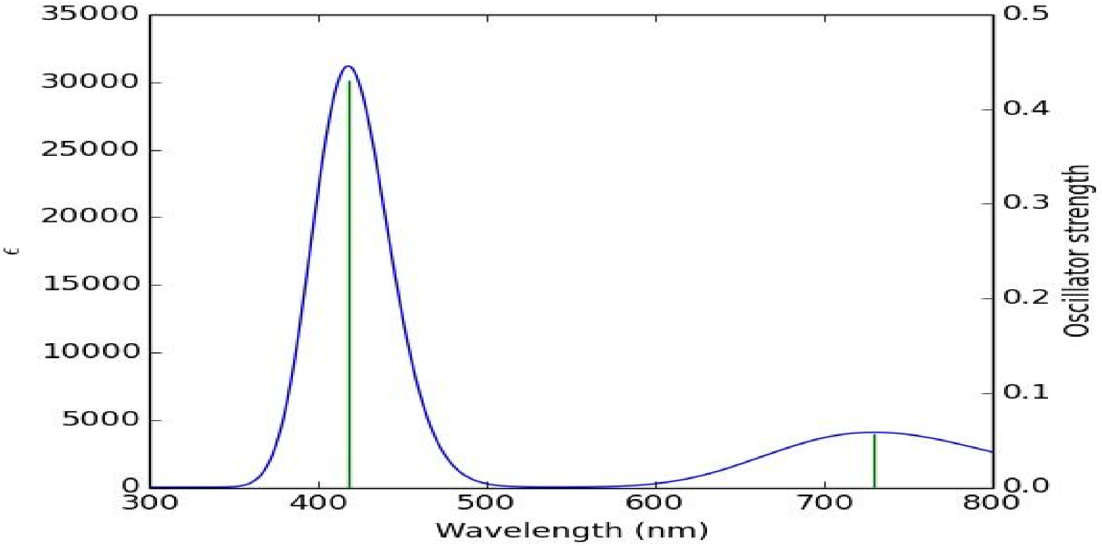


Figure 2e: Ethanol

5.0 CONCLUSION

In conclusion, our theoretical investigation into the most stable structures of neutral, anionic, and cationic perfluoropentacene has yielded insightful findings. We determined that the cationic state of perfluoropentacene exhibits the shortest bond length, indicative of higher bond energy and stronger bonds. Conversely, the anionic state possesses the smallest bond angle, suggesting stronger interactions between substituent atoms. The neutral state features an energy band gap of approximately 2.00 eV in close agreement with a previously reported work that obtained2.02eV signifying high stability and electrical conductivity due to facile electron transition from HOMO to LUMO. Notably, the anionic state demonstrated the highest chemical hardness, implying it is the most stable and least reactive form of the molecule. Our results also indicate that perfluoropentacene has significant non-linear optical (NLO) properties, especially in its anionic state, underscoring its potential for optoelectronic applications. Infrared (IR) spectra analyses showed stable vibrational modes across different states, with notable variations in intensity and type of vibrational modes influenced by the presence of fluorine, which shifts absorption peaks. Furthermore, UV-visible (UV-Vis) spectrum analysis revealed that the choice of solvent significantly impacts the molecule's excitation energy and oscillator strength. Toluene, in particular, produced the most pronounced absorption effects, highlighting the necessity of solvent optimization to enhance the optical properties of perfluoropentacene for electronic and photonic applications.

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