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VIBRATIONAL FREQUENCY AND THERMODYNAMIC PROPERTIES OF NEUTRAL AND IONIC PYRENE AND ITS DERIVATIVES

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ABSTRACT

Thermodynamic properties of pyrene organic compound and its chlorinated derivatives in neutral and ionic state were investigated. Pyrene ($C_{16}H_{10}$) is an organic compound that possesses such properties which are essential in determining the future application of the molecule. The study is based on Density Functional Theory (DFT) using Becke's three and Lee Yang Parr(B3LYP) functional with basis sets 6-311++G (d,p). These computations have been performed using Gaussian 03 software. Austin Model was also used to compute the heat of formation of the molecule and its derivatives in the two states at a temperature of 298K and 1 atm. The results showed that pyrene derivatives are thermally stable than the parent pyrene with 2-chloropyrene as the most stable followed by 1-chloropyrene and then pyrene across the neutral, anionic and cationic molecules. Due to higher entropy, pyrene derivatives tend to react more than the original molecule with 2-chloropyrene having higher reactivity than 1-chloropyrene. Enthalpic stabilization is in the order of 2-chloropyrene > 1-chloropyrene > pyrene. IR spectrum shows insignificant difference among the molecules, the only noticeable difference is the charge status of the molecules; this is indeed what caused the significant variation in the IR spectrum distribution.

Keywords: Pyrene, thermodynamic, organic compound, DF, Gaussian 03, heat capacity, entropy, energy and Heat of Formation.

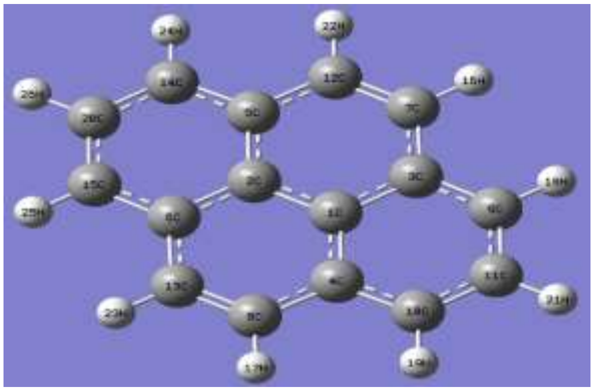
INTRODUCTION

The vast majority of chemical research concerns itself not with individual molecules but instead with macroscopic quantities of matter that are made up of unimaginably large numbers of molecules. The behavior of such ensembles of molecules is governed by the empirically determined laws of thermodynamics, most chemical reactions and many chemical properties are defined in terms of some of the fundamental variables of thermodynamics such as enthalpy, entropy, free energy, and others (Cramer, 2004).An organic material like Pyrene is one of the promising compounds that possess such properties which are essential in determining its future applications. Thermodynamic properties are those that deal with interrelationships between temperature, pressure, volume, and energy. Common thermodynamic properties for solids are heat capacity, density, sublimation pressure, melting point temperature, heat of melting, and heat of sublimation. Thermodynamic properties have a high practical significance because they describe how physical changes in a compound's environment such as pressure and temperature affect the compound and how the compound in return changes the pressure and temperature of its surroundings (Benjamin, 2003).The study of thermodynamics in the late 19th century included the heat-transfer properties of materials and led to the concept of thermal insulation that is, a material that has a relatively low rate of heat transfer. It also contributes to the development of the atomic theory,principles of physical science and conservation of energy. A lot of works were done on molecule's vibrational energy and thermodynamic property of different organic molecules using various theoretical methods including DFT. Kohn *et al* (1996) described Density Functional Theory (DFT) as a theory of electronic structure based on the electron density distribution$n(r)$, instead of the many-electron wave function. He also stated that over the past 30 years, density functional theory has become the physicists' method of choice for electronic structures of solids.This method has now become popular with theoretical and computational calculations by many physicist and chemists.

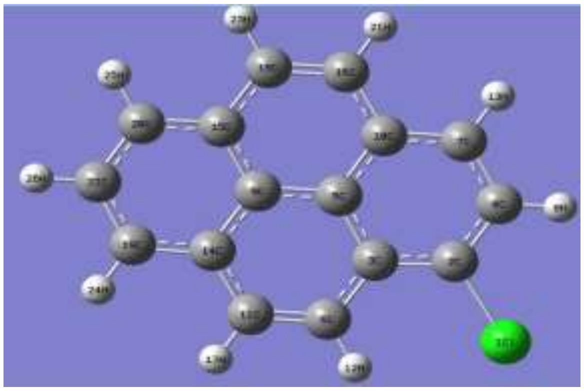
Alshamaileh(2014) performed a DFT calculationat B3LYP/6-311G** level and computed the gas phase energy and heat of formation of pyrene and three of its monochlorinated derivatives at 298K using a combination of isodesmic reactions. All the calculations used the Gaussian 03 program package.

Minenkov (2017) compute the electronic structure calculations and predict thermodynamic properties of various species. Several methods were employed to reproduce 113 accurate formation enthalpies of medium-sized molecules that are important for bio- and combustion chemistry with eight of each B3LYP and MP 2 methods to predict the significantly better enthalpies of formation. Minnesota functionals MO6, MO6-2X and recently developed ωB97X-D3 and ωB97M- V seems to produce better results of formation enthalpies than B3LYP. But performance of the DLPNO–CCSD(T) method can be further improved by running the post-SCF calculations on the B3LYP orbitals.

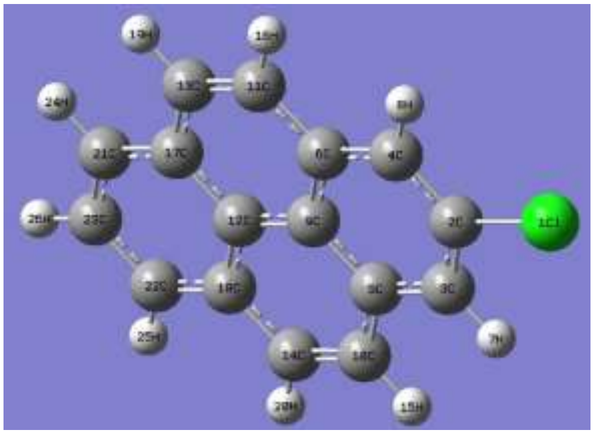
This work uses DFT theoretical method to analyze the vibrational frequency and some of the thermodynamic properties such as heat capacity, C_p, thermal energy, E, and entropy, S, of pyrene and two of its monochlorinated derivatives at a temperature of 298K and 1atm. In DFT, electron density is used in the calculations instead of electron wave function and a lot of computational time is saved. This unique features of DFT makes it dominant over other conventional theoretical methods. Heat of Formation was evaluated using semi-empirical method known as Austin Model 1(AM 1) within the same temperature and pressure. All computations were carried out after the molecule's geometry was optimized.



(a) Pyrene



(b) 1-chloropyrene



(c) 2-chloropyrene

Computational details

The computations of heat capacity, entropy and energy content have been performed using DFT at B3LYP/6-311++G(d,p) level. The computed values of the thermodynamic quantities for each molecule are due to the net group contributions of electronic, translational, rotational and vibrational effect. The quantities were computed utilizing the optimized geometry of the molecules by Gaussian 03 software package.

In many substances electrons do not absorb energy until very high temperatures are reached. Thus most heat capacity effects are interpreted in terms of the motion of the atoms neglecting electronic transitions. The total internal energy of a material is therefore, equal to the sum of the energies due to translational and rotational motion of the molecules and to the vibrational motion of the atoms making up the molecules (Liu, 1965).

$$E = E_T + E_R + E_V \qquad (1)$$

where E_T, E_R, E_V are energies due to translational, rotational and vibrational respectively.

Heat capacity arises because the individual particles comprising a substance are able to move and thus take up kinetic energy and usually also potential energy as the temperature rises. However the electronic contribution is negligible even at high temperatures. Hence the total heat capacity of a gas is given by the sum of the contributions due to translation, rotation and vibration.

The temperature dependence empirical equation of heat capacity of the molecule is given by (Rihani and Doraiswamy, 1965);

$$C_P = \sum a + \sum bT + \sum cT^2 \tag{2}$$

where a, b and c are the characteristic of each gas

The entropy of the molecules under study can be calculated from the Boltzmann relation as;

$$S = K \ln W \tag{3}$$

where K is the Boltzmann constant (1.38 x 10^{-23} J/K), and W is the number of microstates. Microstates are a term used to describe the number of different possible arrangements of molecular position and kinetic energy at a particular thermodynamic state. A process that gives an increase in the number of microstates therefore increases the entropy.

MATERIAL AND METHOD

In this research work, a 32- bit operating system personal computer (PC), Gaussian 03 software, Open Babel software, Gauss-view software and Arguslab 4.1.0 software were used in the computation.

Thermodynamic properties such as heat capacity, entropy and total energy of pyrene molecule and two of its monochlorinated derivatives in neutral and ionic state were calculated.

The molecules were obtained via Ligand Expo Database. Ligand Expo (formerly Ligand Depot) is an online database which provides chemical and structural information about small molecules (so-called Ligand) within the structure entries of protein Data Bank (PDB) (Babaji *et al*, 2016). The obtained molecule format was then converted to Gaussian acceptable format using Open Babel. The Lee, Yang and Parr correlation functional with Becke's three parameters (B3LYP) as exchange correlation functional using 6-311++G(d,p) standard basis set was adopted in the calculations which includes diffuse and polarization functions to ensure even more accurate predictions of the properties.

All the computations were carried out using the density functional theory (DFT) implemented in the Gaussian 03 suite program. The geometrical structures were first optimized to a state of minimum energy before any job is performed.

Vibrational frequency of the molecules was calculated after opening the Gaussian input window by specifying the **Job Type** on the **route section** that is, **opt freq**, after choosing the **method** and **basis sets**. **Charge** and **Multiplicity** of the molecule under investigation were identified given 0 and 1 for neutral, **-1** and **2** for anionic and **+1** and **2** for cationic

Similarly, computations of ionic form (anionic and cationic) of the molecules were performed using the same procedure as described above, but changing the **charge status** of the molecule from **0** for neutral molecule to **-1** for anionic and **+1** for cationic molecule.

The list of the computed frequencies and thermodynamic parameters were extracted from the frequency calculation output file generated by Gaussian.

The gas phase heat of formation of pyrene and its derivatives in neutral and ionic state at 298K and 1atm was also calculated using one of the semi-empirical methods; Austin Model 1 (AM1) with STO-3G as minimal valence basis set. This method is mostly used to model organic molecules after getting the optimize geometry of the molecule. Arguslab 4.0.1 software was used in this calculation.

RESULTS AND DISCUSSION

The statistical thermo chemical analysis of Pyrene and its derivatives was carried out considering the molecules to be at room temperature of 298 K and one atmospheric pressure (1atm). Table 1,2 and 3 describe the thermodynamic properties (i.e. thermal energy, heat capacity and entropy) of neutral, ionic and cationic molecules of pyrene respectively. It is well known that thermal stability is the stability of a molecule at high temperatures; i.e. a molecule with more stability has more resistance to decomposition at high temperatures. Monochlorinated derivatives are considered to have high resistance to temperature than the parent molecule, that is; 2-chloropyrene is considered to be thermally most stable followed by 1-chloropyrene and then parent Pyrene in neutral, anionic and cationic forms of the molecule as indicated in table 1,2 and 3 respectively.

Heat capacity of a defined system is the amount of heat (usually expressed in calories, kilocalories, or joules) needed to raise the system's temperature by one degree (usually expressed in Celsius or Kelvin). It is expressed in units of thermal energy per degree temperature. The heat capacity of a material, along with its total mass and its temperature, tell us how much thermal energy is stored in a material (Bralower and Bice). A material with higher heat capacity absorbs and release heat energy very slowly compared to those ones with lower heat capacity. This phenomenon means that thermal stability is associated with the higher heat capacity which is one important property needed by the organic molecules for a variety of applications. The thermal stability with respect to heat capacity has almost the same order with that of the thermal energy which is in the order of 2-chloropyrene> 1-chloropyrene> Pyrene across the neutral, anionic and cationic molecules.

The larger the entropy, the more the substance is going to be favored in a reaction. By itself, the entropy doesn't fully describe the stability of a molecule. Higher degree of randomness facilitates the reaction process. The reactivity of the molecules due to entropy shows that as the temperature moves higher, Pyrene derivatives tend to react more than the parent molecule. Considering table 1, 2 and 3, 2-chloropyrene is most reactive than the 1-chloropyrene. This means that addition of chlorine to the molecule improve the reactivity of the molecule especially moving to the higher positions in the pyrene ring.

Table1: Thermal energy, E (kcal/mol), Heat Capacity, C_v, (cal/mol-Kelvin) and Entropy, S, (cal/mol-Kelvin) of Neutral Pyrene Molecule at B3LYP/6-311++G(d,p) level

Parameter	Molecule	Electronic	Translational	Rotational	Vibrational	Total
E	Pyrene	0.000	0.889	0.889	133.890	135.667
	1-chloropyrene	0.000	0.889	0.889	128.753	130.531
	2-chloropyrene	0.000	0.889	0.889	128.619	130.397
C_v	Pyrene	0.000	2.981	2.981	38.928	44.889
	1-chloropyrene	0.000	2.981	2.981	42.740	48.702
	2-chloropyrene	0.000	2.981	2.981	42.860	48.822
S	Pyrene	0.000	41.815	28.988	24.135	94.938
	1-chloropyrene	0.000	42.278	32.739	29.700	104.716
	2-chloropyrene	0.000	42.278	32.827	29.783	104.887

Table 2: Thermal energy, E (kcal/mol), Heat Capacity, C_v, (cal/mol-Kelvin) and Entropy, S, (cal/mol-Kelvin) of Anionic form of the Molecule at B3LYP/6-311++G(d,p) level

Parameter	Molecule	Electronic	Translational	Rotational	Vibrational	Total
E	Pyrene	0.000	0.889	0.889	130.753	132.531
	1-chloropyrene	0.000	0.889	0.889	125.946	127.723
	2-chloropyrene	0.000	0.889	0.889	125.702	127.480
C_v	Pyrene	0.000	2.981	2.981	41.229	47.191
	1-chloropyrene	0.000	2.981	2.981	44.884	50.846
	2-chloropyrene	0.000	2.981	2.981	45.160	51.122
S	Pyrene	1.377	41.815	29.012	25.917	98.122
	1-chloropyrene	1.377	42.278	32.768	31.703	108.127
	2-chloropyrene	1.377	42.278	32.851	31.645	108.152

Table 3: Thermal energy, E (kcal/mol), Heat Capacity, C_v, (cal/mol-Kelvin) and Entropy, S, (cal/mol-Kelvin) of Cationic form of the Molecule at B3LYP/6-311++G(d,p) level

Parameter	Molecule	Electronic	Translational	Rotational	Vibrational	Total
E	Pyrene	0.000	0.889	0.889	134.052	135.830
	1-chloropyrene	0.000	0.889	0.889	128.867	130.644
	2-chloropyrene	0.000	0.889	0.889	128.553	130.330
C_v	Pyrene	0.000	2.981	2.981	39.143	45.104
	1-chloropyrene	0.000	2.981	2.981	42.857	48.818
	2-chloropyrene	0.000	2.981	2.981	43.128	49.089
S	Pyrene	1.377	41.815	28.985	24.667	96.844
	1-chloropyrene	1.377	42.278	32.729	30.219	106.604
	2-chloropyrene	1.377	42.278	32.822	30.363	106.841

Heat of formation

Enthalpy or heat of formation refers to the energy involved in the formation of a substance from its elements in their most stable forms. Higher enthalpy means heat had to be absorbed to form the substance, which makes the substance a higher-energy compound. High energy compounds tend to be more reactive, therefore less stable. The reverse is true for lower enthalpies. Table 4 lists the values of heat of formation for pyrene and two of its monochlorinated derivatives obtained from the semi-empirical method. From table 4, pyrene derivatives are considered to be more reactive than the parent pyrene across the neutral and ionic state. So, enthalpic stabilization is in the order of 2-chloropyrene> 1-chloropyrene > pyrene except for the case of cationic molecule. This clearly indicates that, enthalpy stabilization increases due to the introduction of chlorine into the pyrene ring. Ionic molecules possess higher enthalpy which shows that, charging the molecules makes them to become more reactive than the neutral counterparts. Enthalpic effect is more pronounced in charging the molecule than the addition and positioning of chlorine into the molecule.

Table 4: Enthalpy of formation, ΔH_f^o(kcal/mol) of Neutral and Ionic molecules of Pyrene and its derivatives using AM 1 method with STO- 3G basis set.

Molecule	ΔH_f^o(kcal/mol) (Calculated)	ΔH_f^o(kcal/mol) Experimental(Roux *et al*, 2008)
	Neutral	
Pyrene	70.2828	225.5
1-chloropyrene	62.9693	NA
2-chloropyrene	62.0759	NA
	Anionic	
Pyrene	103.6678	NA
1-chloropyrene	84.9459	NA
2-chloropyrene	83.9081	NA
	Cationic	
Pyrene	519.9142	NA
1-chloropyrene	512.4950	NA
2-chloropyrene	517.8685	NA

IR Spectra

The calculated vibrational frequencies of pyrene and its derivatives are shown in Figure 3. 6-311G basis set was chosen for vibrational frequencies with variation in intensity among the studied molecule. The aromatic molecules frequency has both in-plane (1100 – 1700) cm^{-1} and out-of-plane (below 1000 cm^{-1}) (C – H) bending vibration. It was observed that the IR spectrum of pyrene behave in almost the same way to that of the two derivatives, which means addition of chlorine into the parent molecule did not temper with the IR spectrum distribution of the molecule. Although out of plane, strong (C – Cl) stretch was observed at (750 - 850) cm^{-1}, the molecules have an out of plane (C-H) medium bending vibration in the region (870 - 885) cm^{-1}. Strong (C - O) and (C - F) occur at (1000 - 1320) cm^{-1} and (1000 - 1350) cm^{-1}respectively. Generally, the number of vibration modes for each structure agreed with the calculations for non-linear molecular system according to the relation 3N- 6, where N is the number of atoms that the structure included. The same behavior occurred at the anionic and cationic molecules, the difference in the charge status of the molecule is what caused the significant variation in the IR spectrum distribution. Many peaks occurred at the ionic molecules than the neutral molecules, especially at anionic. This clearly indicate the existence of many functional groups that are attached to the ionic molecule which are important portion of the molecule that is capable of characteristic reactions and therefore determine the properties and chemistry of the organic compound. As such, ionic molecules appear to be a potential candidate for optical applications (Abdulaziz *et al*, 2019).

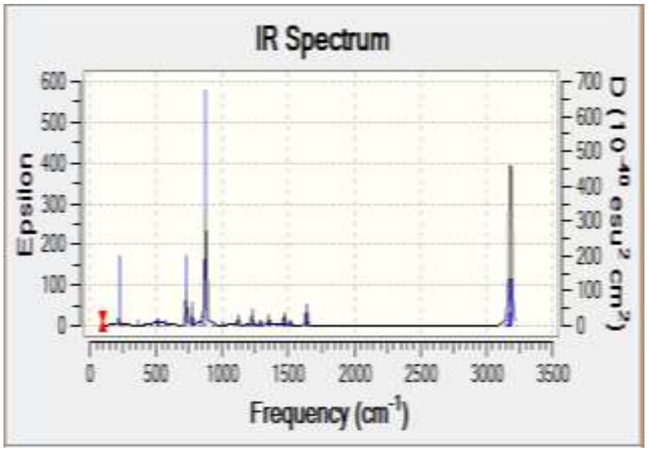


Fig 2: IR spectrum of Neutral pyrene

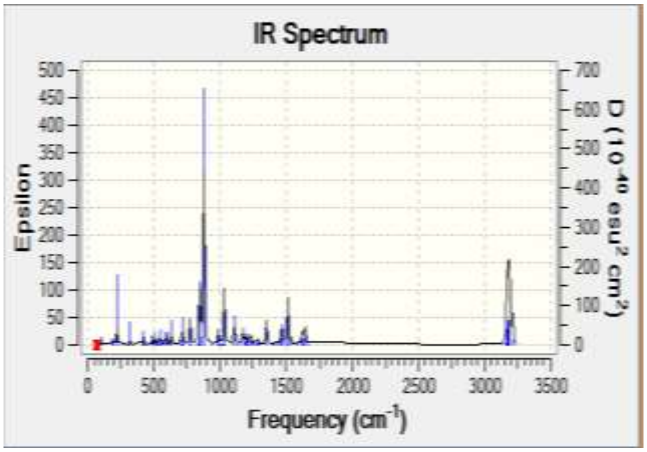


Fig 3: IR spectrum of Neutral 1- Chloropyrene

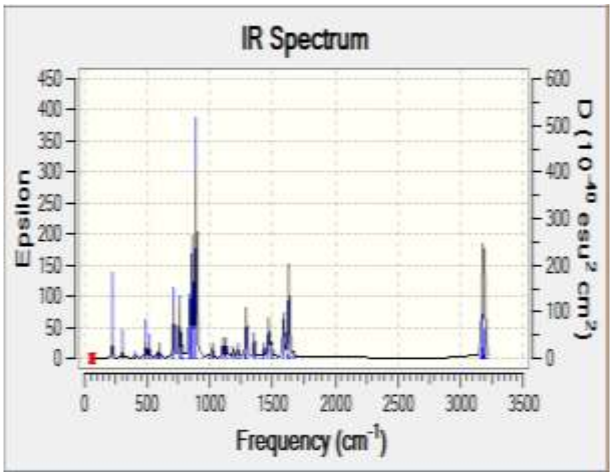


Fig 4: IR spectrum of Neutral 2-Chloropyrene Molecule

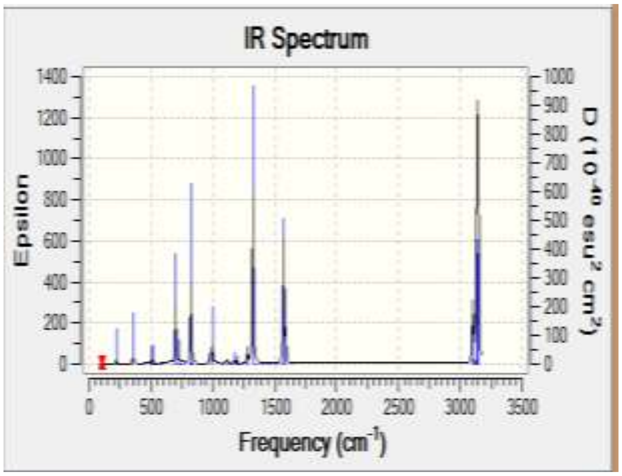


Fig 5: IR spectrum of Neutral Pyrene (anionic)

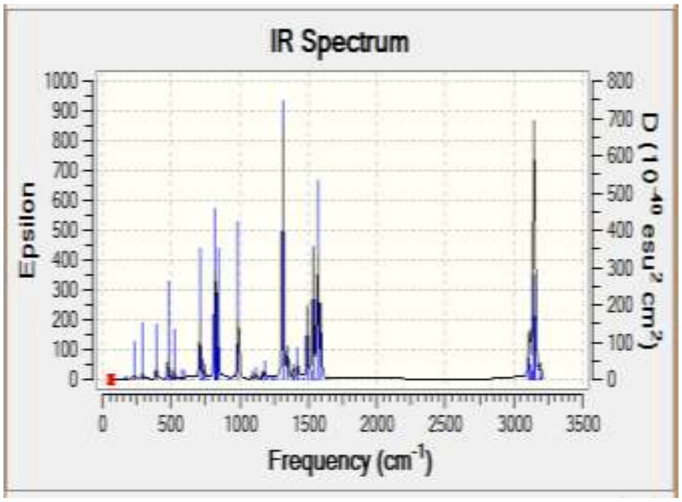


Fig 6: IR spectrum of 1-Chloropyrene Molecule (Anionic)

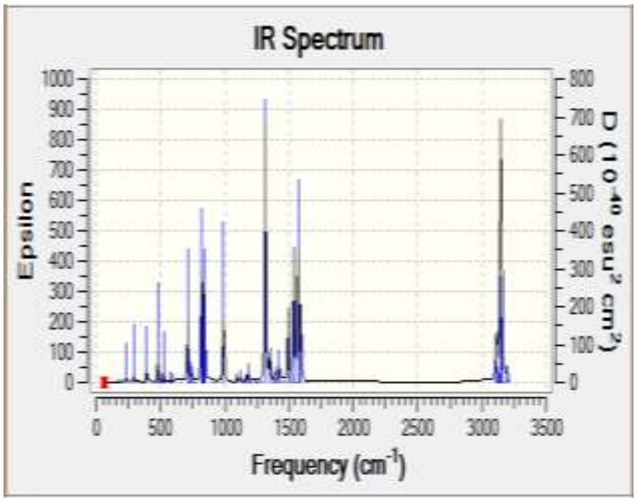


Fig 7: IR Spectrum of 2-Chloropyrene Molecule (Anionic)

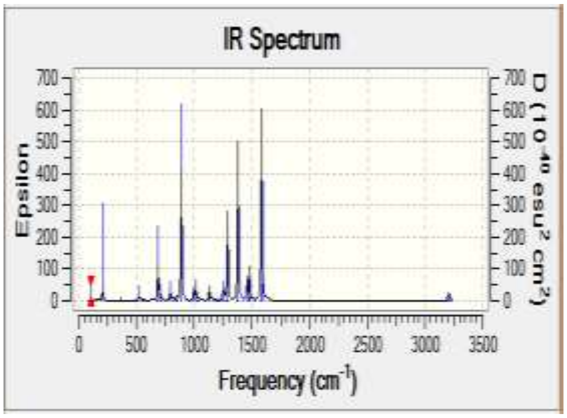


Fig 8: IR Spectrum of Pyrene Molecule (Cationic)

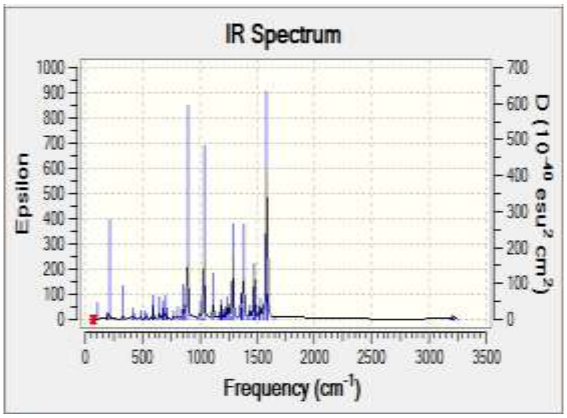


Fig 9: IR Spectrum of 1-Chloropyrene Molecule (Cationic)

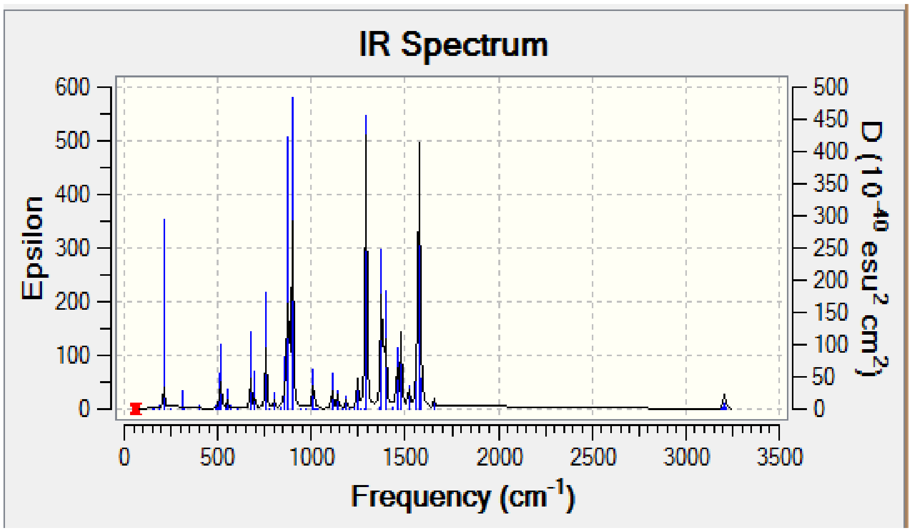


Fig (ref: 3.2 IR Spectra general discussion on fig: 2-10)10: IR Spectrum of 2-Chloropyrene Molecule (Cationic)

CONCLUSION

DFT theory at B3LYP/6-311++G(d,p) level was used to study the effects of chlorination and charging of pyrene molecule on vibrational frequency and some of its thermodynamic properties. The results showed that addition of chlorine to the molecule make the compound to become thermally stable and improve the reactivity of the molecule due to higher entropy especially when placing the chlorine in the higher positions in the ring. Comparing this work with the available literatures, it was found that DFT calculations are more accurate in calculation of heat of formation of this molecule and its monochlorinated derivatives than the semi-empirical method; AM 1(with STO minimum basis set). This is due to the closeness of DFT theoretical value of 227.8 for neutral pyrene in Al-Shamaileh (2014) with the available experimental value of 225.5 in Roux et al (2008). Addition of chlorine into the pyrene ring seems to have insignificant effect in changing its vibrational spectrum; the difference in the charge status of the molecule is what caused the significant variation in the IR spectrum distribution.

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