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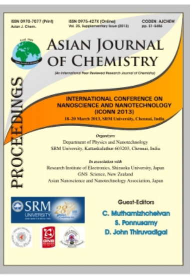

Comparative Study of Thermochemical Properties of Fluorographene at Different Temperatures: A Computational Approach†

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Extraordinary properties of graphene continue to attract intense interest that has expanded into research areas. One of the research directions that have emerged recently is based on the notion of graphene being a giant macromolecule, which as any other molecule can be modified in chemical reactions. Graphene's surface has been decorated with various atoms. One way to create more stable graphene derivatives is to try using agents that bind to carbon stronger than hydrogen. Fluorine is one such candidate. Fluorographene is, in a simplified way, a 2D version of Teflon/PTFE which consists of long 1D poly(tetrafluoroethene) polymer molecules. Like poly(tetrafluoroethene) (PTFE), fluorographene has a high thermal stability and excellent 'non-stick' properties. Also like poly(tetrafluoroethene), it is chemically very stable, *i.e.* very inert, so, combined with its great thermal stability, it can be used as a stable surfacing material over a wide temperature range. In this paper, fluorographene is optimized using Gaussian 03. Fluorographene's thermochemical properties are analyzed over a range of temperatures. The ionization potential is also analyzed and compared to graphene.

Key Words: Fluorographene, Thermal chemistry, Ionization potential.

INTRODUCTION

In recent years great attention is paid to the investigation of properties of one layered membranes of graphene and similar materials. This pertains to their unique heat conducting properties. Among the possible derivatives of graphene are graphane and fluorographene, which result from the hydrogenation and fluorination of graphene have attracted special attention. One way of creating more stable graphene derivatives is to try using agents that bind to carbon stronger than hydrogen. Fluorine is one such candidate. During fluorination process the carbon atoms which are bonded to fluorine have their sp^2 hybridization changes to sp^3 and may provoke the opening of bandgap[1]. This transformation from a planar to a more three dimensional structure brings several new characteristics. A set of outstanding physical and chemical properties for single layer fluorographene has been recently found experimentally and predicted theoretically[1-10]. Quantum chemical calculations for two plane crystalline structures of fluorographene was first carried out in 1993[11] and it was shown that chair configuration is energetically the most favoured. The structure and electronic properties of four crystalline structures of graphene and graphene fluoride have been investigated.

COMPUTATIONAL PROCEDURE

The quantum theoretical basis of thermodynamics is well established and forms the standard approach to statistical mechanics. Theoretical estimates of thermodynamic quantities are derived from theoretical estimates of enthalpy and entropy.

Here, all calculations have been carried out with the Gaussian 03[12] package. Full geometry optimizations have been performed at the Semi empirical AM1 level. The optimized geometry was then used to perform frequency calculations at different temperatures. The structure is stable as the vibrational analysis of the molecule does not show any imaginary frequency.

RESULTS AND DISCUSSION

An arm chair configuration of graphene($C_{24}H_{36}$) sheet is considered and one fluorine is substituted for each carbon atom giving a configuration of $(CF)_{24}H_{12}$. The optimized structure of fluorographene is given in Fig. 1.

Structural parameters: The C-C bond length and the C-H bond length of graphene average about 1.52 Å and 1.12 Å as compared to an average bond length of 1.41 Å and 1.1 Å predicted by Cristina Nava contreras[13].

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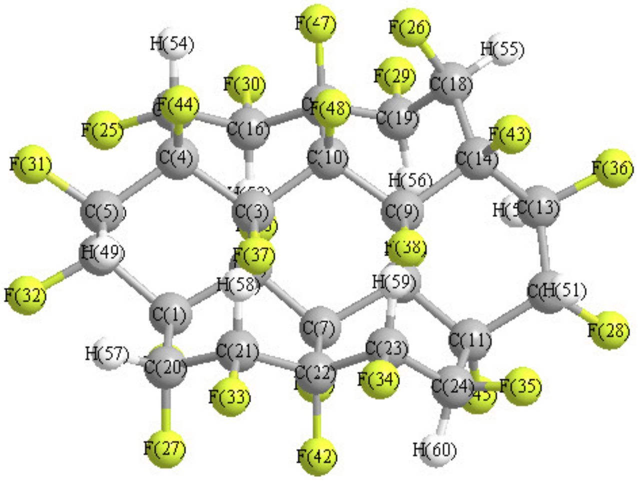

Fig. 1. Optimized structure of fluorographene

On decorating the graphene layer with fluorine it is observed that the C-C bond length varies between 1.36 Å to 1.51 Å as compared to the average C-C bond length of 1.44 Å proposed by Cristina Nava contreras[13] and C-F bond length averages at an 1.43 Å and C-H at 1.10 Å exactly in agreement with the same author.

Ionization potential: HOMO-LUMO gap of graphene is 1.25 eV in close agreement with the value predicted by Cristina Nava contreras[13] for arm chair configuration.

The HOMO-LUMO gap for fluorinated graphene is 8.48 eV slightly overestimated as compared to that predicted by Enyasin[14] but a higher value as compared to the value predicted by Cristina Nava Contreras[13] where a partial fluorination of graphene was carried out.

Thermal chemistry: The thermal chemistry of graphene and its fluorinated derivative were analyzed at a range of temperatures. As the property of fluorinated graphene was found to be identical to Teflon, the operating range of temperature for Teflon has been chosen as reference range here. The analysis was carried out from 100 K to 500 K.

The contributions of external rotations, translations and vibrations to entropies and heat capacities are calculated from scaled vibration frequencies for the AM1 optimized structures. The theoretical formation energies were estimated assuming the formal reactions as followed in their works by Enyashin *et al.*[14] and Zboril *et al.*[15] as:

$$E_{form}(CF)_{24}H_{12} = [E_{tot}(CF)_{24}-1/2\ E_{tot}(24(F_2))-E_{tot}(C_{24}H_{36})]$$

and is tabulated in Table-1.

TABLE-1
ENTHALPY OF FORMATION OF FLUORO GRAPHENE

	100 K	200 K	300 K	400 K	500 K
$E_{tot}(C_{24}H_{36})$	360.9457	364.5231	370.844	380.5804	393.8159
$1/2\ E_{tot}\ 24(F_2)$	31.75447	40.09783	48.50896	57.13846	66.0767
$E_{tot}(CF)_{24}H_{12}$	347.3375	351.4414	358.4388	368.8849	382.8181
$E_{form}(CF)_{24}H_{12}$	-45.3627	-53.1795	-60.9142	-68.834	-77.0745

As seen from Table-1, the enthalpy of formation is increasingly negative indicating exothermic reactions.

The variation of the thermal correction to energy, enthalpy and Gibbs free energy are represented by the graph in Fig. 2. The internal energy and enthalpy increase in a steady manner with the increase in temperature. The Gibbs free energy is found to decrease with increase in temperature as the entropy of reaction increases as listed in Table-1. The increase in entropy from 100 K to 200 K is marginal and as the temperature approaches 400 K, the increase in the entropy of the system is double and then again is marginal approaching 500 K. The constant value heat capacity that is steadily exhibiting an increasing difference between temperatures seems to show a decreasing difference after 400 K. Both these thermal parameters may indicate a change over after 400 K.

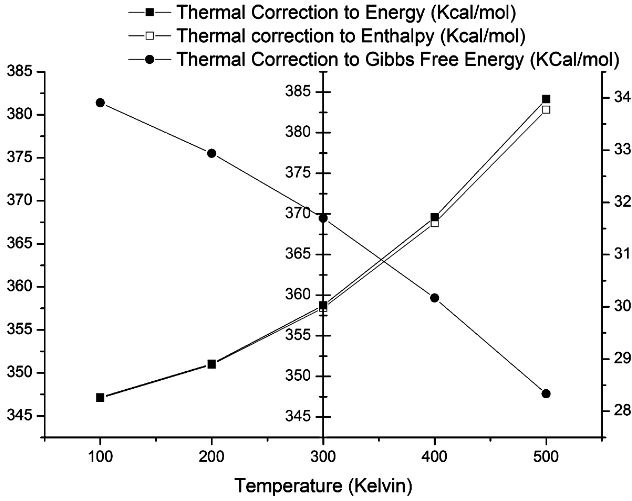

Fig. 2. Variation of thermal correction to energy, enthalpy and Gibbs free energy with temperature

The variation of constant value heat capacity and entropy with temperature are summarized in Table-2.

TABLE-2
VARIATION OF CONSTANT VALUE HEAT CAPACITY AND ENTROPY WITH TEMPERATURE

Temperature	100 K	200 K	300 K	400 K	500 K
C_{tot}	25.701	52.59	84.569	120.387	153.518
S_{tot}	82.895	110.279	138.215	168.019	198.972

Conclusion

We have shown that the exposure of graphene to atomic fluorine results in a stoichiometric derivative that is an excellent insulator with a high thermal and chemical stability. The optical and electrical properties of fluorographene are radically different from those of graphene due to a wide gap opened in the electronic spectrum and this gap manifests itself to be higher in our calculations. According to earlier works, mechanically also fluorographene is remarkably stiff but stretchable. These characteristics rival those of Teflon and allow one to consider fluorographene for a range of technologies, in particular those that employ Teflon. As for electronic applications, there is a promising possibility to use fluorographene as an atomically thin insulator or a tunnel barrier in graphene-based heterostructures. Present work demonstrates a wide band gap for fluorographene. It is planned to further carry on these studies and analyze the dipole moment, charge distribution, population analysis and vibrational analysis.

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