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The Molecular Electrostatic Potential, Density of State and Homo-Lumo Analysis of Single Layered Graphene

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ABSTRACT

In this work, we conducted a quantum chemical investigation of single-layer graphene, examining its structural characteristics. We also studied its UV spectroscopy and molecular electrostatic potential (MESP). We employed the structural and geometrical parameters of single-layer graphene using the B3LYP/6-31+G(d, p) basis set. Electronic transitions were calculated in a water environment using the PCM model and DFT/B3LYP/6-31+G(d,p), which revealed charge transfer within the molecule. The HOMO-LUMO analysis of single-layer graphene provided detailed insights into the density of charge transfer between acceptor and donor groups. The density of states (DOS) of single-layer graphene was also studied.

Keywords:—*Single layered graphene, MESP, DOS and HOMO-LUMO*

I. INTRODUCTION

The invention of graphene by [1], there has been significant interest in its properties and applications. Graphene is highly favored by physicists and materials researchers due to its simple structure and processing capabilities[2]. Computational techniques have proven invaluable for modeling oxygen-containing groups on graphene. Quantum computational methods [3], in particular, have emerged as powerful tools for exploring atomic structures, bonding, stability, and reaction mechanisms.

Advancements in computer hardware and efficient software have greatly enhanced the ability to predict atomic properties through quantum mechanics. Among the most widely used software packages for electronic structure calculations is Gaussian[4, 5]. Various experimental and theoretical studies have provided insights into the bonding and reactivity of graphene systems, often based on empirical observations and established principles. This has highlighted the need for a robust theoretical framework to support these observations. In this study, we utilize Hartree-Fock and B3LYP methods to analyze single-layer graphene (SLG). We focus on evaluating key geometric parameters, structural characteristics, and vibrational properties.

II. EXPERIMENTAL PROCEDURE

Graphite powder was obtained from Merck, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), and hydrochloric acid (HCl). Double ionized (DI) water was used for all

the reactions. Graphene oxide (GO) was synthesized using the modified Hummers method. X-ray diffraction (XRD) measurements were recorded at room temperature with a scan rate of 0.02°/min over the range of 10° to 80° using a PAN alytical X'Pert-Pro diffract to meter with Cu Ká1 radiation (ë = 1.5406 Å). The UV-visible spectra were obtained using a Jasco V-650 spectrophotometer in the wavelength range of 400nm to 800nm. Quantum chemical calculations were performed to predict the molecular electrostatic potential, Density of state and HOMO-LUMO studies using the B3LYP method with the 6-31G(d, p) basis set in the Gaussian 09 software.

III. Structural Analysis

A powder X-ray diffraction (XRD) spectrum of single-layer graphene (SLG) is shown in Figure 1. The diffraction peak at 2θ = 26.3° corresponds to the characteristic graphite structure. The optimized molecular structure parameters, including bond lengths and bond angles of SLG, were calculated using the B3LYP method with the 6-31G(d, p) basis set and are depicted in Figure 1.SLG consists of carbon atoms with sp^2 hybridization, involving both single and double bonds. Typically, in an aromatic ring structure, the C–C bonds do not exhibit uniform bond lengths and angles. The presence of these peaks confirms the formation of graphene oxide. The graphene oxide peak initially observed at 10.3° shifts after reduction to form graphene. Additionally, a new peak appears at approximately 43.3°, corresponding to the (100) plane (JCPDS No. 75-1621).

The chemical reduction process removes other functional groups, impurities, and amorphous carbon. The low crystallinity of graphene suggests the presence of residual oxygen-containing functional groups within the graphene sheets [6].

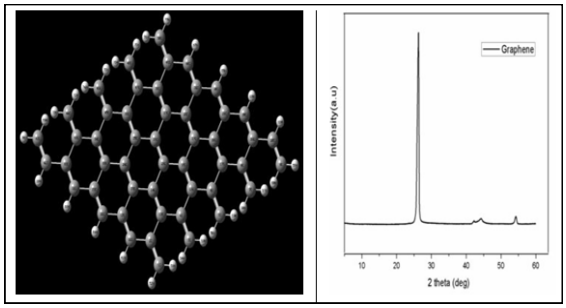

Figure 1: Molecular structure and XRD peak of SLG

IV. Result and Discussion

Molecular Electrostatic Potential (MESP)

The molecular electrostatic potential (MESP) of the molecule was calculated using the B3LYP method with the 6-31G (d,p) basis set, the molecular electrostatic potential (MESP) are shown in Figure 2. MESP is a useful tool for analyzing and predicting the molecular reactivity of various biological systems, particularly in relation to hydrogen bonding interactions [7].

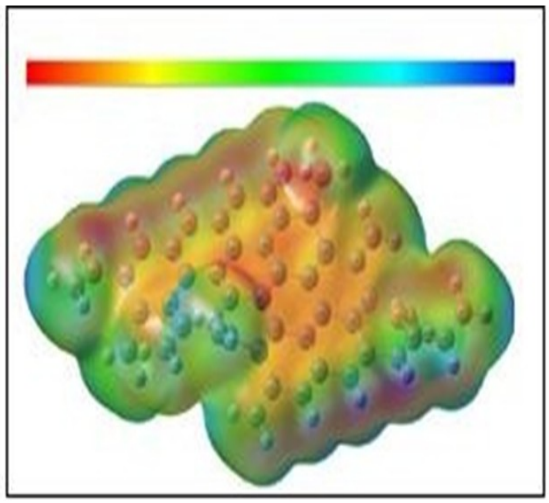

Figure 2: MESP and DOS mapping of SLG

It has been extensively applied to the study of the reactive behavior of nucleic acids and their bases, as well as increasingly larger fragments of DNA and RNA.Electrostatic potential maps provide a three-dimensional illustration of the charge distributions within molecules.

Density of States (DOS)

The Density of states (DOS) of the molecule was calculated using the B3LYP method with the 6-31G(d, p) basis set as shown figure 3. The DOS plot reveals the overlapping population in the molecular orbitals[8], with the OPDOS (overlapping population density of states) results indicating the nature of interactions between atomic orbital groups. A positive OPDOS value suggests bonding interactions, a negative value indicates antibonding interactions, and a zero value corresponds to non-bonding interactions.

The DOS plot highlights the contribution of specific groups of orbitals to the molecular orbitals, with the plot range extending from -1.50 a.u. to +1.50 a.u. This graph illustrates the orbital characteristics across different energy ranges, showing significant contributions from the s and p orbitals of carbon in the frontier molecular orbitals.

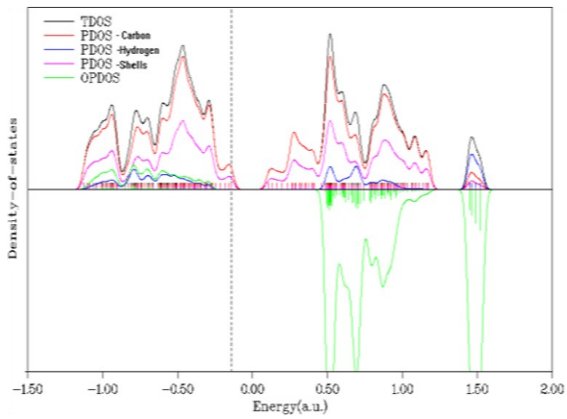

Figure 3: MESP and DOS mapping of SLG

The partial density of states (PDOS) of the carbon atom within the molecule reflects the total density of states, with the carbon atom exhibiting slightly higher positive energy values than negative ones. The OPDOS curve in the negative region indicates the anti-bonding nature of the molecule, which is attributed to unfavourable orbital interactions.

HOMO-LUMO Analysis

The HOMO-LUMO analysis was employed to demonstrate the bioactivities arising from intramolecular charge transfer within the molecule[9]. The molecular orbital energies for the first three energy levels namely HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1, and LUMO+2—are illustrated in Figure 4. The energy values of the HOMO (orbital 164) and LUMO (orbital 165) were calculated to be -0.3829 eV and 2.7736 eV, respectively.

The electron charge transition occurs from the HOMO (orbital 164) to the LUMO (orbital 165), indicating a charge transfer from the C=C bond to the C-C bond within the molecule[10]. The energy gap between the HOMO and LUMO was found to be 3.1565 eV in isolated gas-phase calculations. Additionally, the self-consistent field (SCF) energy of the compound was calculated to be -1886.226 a.u.

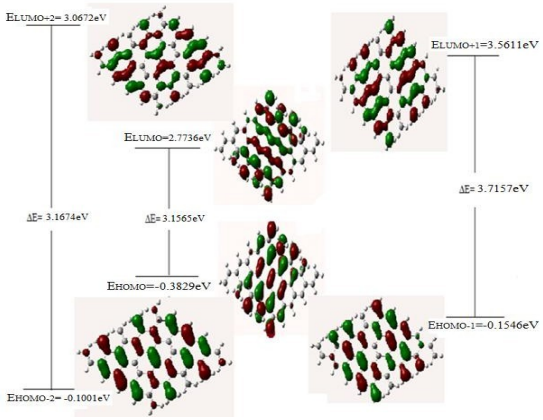

Figure 4: MESP and DOS mapping of SLG

V. CONCLUSION

Graphene was successfully synthesized at an appropriate temperature using the modified Hummers method. The XRD spectra, with a peak at 10.3°, confirm the formation of graphene oxide. The density of states (DOS) analysis of the compound indicates molecular stabilization, which is

influenced by the carbon atoms. The molecular electrostatic potential (MESP) mapping provides insights into the charge density distribution and chemical reactivity of the molecule. The energy gap of the compound was determined to be 3.122 au.

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