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Optical properties of pure graphene in various forms: A time dependent density functional theory study

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Abstract

Time dependent density functional theory (TDDFT) based calculations were performed for two basis sets 6-31G and 6-31G (d) on two sets of Graphene samples: a) Graphene nano-ribbons (GNRs) of different geometries like square, rectangle and triangle containing 48, 53, 60, 68, 70 and 77 atoms, and b) Six isomers of $C_{46}H_{18}$ GNR. UV-visible absorption spectra were obtained from the TDDFT calculations. Optical gaps, excitation wavelengths, oscillator strengths and dominant transitions of all the samples were calculated. The highest oscillator strengths were found for the rectangle shaped GNRs Rectangle60, Rectangle77 (***f*** = 0.826 and 1.512) at the absorption wavelengths 416.5 and 439.2nm. Amongst $C_{46}H_{18}$ isomeric GNRs, ISO4, ISO5 and ISO6 with high ***f*** (>0.6) were found to absorb more light in the visible region. Higher optical absorption has been obtained for all the isomeric GNRs in the range 500-900nm making them suitable for the dye sensitized solar cell applications. The pi→pi* transitions were found to be the dominant transitions in the optical absorption of both the sets of GNRs.

Keywords: TDDFT; Graphene nano-ribbons; Shapes; $C_{46}H_{18}$ Isomers; UV-visible absorption

1. Introduction

Graphene is a very simple, strong, and easily synthesized material, which makes it interesting in basic research and applications engineering [1]. Graphene nano-ribbons (GNRs) have been an exciting area of research allowing the possibility of band gap engineering [2-4] by varying their dimensions/ribbon widths [5], has been studied extensively. Recently there have been experimental reports on the GNRs of varying shapes and sizes produced by diamond-edge-induced nanotomy (nanoscale-cutting) of graphite into graphite nanoblocks [4]. Our group has reported density functional theory based study on various GNR shapes and zig-zag shaped (ZGNR) $C_{46}H_{18}$ isomers [6, 7]. It was concluded that the HOMO-LUMO gap varies with the

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shapes and sizes of semiconducting ZGNRs. There have been reports indicating the shape and size dependence due to the edge states and quantum confinement effects has been found to have effect on the optical, electrical and magnetic properties of graphene nano-ribbons [8-13].

There have been significant research interests on the optical properties of graphene [14-17] owing to their wide applications in photonics and optoelectronics ranging from solar cells and light-emitting devices to touch screens, photo-detectors and ultrafast lasers. Recently first-principles calculations have identified enhanced excitonic effects on optical spectra of pure graphene [18] followed by subsequent experimental evidences [19, 20]. However, most of the studies have usually involved doped Graphene by impurities, defects and substrates etc. [21-25]. Role of graphene in dye sensitized solar cells (DSSCs) has ignited significant research interest. They were first used as a transparent electrode to replace Fluorine doped tin oxide (FTO) at the photoanode of DSSC [26] and have since been used, for example, with the purpose of harvesting light [27]. Kim et al. reported the highest quantum efficiency of DSSC when 1.0 wt % of graphene was used as a working electrode with TiO_2 [28].

In the present study, we intend to study the optical absorption of graphene nano-ribbons using Time dependent density functional theory (TDDFT). For this purpose, we have designed GNRs in two sets: a) Different shapes of squares, rectangles and triangles (2 each), ranging from 48-77 atoms and b) Six isomers of $C_{46}H_{18}$ GNR. Hydrogen atoms are used with the GNRs to terminate the unsaturated carbon bonds. UV-Visible absorption spectra will be determined and HOMO-LUMO gaps, oscillator strengths and dominant orbital transitions will be computed and analyzed.

2. Methodology

In the present study, time dependent density functional theory (TDDFT) calculations are performed on two sets of Graphene nano-ribbons: a) with different shapes (naming convention is “SHAPE*n*”, where n = total number of atoms) and b) Six isomers of $C_{46}H_{18}$ GNR (naming convention is “ISO*n*”, where $n = n^{th}$ isomer (1-6)) All calculations have been performed with the Firefly version 8.1.0, build number 8800 program code [29]. Single point TDDFT calculations were performed on the ground state optimized geometries of all the GNRs invariably taken from the density functional theory calculations performed by our group [6, 7]. The Pople's N-31G split valence basis set 6-31G was used for optimizing the ground state structures. The optimized structures were obtained by first relaxing the structures using the steepest descent algorithm in Avogadro package [30]. It was followed by a more accurate calculation carried out using Becke’s three parameter functional with the Lee-Yang-Parr correlation functional (B3LYP) level of theory [31, 32]. The optimized geometries were confirmed as minima on the potential energy surface (PES) by evaluating the hessian and checking for the presence of all real frequencies.

Later, the electronic transitions between occupied and unoccupied states were calculated at Restricted Hartree Fock (RHF) and TDDFT/B3LYP level of theory using two basis sets 6-31G and 6-31G (d), with 100 singlet excited states that result in the UV-Visible absorption spectra. Also no symmetry constraints were considered in TDDFT calculations. HOMO-LUMO gaps and the dominant molecular orbital transitions along with their oscillator strengths, excitation wavelengths will be calculated.

3. Results and Discussions

In the present study, hydrogen terminated GNRs are considered in two sets a) Six different shapes- Square48, Square70, Triangle53, Triangle68, Rectangle60 and Rectangle77; where the digits signify the number of atoms; and b) Six isomers of $C_{46}H_{18}$ GNR (ISO1-ISO6). **Table I** displays the molecular formula and total number of atoms of all the GNRs. The ground state optimized structures obtained from our recent works using density functional theory calculations [6, 7], can be seen in **Figures 1 and 2**.

TDDFT calculations were performed on both the sets of GNRs and the optical absorption spectra were analyzed as follows:

3.1 For the first set of six GNRs of various shapes and sizes

TDDFT calculations were performed for two basis sets 6-31G and 6-31G (d). **Table II** shows the HOMO-LUMO gap ($\Delta E_{H\text{-}L}$) obtained from the TDDDFT calculations. $\Delta E_{H\text{-}L}$ values were found to be in the range 0.91- 2.37eV for 6-31G basis set and 0.91- 2.33eV for 6-31G (d) basis set. Maximum percentage variation in the $\Delta E_{H\text{-}L}$ values was found to be 2.5% for Rectangle77 GNR and no variation in the ΔE_{H-L} value was found for the Triangle53 GNR. The ΔE_{H-L} values for 6-31G (d) basis set were found to be lower than that of 6-31G basis set ones. The lowest ΔE_{H-L} value was found for the Triangle53 GNR (0.91eV) which indicates the ease of optical absorption. On the other hand Square70 was found to have maximum ΔE_{H-L} value indicating more excitation energy is required for the optical absorption. Moreover the variation in ΔE_{H-L} indicates the differences in the optical absorption characteristics of all the GNRs.

Table III illustrates the computed excitation wavelengths, electronic transition configurations and oscillator strengths, for both the 6-31G and 6-31G (d) basis sets. It is clearly seen that the absorption spectra of all the GNRs lie within the UV, Visible and IR wavelength regions. **Fig. 3** displays the UV-visible spectra of all the GNRs with the y-axis showing the unnormalized absorbance, which would help us in pointing out the GNR promising the maximum optical absorption. There is a red shift in spectra obtained using 6-31G (d) basis set with wavelength shift ($\Delta\lambda_{max}$ = 18.1 nm) as compared to the spectra obtained using 6-31G basis set. And the oscillator strengths have been found to decrease consistently for 6-31G (d) basis sets (Δf_{max} = -0.15). Absorbance values have also found to decrease for these GNRs as compared to that with 6-31G basis set. We shall now discuss in details the dominant transitions occurring in the GNRs when 6-31G (d) basis set was used. The four most dominant orbital transitions for all these GNRs were found to be HOMO→LUMO, H-1→LUMO, H→L+1 and H→L+2, irrespective of their shapes and sizes. However the Square70 GNR preferred more contribution from H-2→L transition than H→L+2. **Fig. 4** displays the isodensity plots of four dominant transitions for these GNRs obtained using 6-31G (d) basis set. The isodensity plots of molecular orbitals were made using MaSK [33] for isosurface value= 0.01 a.u. It is known that the oscillator strength is directly proportional to the absorbed wavelength. Hence a higher oscillator strength is preferred if more optical absorption is needed which makes the corresponding GNR more viable candidate for the photosensitizer in dye sensitized solar cell (DSSC) applications. The solar spectrum predominantly consists of the UV-Vis-IR regions and studying the light absorption in accordance to it would be more meaningful. For Square48, the light absorption is more around 336 and 606 nm, which correspond to the ***f*** values 0.55 and 0.423. For Triangle53, Rectangle60, Triangle68, Square70 and Rectangle77, the light absorption is more around (408, 801) nm, (416.5, 491.5) nm, (325, 356 and 442) nm, (407, 430) nm and (439, 686) nm. Amongst all the GNRs, the highest oscillator strengths (>0.5) were found for the Rectangle shaped GNRs Rectangle60, Rectangle77 (***f*** = 0.826 and 1.512) at the absorption wavelengths 416.5 and 439.2nm. Next higher ***f*** values were obtained for Square48, Triangle53 and Square70 with ***f*** = 0.575, 0.691 and 0.75 at absorption wavelengths 335.9, 408.2 and 430.1nm. For all these GNRs, we attribute all the absorption peaks to the pi-pi* transitions. These peaks are accompanied by very high absorbance values of the order of 10,000. The peaks with lower absorbances seem to be due to the vibrational effects. Also the various shifts in the wavelengths of different GNRs could be due to the difference in the extent conjugation of pi bonds. Some groups have studied the absorption spectrum of graphene experimentally. Bhandari et al. [34] reported the UV-Visibe spectra peaks at 240nm which correspond to pi-pi* transitions of aromatic C-C bonds. Pan et al. and Zhang et. al [35, 36] reported strong absorption peaks around 320nm and 227nm in the UV-vis absorption spectrum of carbon nanoparticles/graphene quantum dots in aqueous solutions, which were attributed to the pi-pi*transitions. Sahu et al. [37] observed the similar peaks for pure graphene around 266nm.

3.2 For the second set of six isomers of $C_{46}H_{18}$ GNRs

TDDFT calculations were again performed on all the isomers for two basis sets 6-31G and 6-31G (d). **Table II** shows the HOMO-LUMO gap ($\Delta E_{H\text{-}L}$) obtained from the TDDFT calculations. $\Delta E_{H\text{-}L}$ values were found to be in the range 0.99- 2.60eV for 6-31G basis set and 0.96- 2.56eV for 6-31G (d) basis set. Maximum percentage variation in the $\Delta E_{H\text{-}L}$ values was found 3.0% for ISO1 GNR and minimum variation of 1.3% in the $\Delta E_{H\text{-}L}$ value was found for the ISO3. The $\Delta E_{H\text{-}L}$ values for 6-31G (d) basis set were found to be lower than that of 6-31G basis set ones. The lowest $\Delta E_{H\text{-}L}$ value was found for the ISO4 GNR (1.48eV) which indicates the ease with which it can undergo optical absorption. On the other hand maximum $\Delta E_{H\text{-}L}$ value was found for ISO2 indicating more excitation energy is required for the optical absorption.

Table IV illustrates the computed excitation wavelengths, electronic transition configurations and oscillator strengths, for all the isomers. Here again it is seen that the absorption spectra of all the isomeric GNRs again lie within the UV, Visible and IR regions. The **Fig. 5** displays the UV-visible spectra of all the isomeric GNRs. There is a red shift in wavelengths ($\Delta\lambda_{max}$ = 23.7 nm) obtained using 6-31G (d) basis set. And the oscillator strengths have been found to decrease consistently for 6-31G (d) basis sets (Δf_{max} = -0.09), except for ISO4 and ISO6 where an increase in ***f*** has been found. Absorbance values have also found to decrease for these GNRs as compared to that with 6-31G basis set. Now the dominant transitions occurring in the GNRs when 6-31G (d) basis set was used will be discussed. The three most dominant orbital transitions for all these GNRs were found to be HOMO→LUMO, H-1→LUMO and H→L+1. H-2→L and H→L+2 were the fourth dominant orbital transitions for (ISO1, ISO3, ISO5, ISO6) and (ISO2, ISO4). **Fig. 6** displays the isodensity plots of three dominant transitions for these GNRs obtained using 6-31G (d) basis set. These were made using MaSK [33] for isosurface value= 0.01 a.u.

It is seen that for ISO1, the light absorption is more around 305.3 and 401.6 nm, which correspond to the ***f*** values 1.683 and 0.612. For ISO2, ISO3, ISO4, ISO5 and ISO6, the light absorption is more around (345.4, 387.8) nm, (316.8, 359.1, 389.1) nm, 651.3nm, (398.7, 660.8) nm and 613nm, corresponding to ***f*** >0.30. High ***f*** **(**> 0.6) transitions found for these isomers are: ISO1 (305.3, 401.6) nm, ISO2 (387.8nm), ISO3 (389.1nm), ISO4 (651.3nm), ISO5 (660.8nm) and ISO6 (613nm). Isomers ISO4-6 seems to absorb more of visible light and could be potential candidates for use in DSSCs. For all these GNRs, we attribute all the absorption peaks to the pi-pi* transitions. pi-pi* transitions were found to be the dominant transitions in the optical absorption of graphene in solvents [34-37]. These peaks are accompanied by very high absorbance values of the order of 10,000. The peaks with lower absorbances seem to be due to the vibrational effects.

Interestingly a closer look at the **Figs (3, 5)** reveal that the absorbance values between 500-900nm of all the isomeric GNRs is nearly 50% higher than the first set GNRs. However the absorbance values of both the sets of GNRs remains almost similar within the range 300-500nm.

4. Conclusion

Optical properties were studied with the help of TDDFT calculations performed on the ground state optimized graphene nanoribbons (GNRs) in two forms: a) Graphene nano-ribbons (GNRs) of different geometries like square, rectangle and triangle containing 48, 53, 60, 68, 70 and 77 atoms, and b) Six isomers of $C_{46}H_{18}$ GNR. All the calculations were performed and compared for two basis sets 6-31G and 6-31G (d). Optical absorption of all the GNRs was found to lie in the UV-Visible-IR range (300-900nm). Absorption spectra were found to vary with the various shapes, sizes and isomeric forms of GNRs. When 6-31G (d) basis sets were used, maximum red shifts of 18.1nm and 23.7nm were found in the excitation wavelengths of first (shapes and sizes) and second sets of GNRs (isomers), with respect to the 6-31G basis set values. Oscillator strengths were also found to be smaller for all the GNRs for the former case.

The lowest HOMO-LUMO gaps (ΔE_{H-L}) were found for the Triangle53 (0.91eV) and ISO4 (1.48eV) GNRs in their categories. However Square70 and ISO2 GNRs were found to have highest ΔE_{H-L} values of 2.33 and 2.56eV, indicating the higher excitation energy needed for the optical absorption. The four most dominant orbital transitions for the first set of GNRs were found to be HOMO→LUMO, H-1→LUMO, H→L+1 and H→L+2, irrespective of their shapes and sizes. The three most dominant orbital transitions for next set of $C_{46}H_{18}$ isomeric GNRs were found to be HOMO→LUMO, H-1→LUMO and H→L+1. The highest oscillator strengths (>0.5) were found for the Rectangle shaped GNRs Rectangle60, Rectangle77 (***f*** = 0.826 and 1.512) at the absorption wavelengths 416.5 and 439.2nm. In the second set of GNRs, isomers ISO4, ISO5 and ISO6 with high ***f*** (>0.6) were found to absorb more light in the visible region. Higher optical absorption has been obtained for the isomeric GNRs in the range 500-900nm. The pi→pi* transitions were found to be the dominant transitions in the optical absorption of both the sets of GNRs.

We hope that these results can improve our understanding of the optical properties of graphene for future applications like photovoltaics or in DSSC applications, where visible-light absorption in the graphene layer is of primary concern.

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