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Electronic and optical properties of graphene adsorbed with methanol molecules: first-principles calculations

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Abstract. Properties of methanol molecules adsorbed on graphene are studied theoretically and various adsorption geometrical structures, density of states as well as the optical properties are obtained by means of first-principles calculations. Electronic characteristics and optical properties of graphene are sensitive to the molecule adsorptions. It is found that band gap appears when the methanol molecules are adsorbed. The dielectric function, refractive index, extinction coefficient, absorption coefficient and the reflectivity are changed. In the case of one methanol molecule adsorption, the peaks for the imaginary of the dielectric function and the adsorption coefficient shift to the high energy region, and new peaks appear in the visible range. The maximum value of extinction coefficient rises, and new peaks appear in the visible range when two methanol molecules are adsorbed.

1. Introduction

Graphene is found to be a magical two-dimensional material with a variety of remarkable functions since it was stripped from graphite in 2004 [1-3]. Graphene has set off a research boom in electronics, optics and biomedicine, et al [4-5]. Graphene is a single layer honeycomb lattice plane which is formed by sp^2 hybrid of carbon atoms, and it has zero band gap, the electronic energy band structure near the Fermi level shows linear dispersion relation [6-8]. Graphene has large specific surface area, outstanding thermal conductivity and perfect quantum tunnelling effect, et al. The rich and novel physical characteristics make graphene a shining star in nanoelectronics and optoelectronic devices [9-10]. What we should know is that some devices involving graphene require non-zero band gaps, that is, the nature of semiconductors. Zero band gap structure limits the development of graphene in the field of nanoelectronics and optoelectronic devices. Only to open the band gap of graphene can it be applied to various aspects. In recent years, the electronic and optical structures of graphene and their derivatives have been studied and significant modifications of graphene were noted [11-14]. There are various methods to adjust the band structure and open the band gap and modify the optical properties of graphene. One method is doping atoms such as N, B and N-B pairs with the condition that the atomic radii of N and B are close to C atoms, and in addition, after doping with these atoms, the electronic and optical properties of graphene will be significantly optimized [14-16]. By contrast, doped atoms usually have different electronic configurations than C atoms, and charge transfer occurs after atomic doping. Another method is adsorbing atoms or molecules, such as CO, NO, NO_2 and thiophene molecule et al. Since graphene has only one atomic layer thickness and is easily exposed to the outside world, the atoms and molecules adsorbed on the surface of graphene can change the structure of graphene by perturbing the π-electron network [17-20]. The topological disorders like ripples and Stone-Wales defects play an important role in optimizing the properties of graphene as well [21-22]. The interest in the study of graphene in photonic and optoelectronics is rising which is shown by its various applications, such as solar cells, lighting-emitting and touch screen et al., and optical properties of graphene have been extensively studied both theoretically and experimentally.

2. Theoretical methods

All our theoretical calculations are done through VASP (Vienna ab-initio Simulation Package) [23-24], PAW (projector-augmented-wave) pseudopotential is used to describe the interaction between ions and electrons [25-26], the GGA (generalized gradient approximation) in the form of PBE (Perdew-Burke-Ernzerh) is used to describe the exchange correlation energy function [27]. The cut-off energy is 400 eV in the process of the structural optimizations and calculations. A 7×7×1 Monkhorst-Pack grid is chosen when calculate the integral in Brillouin zone, and the energy convergence is set to less than 10^{-4}eV. In optimization calculation, the convergence accuracy of nuclear motion is less than 0.2 eV/Å. A 4×4×1 supercell (32 atoms) of pristine graphene is chosen. To avoid interlayer interference, the thickness of the vacuum layer is set to 15 Å. In order to investigate the relationship between the properties of graphene and the adsorption distance of methanol, the methanol molecules are fixed in the Z axis.

Only the interband transition is considered when we calculate the optical properties, so the dielectric function

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may be inaccurate in the Drude region (low frequencies) [27]. The optical properties are general evaluated by the dielectric function which is the sum of real and imaginary parts, $\varepsilon(w) = \varepsilon_1(w) + i\varepsilon_2(w)$. The imaginary part is calculated by the summation of the empty band states using the following equation [29],

$$\varepsilon_2^{\alpha\beta}(w) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\epsilon_{ck} - \epsilon_{vk} - w) \times < u_{ck} + e_{\alpha q} | u_{vk} >< u_{ck} + e_{\beta q} | u_{vk} >^* \quad (1)$$

where the Ωrepresents the volume, v and c is the valence and conduction bands respectively, α and β indicate the Cartesian components, e_α and e_β are the vacuum dielectric constant, ϵ_{ck} and ϵ_{vk} refer to the energy of conduction and valence band respectively , u_{ck} is the cell periodic part of the orbitals at the k-point k. The real part of dielectric tensor is calculated by the Kramers-Kronig relation,

$$\varepsilon_1^{\alpha\beta}(w) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2^{\alpha\beta}(w')w'}{w'^2 - w^2 + i\eta} dw' , \quad (2)$$

where P denotes the principle value. According to the values of real and imaginary parts of dielectric function, the optical properties such as refractive index $n(w)$, the extinction coefficient $k(w)$, the absorption coefficient $\alpha(w)$ and the reflectivity $R(w)$ can be given by [30-31],

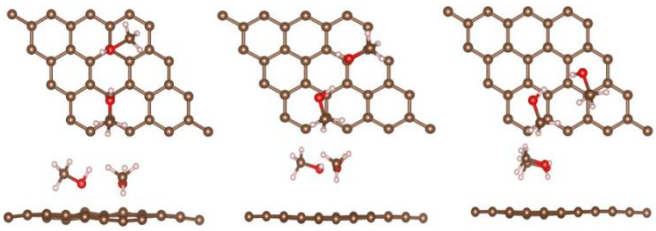
$$\alpha(w) = \frac{\sqrt{2}w}{c} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} - \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (3)$$

$$n(w) = \frac{1}{\sqrt{2}} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} + \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (4)$$

$$R(w) = \left| \frac{\sqrt{\varepsilon_1(w) + i\varepsilon_2(w)} - 1}{\sqrt{\varepsilon_1(w) + i\varepsilon_2(w)} + 1} \right|^2 , \quad (5)$$

$$k(w) = \frac{1}{\sqrt{2}} \left\{ \left[\varepsilon_1^2(w) + \varepsilon_2^2(w)\right]^{\frac{1}{2}} - \varepsilon_1(w) \right\}^{\frac{1}{2}} , \quad (6)$$

3. Results and discussion

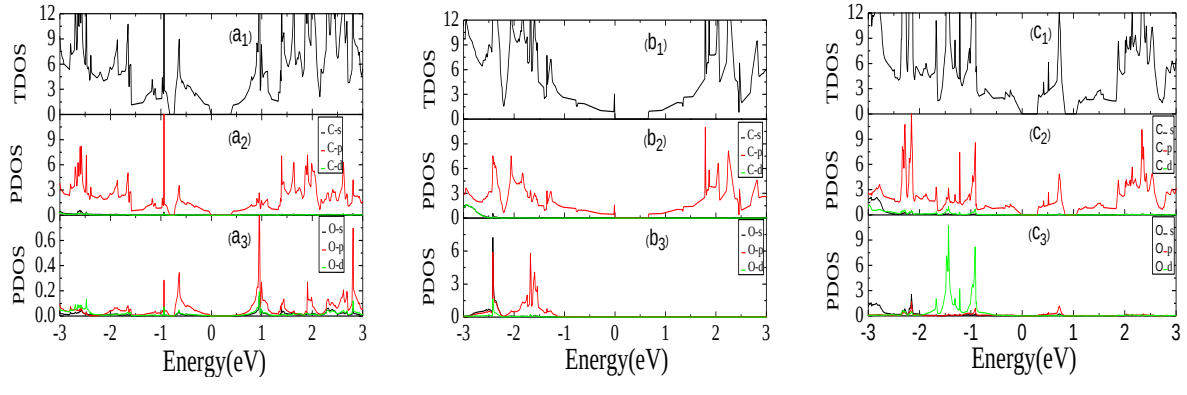


(a) (b) (c)

Figure 3.1: Top and side views of the relaxed structures with two methanol molecules adsorbed on graphene surface on (a) opposite position, (b) meta position, and (c) adjacent position. Red, white and brown spheres represent O, H and C atoms, respectively.

Different adsorption configurations are considered in our calculations. Firstly, one methanol molecule is adsorbed on the graphene surface with the oxygen atom on the top site. Secondly, two methanol molecules are adsorbed on the graphene surface, which contains three configurations, i.e., the two methanol molecules are in opposite, adjacent, and meta positions, respectively. All these two methanol molecules are adsorbed with oxygen atoms on the top site. Fig. 3.1 shows the relaxed configurations when the adsorption distance is 1.6 Å with two methanol molecules adsorptions.

It is well known that pure graphene has a zero band gap. After one methanol molecule is adsorbed on the graphene surface, the electronic properties have been modified, and a band gap appears. In our present work, we calculate the electronic properties of two methanol molecules absorbed on the surface of graphene, which is shown in the Fig. 3.2. Fig. 3.2(a) represents the total electronic density of states (TDOS) and the partial DOS (PDOS) of the two methanol molecules which are in the opposite position, Fig. 3.2(b) and Fig. 3.2(c) represent the TDOS and PDOS of two methanol molecules which are in adjacent position and meta position, respectively. From the TDOS, we can obtain that the electronic properties of graphene are changed significantly. Band gap opens, the value of the band gap in these three cases are 0.40 eV, 0.65 eV and 0.28 eV, respectively. It is thus evident from the figure that the band gap is sensitive to the adsorption sites.



(a) (b) (c)

Figure 3.2: TDOS and PDOS of two methanol molecules adsorbed in graphene in (a) opposite position, (b) meta position, and (c) adjacent position, respectively.