

Energetics and Electronic Structures of Alkanes Adsorbed on Carbon Nanotubes

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1. Introduction

Interactions of organic molecules such as bio-materials with carbon nanotubes (CNTs), graphene, and carbon nanohorns have recently been the subject of a great deal of research with the goal of molecular applications of these nano-scale or low-dimensional carbon allotropes. One of the key interactions is CH/ π interaction, which is an attractive interaction between a C-H bond in the organic molecules and π bonds in such carbon allotropes. Indeed, this has attracted much recent interest [1], especially for multiple CH/ π interactions that can occur in the interaction of hydrocarbon chains and the π face of the carbon allotropes [2]. Because the hydrocarbon chain is a backbone for bio-molecules such as amino acid residues and phospholipids, clarification of its interaction to CNTs becomes a firm bridgehead toward systematic understanding of the interaction between organic molecules and the carbon allotropes. In this study, we thus investigate the energetics and electronic structure of alkane adsorbed on CNT on the basis of density functional theory (DFT).

2. Methods

We consider eight representative types of C_nH_{2n+2} ($n=1\dots 8$) with a linear conformation. These alkane molecules were adsorbed on (17, 0) zigzag carbon nanotube (Fig. 1). To simulate the adsorption of one alkane molecule to the CNT, we used a periodic boundary condition, where the lattice parameter c is set to be 17.04 Å along the tube direction; for the lateral direction, we used a square lattice of 19.73 and 30.40 Å in which the system is separated by more than 6 Å from its periodically repeated images to avoid artificial effects.

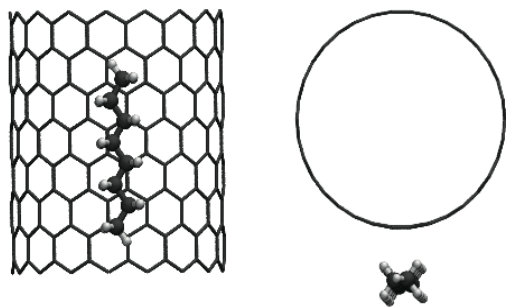


Fig. 1 Side and top views of the structural model of alkanes adsorbed on carbon nanotube. The figure shows C_8H_{18} as an example.

All calculations were performed using DFT. We used the local-density approximation (LDA) to treat the exchange-correlation interactions for electrons. Electron-ion interactions were described using Troullier-Martins norm-conserving pseudopotentials. Valence wave functions were expanded in terms of a plane wave basis set with an energy cutoff of 70 Ry. $1\times 1\times 2$ k -points in one-dimensional Brillouin zone (BZ) were sampled for the BZ integration. During the geometry optimizations, all atoms were relaxed until the residual forces were less than 0.05 eV/Å. The calculations were performed using the CPMD code.

3. Results and Discussion

Figure 2 shows binding energy $\Delta E(n)$ of alkane to CNT as a function of the number of C atoms ($n=1,\dots,8$), defined by the following reaction:



In this reaction, total energies for each constituent are calculated on the fully relaxed geometries in vacuum condition. We found in Fig. 2 that all of the alkanes are bound to the CNT. The distances between the C atoms of the alkane and the CNT wall are in the range of 3.3–3.7 Å (Fig. 3). Very interestingly, the energetics clearly shows that the binding energy is linearly scaled by the length of the alkane molecule. The linear fitting equation is $\Delta E(n) = -0.048n - 0.038$, indicating that the binding energy of a one unit CH_2 is about 50 meV. This also suggests that multiple CH/ π interactions occur in a cooperative manner between alkanes and CNTs. Therefore, when the length of the alkane increases, the molecule is very strongly bound to the CNT.

We next investigate the electronic structures of the alkane-CNT hybrid systems. Figure 4 shows the electronic energy bands of C_8H_{18} adsorbed on CNT as a typical example. The energy band structures of isolated molecule, and pristine CNT are also shown in the same figure. All of the alkane-CNT hybrid systems are semiconductors with a direct gap originating from the E_{11} gap of the semiconducting CNT. It was found that the energy bands near the Fermi level originate primarily from those of the pristine CNT. The energy bands associated with alkane levels do not appear near the energy gap but emerge as occupied and unoccupied states below and above the fundamental gap.

A detailed analysis of the electronic structure can clarify the interesting alterations to the electronic structures of CNT. Figure 5 shows the modulation of the eigenvalues of

the highest occupied (HO) and the lowest unoccupied (LU) states at the Γ point, and the energy gap in the CNT when alkanes of various lengths bound to it. This modulation is defined as

$$\Delta E_{\text{HO/LU/gap}} = E_{\text{HO/LU/gap}}^{\text{Alkane-CNT}} - E_{\text{HO/LU/gap}}^{\text{CNT}}$$

It was found in Fig. 5 that the HO level of a CNT is modulated by a few tens of meV as the alkane length increases, while the LU level is changed by a few meV, thus leading to gap reduction. Interestingly, this gap modulation exhibits similar profile to that of the eigenvalue modulation for the lowest occupied state (Fig. 5), indicating that the self-consistent local potential is decreased in CNT due to the adsorption of alkanes. This is ascribed mainly by the existence of polarized C-H bonds near the nanotube wall, where effective attractive potentials are generated by the positively charged H atoms. These results indicate that the identification of alkane length may be possible by monitoring the energy gap of the CNT.

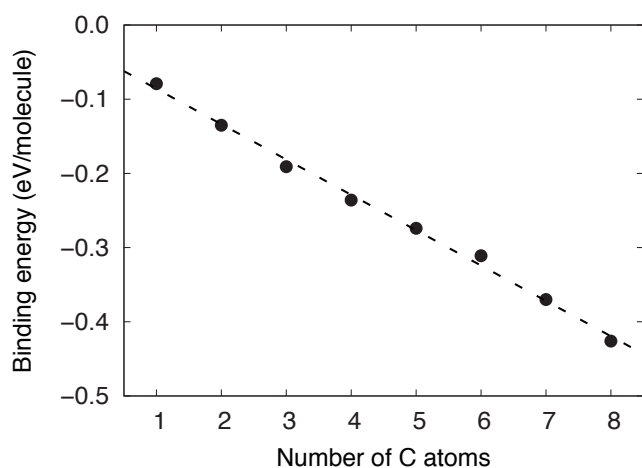


Fig. 2 Adsorption energy as a function of the number of C atoms in alkanes.

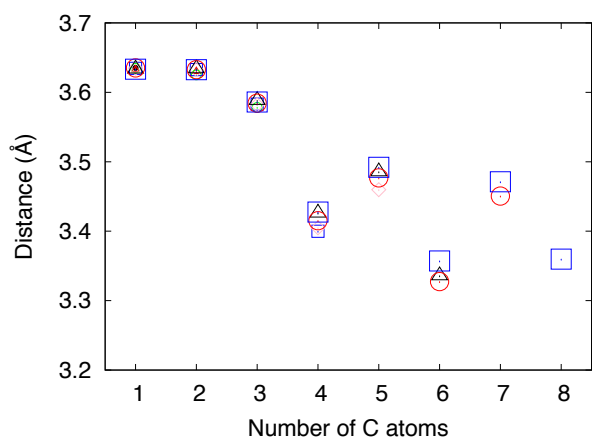


Fig. 3 Distances between the C atoms of the alkane and the CNT wall in optimized geometries of the alkane-CNT hybrid systems as a function of the alkane length.

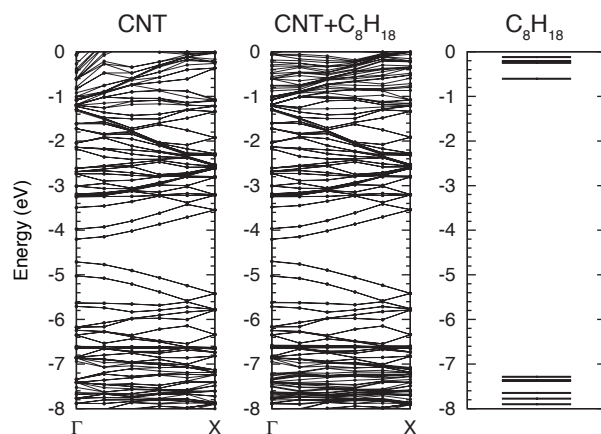


Fig. 4 Energy band structures of isolated CNT, the alkane-CNT hybrid systems, and isolated alkane. Energies are measured from the vacuum levels, which were evaluated from the values of the self-consistent local potential at the edge of the unit cell.

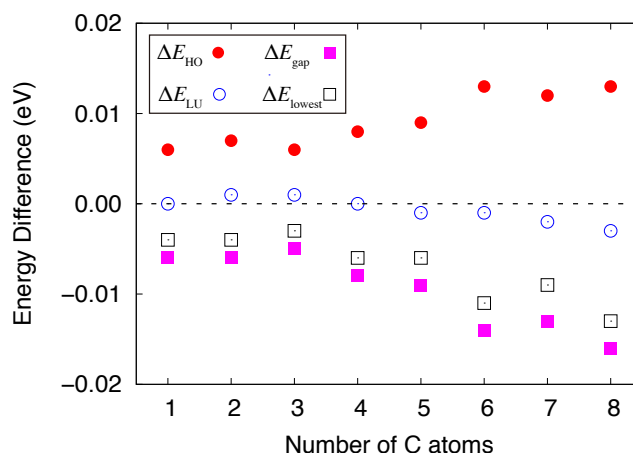


Fig. 5 Difference in the eigenvalues at the Γ point of the lowest occupied, highest occupied, and lowest unoccupied Kohn-Sham states, and in the energy gap for the alkane-CNT hybrid systems, plotted versus the alkane length.

4. Conclusions

We have investigated the energetics and electronic structures of alkanes adsorbed on carbon nanotubes using total-energy electronic structure calculations based on density functional theory. Our calculations showed that the binding energy of the alkane adsorption to the CNT is linearly scaled by the length of the alkane molecule. The electronic structure of the alkane-CNT hybrid systems is qualitatively similar to a simple sum of those of an isolated alkane molecule and a pristine CNT. However, detailed analysis of the electronic structure of the hybrid systems reveals that the adsorption of alkane has effects on the electronic structure of CNT.

References

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- [2] J. Ran and M. W. Wong, J. Phys. Chem. A **110** (2006) 9702.