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Stability of CH_3 molecules trapped on hydrogenated sites of graphene

G.R. Berdiyorov [a,1], M.V. Milošević [b], F.M. Peeters [b,*], Adri C.T. van Duin [c]

[a] Department of Physics, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Saudi Arabia
[b] Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
[c] Department of Mechanical and Nuclear Engineering, Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

We study the effect of a hydrogen atom on the thermal stability of a trapped CH_3 molecule on graphene using ReaxFF molecular dynamics simulations. Due to the hydrogen-molecule interaction, enhanced pinning of the CH_3 molecule is observed when it is positioned adjacent to the graphene site with the hydrogen atom. We discuss the formation process of such a stable configuration, which originates from different adhesion and migration energies of the hydrogen atom and the CH_3 molecule. We also studied the effect of the CH_3–H configuration on the electronic transport properties of graphene nanoribbons using first principles density-functional calculations. We found that the formation of the CH_3–H structure results in extra features in the transmission spectrum due to the formation of strongly localized states, which are absent when the CH_3 molecule is trapped on pristine graphene. Our findings will be useful in exploiting gas sensing properties of graphene, especially for selective detection of individual molecules.

1. Introduction

Graphene has attracted enormous interest in recent years due to its unique physical, chemical and mechanical properties [1–4]. It has a large potential for applications in the field of photonics and electronics [5,6]. Graphene's pristine properties can be modified by decorating it with molecules or adsorbed atoms, which offers a way to control the electronic structure, conductivity and other measurable properties of graphene [7–13]. Tuning the electronic properties of graphene by means of such functionalization is considered as one of the grand challenges for the development of graphene-based nanoelectronics and requires a complete understanding of the interaction between the graphene surface and the adsorbed molecules [14–17].

Although most of the studied elements and molecules have small adhesion and migration energies on graphene, which makes their attachment unstable at room temperature, a recent transmission electron microscopy study has revealed a remarkable enhanced stability of small molecules on suspended graphene [18]. It was shown that the interaction between the molecules and hydrogen atoms leads to a mutual trapping on neighboring graphene sites by forming energetically favorable configurations. Enhanced stability of such “symbiotic” configurations has been confirmed by density-functional theory (DFT) calculations [18]. In this work we implement molecular dynamics (MD) simulations to study the thermal stability and formation process of those structures. We show that once attached, the molecules migrate on graphene and find a stable position at those graphene sites with trapped hydrogen. The resulting configuration is energetically more favorable and allows one to detect the attached molecule experimentally even at room temperature [18].

Exceptionally high surface-to-volume ratio, high electrical conductivity (i.e., massless Dirac fermion character to charge carriers), relatively low contact resistance, [19], low thermal and $1/f$ noise, [13], possibility of tuning the conductivity by the gate make graphene a promising material for gas sensing applications (see, Ref. [20] for review). However, the main drawback of the graphene-based gas sensors is their low selectivity, which requires functionalization of the graphene surface with agents specific to each gas molecule or the use of other properties of graphene, such as low-frequency electronic noise, [21], as an additional gas sensing parameter. Tuning the electronic properties of graphene by means of such functionalization is also considered as one of the grand challenges for the development of graphene-based nanoelectronics and requires a complete understanding of the interaction between the graphene surface and the adsorbed molecules [7–17].

As was shown in recent experiments, supported by density-functional theory, small admolecules can form different stable configurations on the graphene surface due to the interaction with ever present hydrogen atoms [18]. Therefore, one should take into

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* Corresponding author. Tel.: +32 32653664; fax: +32 32653542.
E-mail address: francois.peeters@uantwerpen.be (F.M. Peeters).
[1] Present address: Qatar Environment and Energy Research Institute, Doha, Qatar.

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account the formation of such thermally stable configurations when exploiting the gas sensing properties of graphene, especially in the selective detection of individual molecules. Here, using DFT and quantum transport calculations based on the nonequilibrium Green's function formalism, we study the effect of the CH_3–H configuration on the transport properties of a graphene nanoribbon. Prominent changes in the electron transmission spectrum of the system are found due to the formation of localized states near such molecule-hydrogen complexes, which are absent when they are trapped at carbon sites that are apart from each other. Since the resistivity is one of the key parameters for gas sensing applications, [20], our findings will be useful in understanding the properties of graphene-based sensors.

2. Computational method

MD simulations were performed using the reactive force-field ReaxFF, which is a general bond-order dependent potential that provides an accurate description of bond breaking and bond formation during chemical reactions [22]. The connectivity in the entire system is recalculated in every iteration, enabling dissociation and formation of chemical bonds during the simulations. Non-bounded interactions (van der Waals and Coulomb) are calculated between all atom pairs, irrespective of connectivity, with a short range shielding term [22]. Since ReaxFF parameters are derived from quantum chemical calculations, such force field gives energies, transition states, reaction pathways and reactivity trends in agreement with quantum mechanical calculations and experiments [23–25].

As a representative sample, we consider graphene (a supercell containing 200 atoms) with a single hydrogen atom and a methyl (CH_3) molecule attached (see Fig. 1). We implement periodic boundary conditions along the graphene basal plane to avoid edge effects [26]. Studied systems were first energy-optimized using the conjugate gradient method, the results of which are shown in Fig. 1. The temperature of the equilibrated system was then ramped up to 2500 K at a rate of 20 K/ps using an isothermal isobaric (NPT) ensemble with a Berendsen thermostat for temperature control. The damping constants for temperature and pressure were 0.25 fs and 1 ps, respectively. When the desired temperature is reached, constant temperature MD simulations were conducted using the NPT ensemble for 500 ps with temperature and pressure damping of 100 fs and 5 ps, respectively. The time step was 0.25 fs in all simulations. For a given temperature we conducted a statistical analysis and the results presented in this manuscript are averaged over an ensemble of 10 different initial distributions of velocities of the atoms. Note that ReaxFF simulations were conducted at higher temperatures to allow chemical reactions to occur within a reasonable time scale (in the picoseconds range) with the expectation of exhibiting similar reaction processes as in a real experiment. Therefore, elevated temperature has to be invoked for a quantitative analysis of the reaction kinetics.

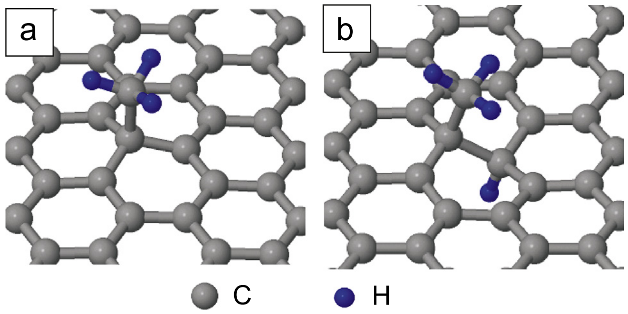

Fig. 1. Equilibrium structure of a CH_3 molecule trapped on graphene without (a) and with (b) a hydrogen atom bound to the adjacent carbon atom.

3. Effect of a hydrogen atom on the thermal stability of CH_3 molecule on graphene

Our main results are presented in Fig. 2, where we plot the time necessary for the migration (solid black dots) and desorption (open red dots) of the CH_3 molecule from the graphene surface as a function of temperature. The migration/desorption time is calculated as the time the migration/desorption process first occurs. For the considered maximal simulation time ($t_{max} = 0.5$ ns) the methyl molecule is stable on graphene up to 1300 K in the absence of the H atom [see Fig. 2(a)]. With increasing temperature, the CH_3 molecule starts to migrate on the surface of graphene, while remaining trapped for longer time [compare filled and open dots in Fig. 2(a)]. This indicates that the migration barrier for the methyl molecule is smaller than the desorption barrier. However, we observed only short-range diffusion of the molecule: in our 0.5-ns-long simulations the maximal net displacement of the molecule was less than 10 graphene sites [see Fig. 3(a)]. There is a noticeable time interval Δt between the start of migration and the final desorption of the CH_3 molecule, which vanishes at higher temperatures. Both migration and desorption times decreases dramatically (with a sharp drop at $T = 1700$ K) with further increasing temperature.

The situation changes drastically in the presence of a hydrogen atom at the neighboring site to the methyl molecule at the opposite side of the graphene plane [Fig. 2(b)]. Such CH_3–H configuration is stable up to $T = 1700$ K, where no migration or desorption is observed within 0.5 ns. We would like to mention that the migration/desorption of the molecule can occur at lower

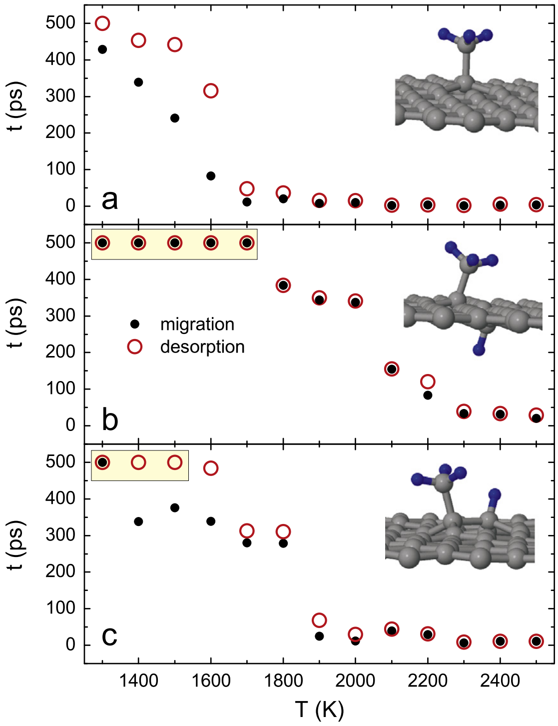

Fig. 2. Migration (filled dots) and desorption (open dots) time of a CH_3 molecule on graphene as a function of temperature, without (a) and with (b,c) a hydrogen atom attached to an adjacent graphene site. Insets show the atomistic configurations. The maximal simulation time was 500 ps, therefore yellow shaded points shown at 500 ps indicate that no migration and/or desorption of the molecule was observed in the simulations for $t \leq 500$ ps. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)