First Principles Study of Gas Adsorption Dynamics on Pristine and Defected Graphene

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We present the results of *ab initio* calculations of gas adsorption processes on graphene. Static density functional theory framework is used to obtain adsorption energies of several species on a Stone–Wales defected graphene monolayer. The Van der Waals interaction is taken into account by a semi-empirical correction. Sites closer to the defect are found to induce stronger adsorption compared to sites further away, where the graphene crystal structure is intact. The Car–Parrinello *ab initio* molecular dynamics simulations are performed at high temperatures. CH_3 is found to be stably physisorbed or chemisorbed at 300 K.

1. Introduction

Covalent and non-covalent functionalization of graphene has been of long-standing interest because of its potential applications. Mechanical and electronic properties of the material can be finely tuned with varying adsorbate types and concentrations. As part of ongoing research, studies of the processes that lead to functionalization of graphene are performed. Evaluation of adsorption energies from first principles (*ab initio*) is combined with the Car–Parrinello molecular dynamics (CPMD) simulations to give a clearer view of how adsorption occurs.

The aim of this work is to study the adsorption processes of two constituents of methane (CH_4) gas– hydrogen atoms (H) and methane radicals (CH_3). Because they possess unpaired electrons, they are expected to be highly reactive and form covalent bonds with ease. It is unclear, however, whether the magnitude of the chemisorption (adsorption by covalent bonding) effects are strong enough to dominate physisorption (van der Waals bonding) of the species.

2. Calculation methods

To carry out the calculations, density functional theory (DFT) is used as implemented in the CPMD planewave/pseudopotential code [1]. The electron exchange-correlation (x-c) interaction is implemented as the generalized gradient approximation (GGA) with correct asymptotic behavior, as developed by Becke [2], Lee, Yang and Parr (BLYP) [3]. In some cases, supplementary calculations have been performed with the use of the basic GGA functional (GGA/PW91) [4], revised Perdew–Burke–Ernzerhof functional (revPBE) [5], as well as in the local density approximation (LDA) approach [6]. None of these functionals correctly describe dispersive forces. In this work, a practical approach has been taken, which is to introduce a pairwise semi-empirical dispersion correction to the Kohn–Sham DFT energy (E^{K-S}):

$$E^{DFT-D2} = E^{K-S} + E_{disp}^{(2)}, \qquad (1)$$

$$E_{disp}^{(2)} = -s_6 \sum_{A<B} \frac{C_6^{AB}}{R_{AB}^6} f_{damp}(R_{AB}, R_{0AB}), \qquad (2)$$

which defines the DFT-D2 correction according to Grimme [7]. A and B are labels of atoms. R_{AB} is the interatomic distance. C_6^{AB} parameters are determined for each atomic pair in time-dependent DFT calculations. f_{damp} is the damping function introduced to cut off unnecessary short-range interactions. It depends parametrically on R_{0AB} which is the sum of van der Waals radii of elements A and B. C_6 and R_0 values are taken from Grimme's work [7] and s_6 is fitted in benchmark calculations (it depends slightly on the density functional used). The DFT-D2 correction scheme supports a small number of functionals, among which are the BLYP and revPBE functionals used in this work.

Two general types of calculations have been performed: static calculations of the total energy of the system and CPMD simulations of species adsorbed on the graphene surface in microcanonical (NVE) and canonical (NVT) ensembles with Nosé-Hoover thermostats [8, 9].

3. Results and discussion

3.1. Chemisorption energies

In order to evaluate the influence of crystallographic defects on adsorption, 4×4 graphene supercells with Stone–Wales (SW) defects were studied. The defect is described as the rotation of two atoms by 90 degrees around the middle point of the bond. It results in a geometrical transformation of four neighboring hexagons into two heptagons and two pentagons. Hence, it is sometimes referred to as the 5-7-7-5 defect. Different species were placed above three different atoms around the defect — above one of the atoms that has been rotated, his nearest neighbor, and his third nearest neighbor. The first atom is a part of two heptagonal graphene rings and one pentagonal ring, the second is a part of one heptagonal, one pentagonal and one hexagonal ring, and the third is a part of three hexagonal rings. Because ideal graphene has

all its atoms in hexagonal rings, the last atom will be referred to as the *bulk* site, while the other two will be called the *defect core* site and the *defect neighbor* site. The inset in Fig. 1 depicts the atomic arrangement obtained from pristine graphene with a Stone–Wales transformation and subsequent geometry optimization. In the relaxed structure, the defect core bond is slightly compressed.
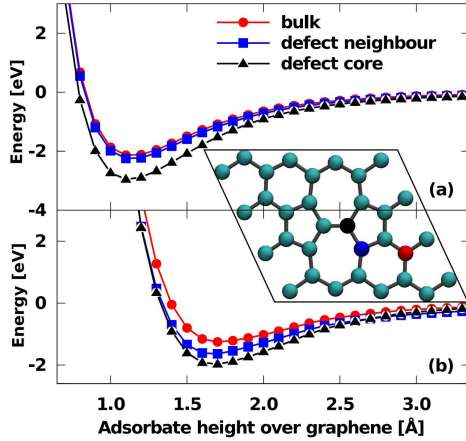

Fig. 1. Chemisorption curves of (a) H, (b) CH_3, over Stone–Wales-defected graphene, BLYP+vdW calculation. Inset: Molecular scheme of the adsorption sites on 4×4 graphene supercell with a Stone–Wales defect.

Provided that the technical parameters of the calculations are kept constant, the adsorption energy of a molecule/species on the graphene surface can be calculated as

$$E_{ads} = E_{surf.+species} - (E_{surf.} + E_{species}), \qquad (3)$$

where $E_{surf.}$ and $E_{species}$ are the energies of the isolated surface and isolated species, respectively, and $E_{surf.+species}$ is the energy of the whole system.

Chemisorption requires the adsorbed molecule to possess at least one free electron. Two such species which are the constituents of methane gas have been studied. They are atomic hydrogen (H) and methane radical (CH_3). They were placed over the adsorption site with 0.6 to 7.5 Å separation. Energy optimization was then performed for distances in this range. The wide range of distances allowed the study of both covalent and van der Waals bonding. The graphene plane was deformed at the adsorption site. The in-plane carbon atom has been moved 0.35 Å out of plane due to $sp^2 \rightarrow sp^3$ rehybridization that occurs when the covalent bond is formed. The magnitude of the out-of-plane deformation due to chemisorption is consistent across all geometry optimization and molecular dynamics calculations.

Across all chemisorption calculations, the *defect core* site induces the strongest bonding, followed by the *defect neighbor* site and, finally, the *bulk* site. Hydrogen was more strongly adsorbed in every setup as well. The difference in CH_3 and H adsorption energies varies from 0.5 to 1.3 eV per molecule, depending on the adsorption site and x-c functional. Detailed results are given in Table I.

3.2. Physisorption energies and dynamics

TABLE I

Chemisorption energies (in eV per molecule) of H and CH_3 on different sites near the Stone–Wales defect.

Adsorbate@site	LDA	PW91	BLYP	revPBE	BLYP +vdW	revPBE +vdW
H@bulk	-2.452	-2.206	-2.027	-2.045	-2.134	-2.152
H@neighbor	-2.550	-2.310	-2.141	-2.148	-2.245	-2.252
H@core	-3.267	-3.032	-2.855	-2.873	-2.952	-2.970
CH$_3$@bulk	-1.833	-1.263	-0.852	-0.994	-1.282	-1.441
CH$_3$@neighbor	-2.036	-1.465	-1.066	-1.194	-1.620	-1.762
CH$_3$@core	-2.504	-1.945	-1.526	-1.683	-1.948	-2.121

Including the vdW correction in the calculations results in a systematic decrease of the total energy, as seen for the case of CO_2 over graphene presented in Fig. 2. A weak energy minimum appears around $2R_{0C}$, the double of van der Waals radius for carbon. Similar influence of the vdW energy is observed also for previously discussed cases of the adsorption of H and CH_3. To illustrate the effects of vdW energy on bonding of H and CH_3 to the graphene surface in a more detailed manner, we plot the vdW contribution to the adsorption energy of the systems in Fig. 3.
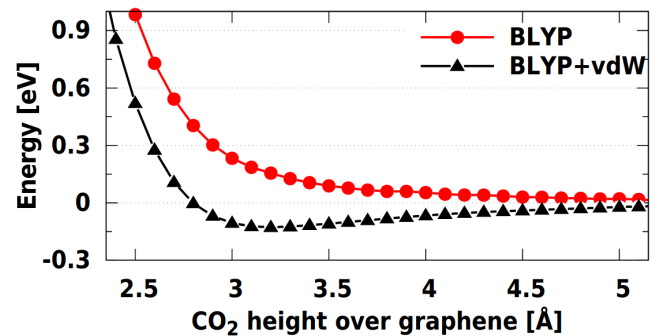

Fig. 2. Physisorption curves for CO_2 obtained in calculations with (BLYP+vdW) and without (BLYP) the vdW correction.

From Fig. 3, we can ascertain the type of dominant bonding of the two species. For all adsorption sites, vdW energy minima in case of H lie in the intermediate region between covalent and vdW bonding regimes. This result suggests that vdW interaction may stabilize chemisorption of H, but make the equilibrium distance larger. For CH_3, a deeper minimum is observed for the defect neighbour site. It lies close to the equilibrium bond length (boundary between shaded and unshaded regions of the graph). Therefore, it is likely that vdW interaction strengthens the C–C bond with minimal change in equilibrium distance. No minima appear on the other two energy curves, leading us to believe that vdW interaction does not stabilize chemical bonding at the other adsorption sites.

Dynamics of CH_3 on graphene have been simulated in CPMD simulations. The CH_3 molecule was placed
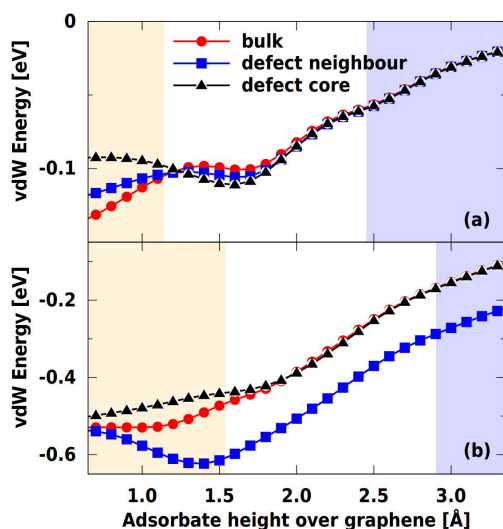
Fig. 3. Van der Waals energy curves of (a) H, (b) CH_3, over Stone–Wales-defected graphene. Values were obtained as the difference in energy in a vdW-corrected calculation and one without vdW correction. The boundaries of shaded regions correspond to the sum of covalent (from [10]) and vdW (from [7]) radii of relevant atoms.

4. Conclusions

Species with free electrons exhibit preference towards covalent bonding over van der Waals bonding. Looking at the results of static calculations, we can see that the energy landscape in the chemisorption regime is quite different from physisorption. The minima of physisorption energy are on the order of two magnitudes more shallow than for chemisorption. However, we observe a significant lowering of total energy when comparing the results of calculations with and without the DFT-D2 correction.

The results of molecular dynamics simulations reveal that while van der Waals-type bonding is a much weaker effect than covalent bonding, species with unpaired electrons can be stably bonded in the physisorption regime. If the initial distance from the graphene plane is suitable for physisorption, they remain in that state for long periods of time. In order to induce chemisorption, molecule has to possess an excess velocity in the direction of the surface.

at a given distance from the graphene plane, which exceeded the double of the van der Waals radius for carbon (as obtained from [7]). Upon starting a molecular dynamics simulation, the molecule relaxed to a physisorbed state. The movement in the direction perpendicular to graphene (z direction) has stopped almost entirely. The molecule exhibited translational motion in the xy plane. Throughout the simulation, the bending modes of the three hydrogen atoms were active and very pronounced.

The physisorption of CH_3 had been maintained for a period of 9 ps in a thermostatted simulation at 300 K. In particular, neither spontaneous chemisorption nor separation from the graphene surface has been observed. To obtain a simulation of the transition between physisorption and chemisorption regimes, adding artificial motion in the z direction was necessary. These results suggest that the physisorbed state is a stable configuration for CH_3 over graphene and that an energy barrier needs to be overcome for chemisorption to occur. This barrier is attributed to the rehybridization of an in-plane carbon atom and therefore it is not present in the energy curves depicted in Fig. 1.

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