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Density functional calculations of graphene-based humidity and carbon dioxide sensors: effect of silica and sapphire substrates

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ABSTRACT

We present dispersion-corrected density functional calculations of water and carbon dioxide molecules adsorption on graphene residing on silica and sapphire substrates. The equilibrium positions and bonding distances for the molecules are determined. Water is found to prefer the hollow site in the center of the graphene hexagon, whereas carbon dioxide prefers sites bridging carbon-carbon bonds as well as sites directly on top of carbon atoms. The energy differences between different sites are however minute – typically just a few tenths of a millielectronvolt. Overall, the molecule-graphene bonding distances are found to be in the range 3.1–3.3 Å. The carbon dioxide binding energy to graphene is found to be almost twice that of the water binding energy (around 0.17 eV compared to around 0.09 eV). The present results compare well with previous calculations, where available. Using charge density differences, we also qualitatively illustrate the effect of the different substrates and molecules on the electronic structure of the graphene sheet.

1. Introduction

It is well established that the resistance of graphene is sensitive to adsorbates at its surface [1], making it a viable option as gas sensor material. On the other hand, the same properties that make graphene an excellent molecular sensor material has negative consequences for the performance of graphene field effect transistors (GFETs) since adsorbates at the graphene surface leads to unwanted variations in device performance [2].

Graphene's high sensitivity to adsorbates has spurred a large activity focused on constructing and characterizing graphene based sensors [3,4]. For example, a graphene sensor for detecting humidity was recently constructed and characterized [5,6]. However, initial electronic structure computations of the charge doping of graphene by small molecules such as, e.g., water, carbon dioxide, and nitrogen dioxide found that the net charge transfer between the molecules and the graphene is typically very small, and insufficient to explain the apparent sensor properties of graphene [7–9]. It was later suggested that the substrate might play an important role in the observed resistance changes. Specifically, it was demonstrated that water molecules interact with silicon dioxide surface defects to produce an effective doping of the graphene sheet [10].

Silica and alumina are widely used dielectrics in electronic device construction. In graphene devices these materials often have direct contact with graphene, in roles such as substrate, passivation layer [11] or gate dielectric [4]. It is therefore of interest to analyse the bonding between graphene and these oxides in some detail. Furthermore, in the view of improving the understanding of how molecules interact with graphene in close contact with these dielectrics, a systematic computational study of the basic properties of the combined systems (substrate/graphene/molecule) is relevant.

Here, we use a dispersion corrected density functional to compute, at the quantum mechanical level, the equilibrium geometries and binding energies of water and carbon dioxide molecules adsorbed on

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top of graphene, residing on either silica or alumina. Specifically, we address α-quartz, cristobalite and sapphire as substrates. The employed dispersion corrected density functional enables us to compute equilibrium geometries and binding energies with some precision, which as far as we are aware is still lacking in the literature. We also illustrate qualitatively, with the help of charge density differences, how the electronic structure of the graphene sheet is affected by the combined interaction of the molecule and the substrate.

2. Computational details

Ground-state density functional theory (DFT) calculations in a repeated slab geometry were performed using pseudopotentials combined with a plane-wave basis set. Specifically, we used the Quantum Espresso (QE) [12] package as downloaded from [13] together with Hamann, Schluter, Chiang and Vanderbilt (HSCV) [14] norm-conserving pseudo-potentials (as downloaded from [15]) for all atoms. The kinetic energy cut-off for the wave function was set to 130 Ry. The Perdew, Burke and Ernzerhof (PBE) functional [16] for the exchange-correlation part of the density functional was used together with semi-empirical Grimme corrections [17,18] accounting for van der Waals corrections. All calculations were spin polarized. The Brillouin zone was sampled with a Monkhorst-Pack [19] k-point grid corresponding to a mesh density of 32×32×1 when folded onto the simple graphene unit cell. Furthermore, a Methfessel-Paxton (MP) smearing of 3.7 mRy was introduced.

2.1. Geometry considerations

The calculations were performed for three different systems, classified according to the substrate used. We will refer to those three systems as I, II and III. System I is based on a (111) plane cut in bulk silicon dioxide (SiO_2) of cristobalite type forming a slab with silicon atoms on the surface. System II is a cut in bulk SiO_2 of α-quartz type forming a slab with silicon atoms on the surface. Similarly, system III is a cut in bulk sapphire (Al_2O_3) with aluminum atoms on the surface of the slab. The input geometries for the substrates (SiO_2 [20], sapphire [21]) and pristine graphene [22] were extracted in the Crystallographic Information Framework (CIF) format from the materials project repositories [23,24], where they were already relaxed as bulk structures. The CIF files were in turn fetched by the materials project from the Inorganic Crystal Structure Database (ICSD) [25] library [26] and then relaxed. The CIF formats were converted to crystal file formats using the CIF2Cell code [27]. Supercell generation, cuts and vacuum setup were all performed using the CIF2CELL code as downloaded from [28]. In Table 1, we list the slab thicknesses and vacuum distances employed. The two slab surfaces were treated symmetrically.

A pristine graphene sheet was relaxed on top of each substrate. In all cases, a monolayer of graphene with a 2×2 supercell was used. In the addressed systems, there is a certain lateral lattice mismatch between the substrate and the graphene. In all calculations, we opted to use the equilibrium graphene lattice parameter (2.46 Å). For each system, two different adsorbate molecules (H_2O or CO_2) were addressed. The surface was populated with one molecule per 2×2 graphene supercell. The adsorbate molecules were relaxed on top of the already relaxed substrate-graphene system. For simplicity, a flat molecular configuration with respect to the surface was adopted. At ambient temperature, the molecules can be expected to rotate and vibrate, and therefore effectively average over many different orientational configurations. Different lateral positions of the molecules were addressed. Additional details, specific for each individual system, are given below.

Table 1
Slab thickness and vacuum distances used, expressed in ångström.

	System I	System II	System III
Slab thickness (Å)	9.7	10.8	12.6
Vacuum distance (Å)	23.6	21.2	15.8

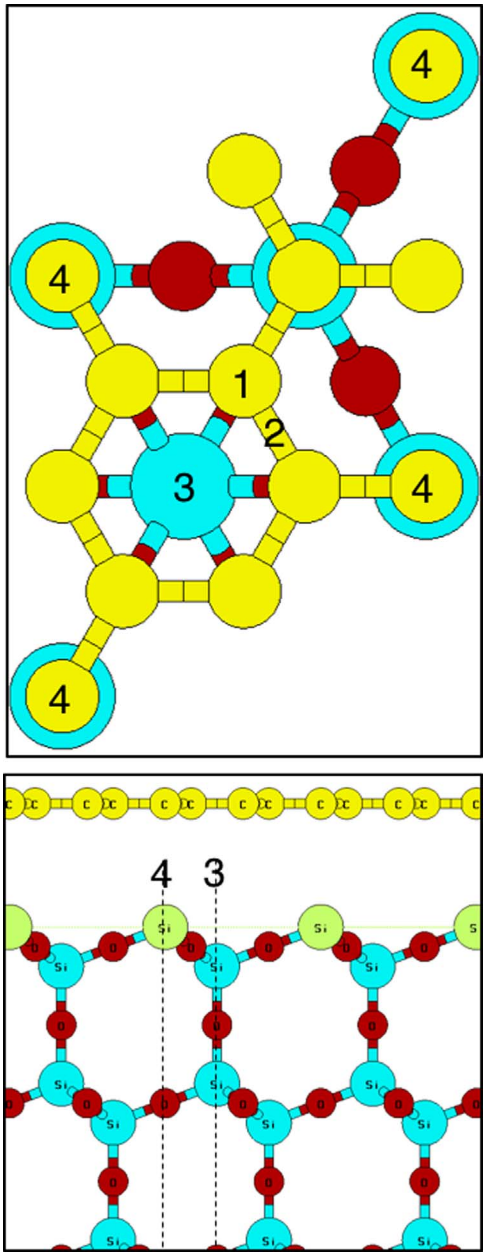

Fig. 1. System I geometry. The Q_3^0 defective silicon atoms are shown in green, carbon atoms in yellow, oxygen atoms in red and silicon atoms in blue. The addressed adsorbate configurations are numbered from 1 to 4. The positions refer to the lateral position of the central adsorbate atom, i.e. the oxygen atom in H_2O, and the carbon atom in CO_2. The plots were rendered with the XCrySDen [37] visualization program as downloaded from [38]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.1.1. System I: cristobalite substrate

A cut in the (111) plane in the cristobalite SiO_2 cubic bulk results in a hexagonal substrate surface. Such a cut causes the substrate to have under-coordinated silicon atoms at the surface, which are referred to as Q_3^0 defective [29–30] silicon atoms. The 0 and 3 mean that the silicon atom is connected to 3 non-dangling (0) oxygen atoms. The substrate surface silicon atoms are either defective under-coordinated silicon atoms of type Q_3^0 or fully-coordinated silicon atoms. The lattice