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Methylbenzenes on graphene

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ABSTRACT

We present a theory study of the physisorption of the series of methylbenzenes (toluene, xylene and mesitylene), as well as benzene, on graphene. The aim is two fold: we provide data that will be used as input to larger-scale methods like molecular-dynamics simulations, and at the same time we enhance the basic understanding of graphene used as a material for sensors and as an idealized model for the carbon in active carbon filters. The molecules are studied in a number of positions and orientations relative to graphene, using density functional theory with the van der Waals functional vdW-DF. The molecules are adsorbed fractional coverage. We focus on the vdW-DF1 and vdW-DF-cx functionals, and find that the binding energy of the molecules on graphene grows linearly with the number of methyl groups, at the rate of 0.09 eV (vdW-DF1) to 0.11 eV (vdW-DF-cx) per added methyl group. We further find that the orientation of the methyl groups of the molecules relative to graphene is at least as important as the lateral position of the whole molecule on graphene.

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1. Introduction

For environmental safety carbon-based filters play an important role for removal of toxic and hazardous substances, e.g., from the air or drinking or waste water. Smooth, defectless graphene may be used as a simplified model for the active carbon and similar material that is often used as filter material in air and water filters. Although defects and impurities influence how active carbon acts as an adsorbent, already the calculated adsorption energy for adsorption on clean, perfect graphene will be an indication of strength of adsorption in filters [1–4].

At the same time, graphene-based sensors may be used for detection of specific molecules in gases and fluids. The sensor must respond selectively to the various molecules. Both applications thus call for the need of understanding, on a fundamental level, the interaction of a number of molecules with graphene.

Here we focus on the adsorption of the group of methylbenzenes on graphene. We use density functional theory (DFT) calculations and the method vdW-DF [5–11] to include the long-ranged dispersion interactions that are crucial for physisorption. We find the adsorption energy and the structure (positions of atoms) of the methylbenzenes when adsorbed in isolated positions on graphene.

With the same method, using functionals within the vdW-DF family, we have previously investigated the adsorption of other relatively small but important molecules on to graphene, such as benzene and naphthalene [12], phenol [13], adenine [14] and the other nucleobases [15], chloroform and other trihalomethanes [16], methanol [17], and the first ten of the series of n-alkanes [18], all at low coverage. These and similar results are useful as input for larger-scale force-field molecular dynamics calculations, as well as providing fundamental knowledge on the binding properties at the single molecule level.

The outline for the rest of the paper is as follows: Section 2 describes methylbenzenes, and Section 3 describes the method of computation, and the choices made in carrying out the calculations. Section 4 reports the results of our calculations, Section 5 discusses our research results, and finally we summarize the study in Section 6.

2. Methylbenzenes

Methylbenzenes is a group of small, aromatic molecules that are volatile and hazardous. They are benzene molecules that have one or more methyl groups attached. We here focus on benzene and the methylbenzenes toluene, para-xylene (1,4-dimethylbenzene) and mesitylene (1,3,5-trimethylbenzene), with one, two, and three methyl (CH_3) groups. The atomic structures are shown in Fig. 1. To see the effects of isomers we also study and compare the adsorption energies of xylene with the methyl groups placed closer together: the ortho-xylene (1,2-dimethylbenzene) and meta-xylene (1,3-dimethylbenzene). Trimethylbenzene also exists as the isomers 1,2,3-trimethylbenzene (hemellitene) and 1,2,4-trimethylbenzene (pseudocumene), but these will not be discussed here. In this paper benzene is included as part

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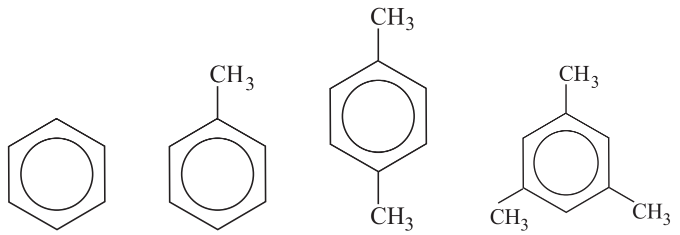

Fig. 1. The atomic structures of benzene, and the methylbenzenes toluene, para-xylene, and mesitylene.

of the group of methylbenzenes, although strictly taken benzene is not a methylbenzene.

Toluene is a colorless liquid, and is used as raw material for the industry and as a solvent. Toluene is believed to be neurotoxic [19], and thus definitely not suitable neither in drinking water nor should it be inhaled. However, it is still much less toxic than benzene, and thus in some cases replaces benzene as an aromatic solvent. Xylene may also for some applications be used as a solvent even less toxic than toluene.

Graphene is a special material because it consists entirely of surface atoms. The possible amount of adsorbed molecules per volume or weight of carbon is therefore high, compared to other materials with similar adsorption energies per adsorbed molecule.

3. Method of computation

The DFT calculations are carried out with the vdW-DF method [5–8,11] in which the exchange-correlation approximation includes long-range dispersion interactions. We mainly use the versions vdW-DF1 [5,6] and vdW-DF-cx [9]. We also report some vdW-DF2 [8] results. The vdW-DF1 and vdW-DF2 calculations are carried out with the DFT code GPAW [20,21] in the Atomic Simulation Environment (ASE) [22,23]. For calculations using the newer functional vdW-DF-cx [9] we use the DFT code Quantum Espresso (QE) [24,25] because vdW-DF-cx was not implemented in GPAW when we carried out the calculations. However, by using GPAW with the latest libxc library it should now be possible to use vdW-DF-cx also in GPAW. All calculations use a fast-Fourier-transform implementation of the central integral in the nonlocal correlation calculations [26].

In all calculations we use periodically repeated orthorhombic unit cells with 60 C atoms in graphene and one methylbenzene molecule. In the lateral plane the size of the unit cell is $3\sqrt{3}a_g \times 5a_g$ with $a_g = \sqrt{3}\,a_c$, where a_c is the C-to-C distance. For our GPAW vdW-DF1 calculations we find $a_c = 1.430$ Å, leading to a lateral unit cell size 12.87 Å × 12.38 Å, checked not to deviate for the vdW-DF2 calculations. For the QE vdW-DF-cx calculations we find $a_c = 1.423$ Å, yielding the size 12.81 Å × 12.32 Å. In the direction perpendicular to graphene the unit cell size is 23 Å in all calculations. The unit cell is illustrated in Fig. 2.

In the GPAW calculations we use a fast-Fourier transform grid with approximately 0.12 Å between grid points for the wave functions, and half this distance for the electron density. We use a 4 × 4 × 1 *k*-point Monkhorst-Pack (MP) sampling over the Brillouin zone (BZ) [27]. The atomic positions are optimized by minimizing the forces acting on them. The positions are considered relaxed when the remaining forces are less than 0.005 eV/Å, which is 10% of the GPAW default threshold value. The electron density is considered converged when the change in total energy in three iterations is less than 4×10^{-7} eV per valence electron, which for the system of 60 graphene C atoms and one toluene molecule means that the threshold for the system energy is 0.1 meV. Our choice of energy change threshold is less than 0.1% of the GPAW default value. We need to use finer thresholds than the defaults due to the small forces and energy changes involved in these systems. Other threshold values not mentioned here are used at their default values.

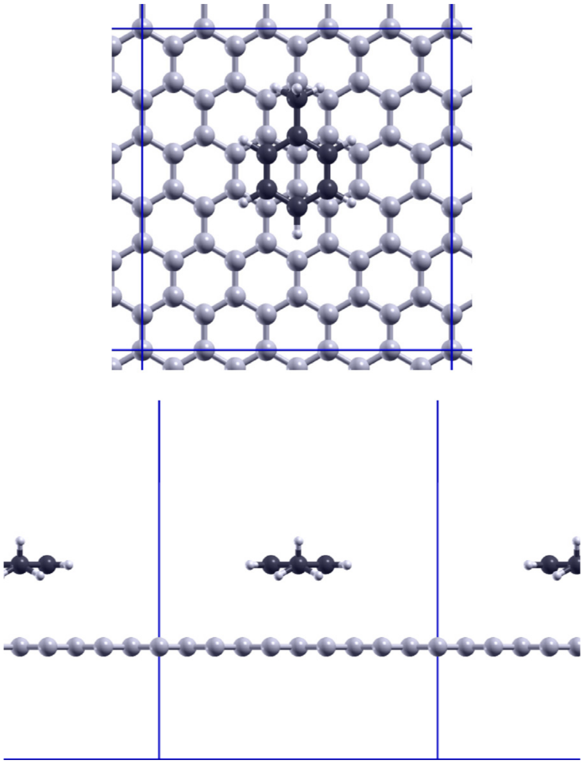

Fig. 2. Sketch of unit cell for toluene adsorption. The height of the unit cell is larger than shown in the lower panel. Light gray spheres are C atoms in graphene, dark gray spheres illustrate C atoms of toluene, and small circles show positions of H on toluene. Shown is the configuration with two H atoms of the methyl group H-tripod pointing towards graphene ('edge') and with the center of the aromatic ring positioned on the bridge between two graphene C atoms ('bridge').

In the QE calculations the sampling of the wave functions and electron density is given by the energy cutoff values for the wave functions (electron density) 50 Ry (400 Ry), yielding 0.17 Å (0.06 Å) between grid points. We use ultrasoft PBE pseudopotentials from the GBRV package [28]. Energy convergence for each atomic configuration is obtained when the total energy changes less than 10^{-8} Ry per iteration, or approximately 10^{-7} eV. Force convergence for the atomic positions is obtained when all components of all forces are smaller than 10^{-4} a.u. (≈ 0.005 eV/Å), which is 10% of the QE default. Like for the GPAW calculations, we use a 4 × 4 × 1 *k*-point MP sampling over the BZ.

The atomic positions are determined by minimizing the forces acting on the atoms. However, this is only a local optimization that cannot rotate the methyl groups or change the position of the aromatic ring on graphene, because the forces are too small, and we therefore use a series of different starting positions and orientation, as illustrated in the Supplementary Material.

4. Results of the calculations

Our main focus is the calculation of optimal adsorption configurations of the methylbenzenes, and their adsorption energies. For each of the molecules we survey a number of systematically prepared configurations, all of which have their atomic positions further locally optimized, as explained in the previous section.

We define the adsorption energy E_a as the gain in total energy of a molecule adsorbed on graphene compared to the sum of total energies of isolated graphene and the isolated molecule, in all calculations using the same periodic unit cell. Binding thus results in a positive value of E_a. Our study provides adsorption energies, given in Table 1 and the Supplementary Material, as well as the changes in adsorption energies when varying orientations, isomers, and positions relative to graphene.

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