Methane adsorption on graphene from *first principles* including dispersion interaction

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ABSTRACT

The methane–graphene interaction is studied using density functional theory complemented with a semiempirical dispersion correction scheme (DFT-D), an *ab initio* van der Waals density functional (vdW-DF) ansatz as well as using Møller Plesset perturbation theory (MP2). The adsorption energy of 0.17 eV and the molecular distance of 3.28 Å obtained from the MP2 calculations are close to the experimental data, while the vdW-DF scheme results either in a realistic adsorption energy or a realistic adsorption geometry, depending on the underlying exchange-correlation functional. The present implementation of DFT-D overbinds about as much as bare DFT calculations underbind, but yields a meaningful adsorption height.

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1. Introduction

The adsorption of methane on graphite has been extensively studied for quite some time [1–3]. Historically, the system served as a model system for physical adsorption phenomena. More recently, the study of methane adsorption on carbonaceous materials is motivated by the search for new storage systems for natural gas. Among others, it was investigated by heat capacity experiments [4], adsorption isotherms [5], Nuclear Magnetic Resonance [6], Positron Annihilation Spectroscopy [7], Neutron Scattering [8] and Electron Diffraction [9]. Theoretical investigations typically rest on empirical potentials [10–12]. In fact, we are aware of only two *ab initio*, i.e., density-functional theory (DFT) calculations of methane adsorbed on graphite(0001) [13] and carbon nanotubes [14]. On the other hand, molecular adsorption on graphite(0001) is frequently used as a testbed to study molecule–molecule and molecule–substrate interactions using state-of-the-art surface science analysis techniques as well as computational approaches. In particular, it has been used to benchmark the validity of models used to describe the dispersion interaction [15–17].

Dispersion or van der Waals (vdW) interaction does not only affect the adsorption geometry and energetics of surface adsorbed molecules [18–26], it is often decisive as well for the intermolecular interactions [27,28] and may even determine chemical reaction pathways [29,30]. At present, the ubiquitous dispersion interaction can be accounted for by performing high-level quantum-chemical wave function or quantum Monte Carlo methods or by the combination of exact exchange plus correlation energy within the adiabatic-connection fluctuation–dissipation theorem. In contrast, the currently used approximations to the electron exchange and correlation (XC) energy in DFT calculations – due to its numerical efficiency the method of choice for large and complex structures such as surface adsorbed molecules – do not properly describe the long-range vdW interactions. Therefore the accurate modeling of loosely bonded adsorbates is a major challenge for DFT. Many concepts have been proposed to include vdW interaction in DFT calculations in order to overcome this problem. The addition of a pairwise interaction energy $\sim C_6 R^{-6}$ with a suitable cutoff function for small atomic distances R is one of the most popular remedies in this respect, see, e.g. Refs. [31–34]. This so-called DFT-D scheme was recently refined by introducing an electron density dependence in the C_6 coefficients [35,36] and is expected to deliver information on the influence of vdW forces at virtually no additional computational costs. In a recent study of Azobenzene at coinage metal surfaces by McNellis and co-workers [37] they found that various semiempirical dispersion correction schemes provide an improvement compared to the GGA-PBE data and that DFT-D values come close to experimental values.

On the other hand – "seamless" van der Waals density functional (vdW-DF) approaches [22,38,39] allow for a *first-principles* description of dispersion interaction. They are substantially more expensive, but meanwhile relatively efficient implementations have been proposed [40,42]. The aims of the present study are to provide theoretical data for an experimentally extensively investigated model system for physical adsorption phenomena – the theoretical results for methane adsorption on graphene hold also for adsorption on graphite(0001) as discussed below. In the following we present calculations for single methane molecules adsorbed on graphene. This system is on the one

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hand sufficiently complex to allow for conclusions on real adsorption phenomena and on the other hand still small enough to be modeled using quantum chemistry methods in order to assess the accuracy of the results not exclusively by means of comparison with experimental data.

2. Methodology

The DFT calculations are performed using the Vienna Ab Initio Simulation Package (VASP) [43] using the Perdew–Burke–Ernzerhof (PBE) functional [44] to model the electron exchange and correlation interaction within the generalized gradient approximation (GGA). The electron–ion interaction is described by the projector-augmented wave (PAW) method [45], which allows for an accurate treatment of the first-row elements with a relatively moderate energy cutoff of 500 eV. The surface Brillouin zone is sampled using the Γ point for the noble-gas calculations as well as the cluster calculations and a $4 \times 4 \times 1$ Monkhorst–Pack mesh for the surface structures. The adsystem was modeled by a single graphene sheet, the adsorbed molecule and a vacuum region of 15 Å.

The (semi)local exchange-correlation functional in GGA cannot account for nonlocal dispersion interaction. Dion et al. [38] proposed a fully nonlocal energy functional (vdW-DF) based on *first principles* which could be easily implemented. The vdW-DF consists of the PBE exchange, the LDA correlation and a correlation term $E_c^{nl}[n]$ defined as

$$E_c^{nl}[n] = \frac{1}{2} \int d^3 r d^3 r' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'),$$

(1)

where a non-local electron-density dependent kernel $\phi(\mathbf{r}, \mathbf{r}')$ enters. In the present study we use the JuNoLo post processing tool [40] with the DFT-GGA charge densities to calculate the dispersion contribution to the total energy. We also present calculations where the exchange energy contributions in the vdW-DF scheme were calculated according to the revPBE energy functional [46].

Alternatively, we approximate the vdW interaction within the DFT-D approach by the pairwise attraction of instantaneously fluctuating atomic dipoles resulting in an asymptotic behavior of $\sim R^{-6}$. The energy for each pair of atoms at $\mathbf{R}_i$ and $\mathbf{R}_j$ with $R = |\mathbf{R}_i - \mathbf{R}_j|$ is calculated from [47]

$$\epsilon_{ij}^{vdW} = -f_{ij}(R) \frac{C_6^{ij}}{R^6}$$

(2)

where $f_{ij}(R)$ represents a damping function and the virial coefficients C_6^{ij} are obtained from the atomic polarizabilities and ionization potentials. Here we use the comparatively simple scheme and implementation proposed by Ortmann et al. [32].

In Hartree–Fock-based schemes, on the other hand, dispersion interaction arises in a natural way from the configuration interaction (CI) between the electronic ground state and excited electronic configurations. Second order Møller–Plesset perturbation theory (MP2) includes the energetic repulsion between the ground state
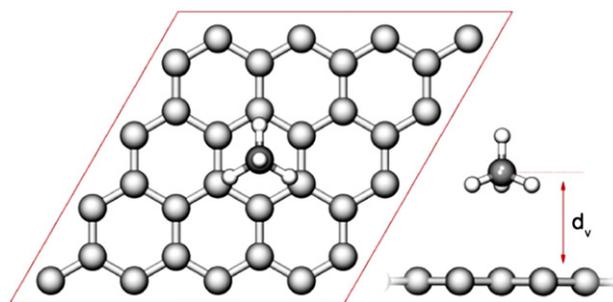

Fig. 1. Adsorption of methane on graphene in a 4×4 periodicity. Top and side views are visualized.

and double excited states in a perturbative way [48]. As more advanced coupled-cluster schemes accounting for CI scale much worse with the system size, MP2 emerges as a suitable compromise for an investigation of the influence of dispersion interaction on molecular adsorption phenomena. Here MP2 calculations were performed using Gaussian-type, correlation consistent, triple-zeta basis sets for all atoms. To account for the dispersive interaction all basis sets were furthermore augmented (aug-cc-pVTZ). The program package Gaussian03 [49] was used for all MP2 calculations.

In a first step we perform a small benchmark test of the four schemes. Here we use noble gas dimers as they are prototypical examples for vdW-bonded systems, due to their closed-shell electronic structure and the absence of permanent multipole moments. The implementations of DFT-GGA, DFT-D, vdW-DF, and MP2 described above are applied to Ne_2, Ar_2, and Kr_2, see Table 1. As expected, the DFT-GGA results generally overestimate the dimer length and underestimate the binding energy rather dramatically, apart from Ne_2, the length of which seems relatively well described already at the GGA level of theory. DFT-D calculations improve the agreement with experiment only marginally, as was noted previously [32]. Calculations with vdW-DF(PBE), in contrast, result in bond lengths that agree reasonably with experiment, especially for Ar_2 and Kr_2 where the deviations from experiment now amount to less than 3%. Unfortunately, the binding energies are overestimated substantially, by up to a factor of six. A similar behavior was noted in Refs. [38,40,41] and attributed to the spurious binding that occurs when using the PBE functional. The use of another GGA functional – revPBE [46] – in conjunction with the vdW-DF calculations leads to a much better description of the binding energy, but at the expense of a slightly worse description of the Ar_2 and Kr_2 bond lengths. The present MP2 results, correlating all orbitals and using the counterpoise correction to correct for the basis set superposition error (BSSE), yield overall the best agreement with the experimental data. The largest deviation occurs for Ne_2, where the binding energy is underestimated by 21% and the bond length overestimated by 3%.

3. Results and discussion

Using periodic supercells, the adsorption of single methane molecules on graphene is modeled within the 4×4 surface unit cell

Table 1
Calculated and measured equilibrium bond length d (Å) and binding energy E_b (meV) for Ne_2, Ar_2 and Kr_2. The percentage of the deviation from the experimental data taken from Ref. [50] is given in brackets.

Method	Ne_2		Ar_2		Kr_2	
	d	E_b	d	E_b	d	E_b
DFT-GGA	3.10 (0.3)	−5.73 (57.4)	4.00 (6.4)	−6.13 (−50.3)	4.35 (8.5)	−6.97 (−59.8)
DFT-D	3.09 (0.0)	−5.73 (57.4)	4.00 (6.4)	−6.24 (−49.4)	4.35 (8.5)	−7.03 (−59.4)
vdW-DF(PBE)	2.85 (−7.8)	−24.45 (571.7)	3.65 (−2.9)	−37.26 (201.9)	3.96 (−1.2)	−42.87 (147.4)
vdW-DF(revPBE)	3.05 (−1.3)	−14.82 (307.1)	3.89 (3.4)	−22.62 (83.1)	4.24 (5.7)	−25.39 (46.5)
MP2	3.17 (2.6)	−2.88 (−20.9)	3.80 (1.1)	−11.78 (−4.5)	3.97 (−1.0)	−16.38 (−5.5)
Exp.	3.09	−3.64	3.76	−12.34	4.01	−17.33
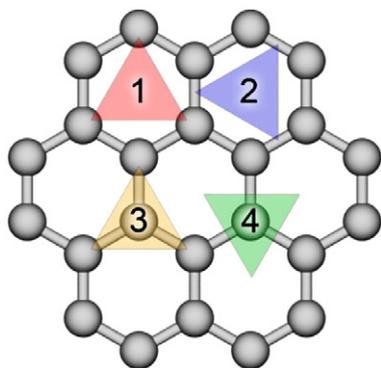
Fig. 2. The four different high-symmetry adsorption sites of methane on graphene. All four sites may be occupied with either the H tripod oriented toward the substrate (d configuration) or towards the vacuum (u configuration).
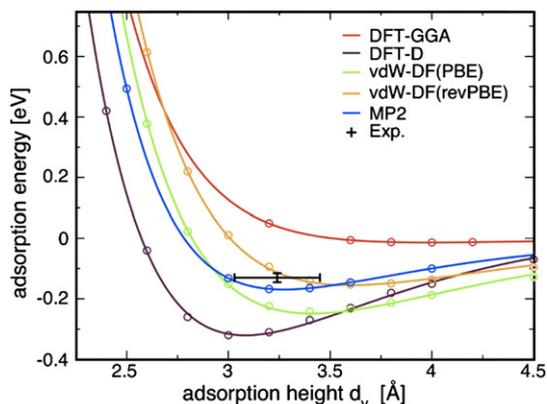
Table 3
Calculated equilibrium distances (Å) and energies (eV) for methane adsorbed on graphene for the most favored adsorption configurations are compared with experimental data from Ref. [2].

Config.	Method	d_v	E_{ads}
1d	DFT-GGA	4.02	−0.01
	DFT-D	3.13	−0.30
	vdW-DF(PBE)	3.41	−0.26
	vdW-DF(revPBE)	3.60	−0.14
	MP2	3.28	−0.17
4d	DFT-GGA	3.99	−0.01
	DFT-D	3.05	−0.32
	vdW-DF(PBE)	3.39	−0.25
	vdW-DF(revPBE)	3.64	−0.16
	MP2	3.29	−0.13
	Exp.	3.03 ... 3.45	−0.12 ... −0.14

indicated in Fig. 1, in order to avoid intermolecular interactions. Given the geometry of the molecule and the substrate, eight high-symmetry adsorption configurations are conceivable. The molecule may occupy one of the four adsorption sites shown in Fig. 2, with the hydrogen tripod either directed to the surface (down configuration, d) or to the vacuum (up configuration, u). The eight adsorption configurations are energetically nearly degenerate within DFT-GGA, with adsorption energies of about 13 meV. This is about the same as found in recent DFT-GGA studies on the adsorption of methane on graphite and carbon nanotubes [13,14]. In agreement with Refs. [11,13] where the 4d configurations was calculated to be most favored, we find the down configuration to be slightly preferred.

The inclusion of dispersion interaction lifts the near energetic degeneracy of the adsorption configurations. However, the maximum energy difference of 86 meV between different geometries – calculated in DFT-D – is still sufficiently small to allow for the considerable translation and rotational mobility of methane adsorbed on graphite observed experimentally [6]. The usage of different approximation schemes for the dispersion interaction leads to different minimum energy adsorption structures. The 1d configuration is favored within vdW-DF(PBE), while vdW-DF(revPBE) as well as DFT-D predict the 4d configuration to be most stable. In order to decide upon the correct structure, more accurate calculations are needed.

Unfortunately, our MP2 approach is restricted to cluster calculations. In order to compare with the previous results that were obtained for periodic supercells, we first determine the influence of the boundary conditions. DFT-D and vdW-DF calculations for configuration 1d are performed using both periodic boundary conditions within a 4×4 translational symmetry as well as for a hydrogen-saturated carbon-cluster of the same lateral dimensions. The calculated adsorption geometries and binding energies do not change qualitatively upon modifying the boundary conditions, but the error bars of about 0.2 Å and 0.05 eV are certainly not negligible, cf. Table 2.

Table 3 summarizes the adsorption height – defined as shown in Fig. 1 – and the adsorption energies for the two most stable adsorption configurations obtained from DFT-GGA, DFT-D, vdW-DF and MP2. The respective minimum energy adsorption pathways are shown in Fig. 3. In order to make the MP2 calculations feasible, we performed single point calculations, using methane and graphene geometries as relaxed within

the DFT-D method. Given the small relaxation of both substrate and adsorbate of the order of picometers, this approximation is not expected to affect the results noticeable. Comparison is made with the measured results summarized in Ref. [2]. These experimental data were obtained for methane adsorption on graphite(0001) surfaces, rather than graphene. However, the comparison is still meaningful: we find the addition of further graphene sheets for the modeling of the graphite substrate to lead to very small modifications (< 0.01 eV) of the methane interaction with the graphite surface, both within vdW-DF and DFT-D. This finding agrees with earlier results for vdW-bonded adsorbates on graphite, see, e.g. Refs. [13,16,17,51].

The comparison between theory and experiment shows that all four schemes certainly provide an improvement compared to the DFT-GGA data.

The molecular distance from the surface obtained from either DFT-D, vdW-DF(PBE) and MP2 calculations is within the scatter of experimental results, whereas only MP2 and vdW-DF(revPBE) calculations yield adsorption energies that are close to the measured data. The vdW-DF (PBE) and in particular the DFT-D approximation tends to overestimate the binding energy. On the other hand, DFT-D and vdW-DF(revPBE) predict an energetic order of the adsorption structures that is different from the MP2 calculations, whereas the trend obtained from vdW-DF (PBE) agrees with MP2. However, it needs to be stressed that the uncertainty introduced by the comparison of cluster and periodic supercell calculations is of the same order as the energy differences between different adsorption geometries. Finally, we mention that DFT calculations using the local density approximation (LDA) [52] to describe the XC functional result in adsorption geometries and adsorption energies that are close to experiment: we calculate vertical distances of 3.25/3.18 Å and adsorption energies of −0.14/−0.15 eV for the 1d/4d configuration. We note that it has been realized earlier already that the

Table 2
Influence of the boundary conditions on the calculated adsorption geometry (d_v in Å) energy (in eV) for configuration 1d.

Method	$d_{periodic}$	$d_{cluster}$	$E_{periodic}$	$E_{cluster}$
DFT-D	3.13	3.39	−0.30	−0.32
vdW-DF(PBE)	3.41	3.39	−0.26	−0.31

Fig. 3. Calculated methane adsorption pathway in comparison with measured data from Ref. [2].

"simple" local density approximation (LDA) seemingly improves the binding properties in some weakly interacting systems, however, for the wrong physical reason [15,53–55].

In summary, we present a microscopic picture of the methane adsorption on graphene. It is essentially driven by dispersion interaction and therefore cannot be modeled sufficiently accurate within DFT-GGA. The present MP2 calculations predict the molecule to adsorb with the hydrogen tripod down about 3.3 Å above the surface with a binding energy of 0.17 eV. The reliability of approximate schemes that model van der Waals forces such as DFT-D or vdW-DF is limited. DFT-D calculations – at least within the present implementation – and the vdW-DF scheme used in conjunction with the PBE functional overestimate considerably the adsorption energy. Replacing the exchange functional used in the vdW-DF calculation by revPBE improves the accuracy of the calculated adsorption energies, but at the expense of the comparison between measured and calculated adsorption height.

Acknowledgments

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