

Attracted by Long-Range Electron Correlation: Adenine on Graphite

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The adsorption of adenine on graphite is analyzed from *first-principles* calculations as a model case for the interaction between organic molecules and chemically inert surfaces. Within density-functional theory we find no chemical bonding due to ionic or covalent interactions, only a very weak attraction at distances beyond the equilibrium position due to the lowering of the kinetic energy of the valence electrons. Electron exchange and correlation effects are much more important for the stabilization of the adsystem. They are modeled by the local density or generalized gradient approximation supplemented by the London dispersion formula for the van der Waals interaction.

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Molecular adsorption on inert surfaces provides an excellent model to probe single molecules and intermolecular interactions by means of sophisticated surface analysis techniques. Questions of fundamental interest such as the role of hydrogen bonds between the nucleic bases in DNA replication and for the origin of life [1] can be addressed by single molecule manipulation using techniques like scanning tunneling microscopy (STM). The self-assembly of DNA base molecules on template surfaces is assumed to play an essential role for the emergence of life under prebiotic conditions. The adsorption and self-organization of adenine molecules on the graphite(0001) surface serves as a model in this context. It has been investigated intensively using STM [2–4], atomic force microscopy (AFM) [5], thermal desorption spectroscopy (TDS) [6], and low energy electron diffraction [7]. While the evaluation of the structural data was assisted by molecular mechanics (MM) calculations [8], quantum mechanics is required to really understand the molecule-substrate interactions and the related changes of the molecular properties.

Obviously, covalent bonds may significantly modify the properties of surface adsorbed molecules [9–11]. However, substantial intramolecular charge transfer and rehybridization processes also take place in the case of organic molecule adsorption on metal substrates [12–14], despite often comparatively small adsorption energies. Even long-range, substrate mediated intermolecular interaction and ordering processes are observed [15]. Similar effects may be expected for molecules adsorbed on a chemically inert surface.

Charge transfer and chemical bonds are, in most cases, well described within density-functional theory (DFT) with either the local-density approximation (LDA) or the generalized gradient approximation (GGA) to account for the exchange and correlation (XC) energy of the electrons. This does not hold for dispersion or van der Waals (vdW) forces. Local (LDA) or semilocal XC functionals (GGA) fail to correctly describe the nonclassical electronic interactions across regions of very sparse electron densities

[16,17]. Such regions between, for example, molecular layers and graphene sheets, enhance the relative importance of vdW coupling for the adsorption. Its calculation from *first principles* requires the self-consistent evaluation of the screening [18,19], which—due to its nonlocality and energy dependence—exceeds the limits of what can presently be handled numerically for complex systems, despite encouraging attempts to employ models for the screening response [16,20].

The present study aims at delivering detailed information on the interaction between organic molecules with chemically inert surfaces, using the adsorption of single adenine molecules on the graphite(0001) surface as model case. To overcome the limitations of the LDA and GGA with respect to long-range electron correlations, we use a modified London dispersion formula [21] to account for the vdW forces. Irrespective of the approximation used, the molecule-surface attraction is largely attributed to the lowering of the XC energy of the inhomogeneous electron gas.

In detail, we use the Vienna *ab initio* Simulation Package (VASP) [22] to perform DFT calculations within either the LDA [23] or the GGA [24]. Ultrasoft pseudopotentials allow for a plane-wave cutoff of 32 Ry for the wave function expansion. The substrate is modeled with a periodic supercell containing 144 C atoms in a single graphene sheet. A

$$\begin{pmatrix} 9 & 0 \\ -4 & 8 \end{pmatrix}$$

periodicity with respect to the graphite surface unit cell is chosen. Using more than one layer of graphite modifies the results far less than the change of the XC potential (see also Ref. [25]). The London dispersion formula [21]

$$E_{ij}^{\text{vdW}}(r) = -\frac{3}{2r^6} \frac{\alpha_i \alpha_j I_i I_j}{I_i + I_j} \quad (1)$$

is used to approximate the vdW interaction within pairs of atomic constituents i, j from their respective polarizabil-

ities α and ionization energies I for large atomic distances r . In order to avoid the r^{-6} singularity, and because the short-range correlations are already contained in the GGA, we use a cutoff function that quenches the interaction for distances below the sum of the covalent radii r_{ij} of atoms i and j

$$f(r) = 1 - \exp\left[-\lambda\left(\frac{r}{r_{ij}}\right)^8\right]. \quad (2)$$

The parameter λ is obtained once from the requirement that $f(r)E_{ij}^{\text{vdW}}(r)$ leads to the correct graphite c lattice constant. Similar approximations have been used in other recent calculations, e.g., Refs. [26,27].

The seamless transition from the long-range dispersion forces to the chemical interactions is a serious challenge for a model that assumes the interacting fragments to be distinct entities. Its validity needs to be tested for the materials of interest. For covalently bonded systems, our implementation leads to only slight changes with respect to the GGA results, e.g., a reduction of the diamond lattice constant by 0.5%. For vdW-bonded systems such as graphite a systematic improvement upon the GGA results for structural and vibrational parameters is found. The structural properties of graphite are fortuitously well described within LDA, even if the interlayer binding energy is underestimated [27]. This underestimation becomes critical within GGA that fails to account for the interlayer binding [16]. The bonding between the graphene sheets, however, is recovered within the GGA + vdW approach described above, yielding a LO phonon mode parallel to the [0001] direction with a frequency of 17.0 meV, close to the experimental value of 15.6 meV [28]. This suggests the London dispersion formula as a simple but reasonably accurate tool to supplement the GGA in systems that can be considered to be assembled from single polarizable entities for interaction distances that are clearly beyond covalent bond lengths.

We start the study of adenine adsorption by mapping the potential energy surface (PES) shown in Fig. 1. Hereby the lateral positions of one graphene layer carbon atom and of the amino group nitrogen were fixed for a mesh of sampling points, whereas their vertical spacing as well as the coordinates of all other atoms were free to relax. The molecule was allowed to rotate. However, the orientation of the molecule in the starting configuration was always chosen to be the one of Fig. 1(a). This orientation changed only little for the local energy minimum reached from the respective lateral position. The mapping of these local minima results in a PES that does not show the full symmetry of the surface, but reflects the lower symmetry of the molecule. Its energy corrugation depends strongly on the XC functional used: We determine maximum values of 0.11, 0.08, and 0.01 eV within LDA, GGA + vdW, and GGA, respectively. The LDA and GGA + vdW values are

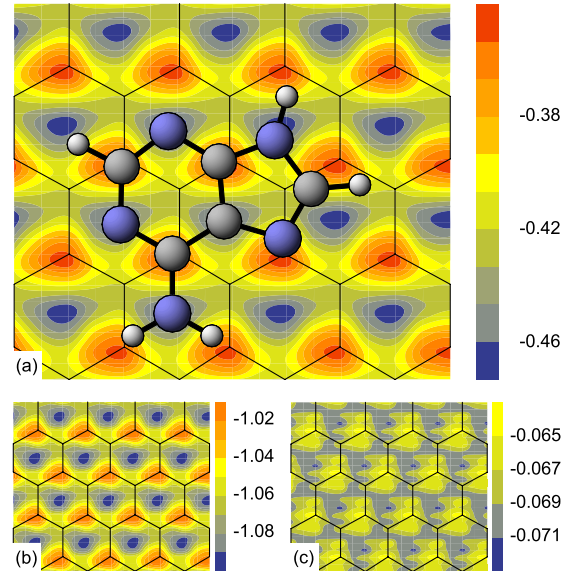


FIG. 1 (color online). PES (in eV) for adenine adsorbed on graphite calculated within LDA (a), GGA + vdW (b), and GGA (c). The minimum energy adsorption position is indicated in (a).

significantly larger than the PES corrugation of 0.03 eV obtained from MM calculations [8].

All rotational degrees of freedom as well as molecular deformations were used to generate alternative starting configurations to verify the minimum energy position shown in Fig. 1(a). We find the molecule to adapt a planar geometry, parallel to the graphite surface. The deviations of the molecular structure from the gas-phase geometry [29] are negligible. The lateral position of the pyrimidine ring of adsorbed adenine is reminiscent of Bernal's AB stacking of graphite. Slight deviations are observed with respect to the adenine positions experimentally determined for monolayers [4,5]. These are most likely related to hydrogen bonds formed within the two-dimensional adenine crystal. They lead to small rotations and shifts of the adenine molecules with respect to the minimum energy position of single molecules.

While the lateral position of the molecule does not depend on the choice of the XC functional, there is a significant influence on the vertical position. We determine substrate-molecule separations of 3.1, 3.4, and 4.0 Å within LDA, GGA + vdW, and GGA, respectively. AFM studies [5] found the thickness of adenine monolayers on graphite to be about 3 Å, i.e., close to our LDA and GGA + vdW results. We obtain adsorption energies of 0.46, 1.09, and 0.07 eV within LDA, GGA + vdW, and GGA, respectively. The GGA + vdW value is close to the energy of 1.01 eV extracted from TDS data [6].

Next we turn to investigate the origin of the bonding. The adsorption energy is of similar magnitude as predicted for adenine adsorbed on Cu(110). In this case, the adsorp-

tion was traced back to the mutual polarization of molecule and substrate [14]. As shown in Fig. 2, the adsorption causes some charge redistribution also in the present case. However, the electron transfer is 3 orders of magnitude smaller than for adenine on copper. Since the orbitals of the heterocyclic molecule are more easily polarized than the delocalized graphite electronic states, the charge redistribution mainly occurs within the molecule. Moreover, it basically occurs within the molecular plane, i.e., it does not lead to a net force along the surface normal. For that reason we can exclude the mutual polarization of molecule and graphite as a noticeable contribution to the molecule-surface attraction.

Do weak covalent interactions bond adenine to graphene? We compared the orbital energies of adsorbed and gas-phase molecules. Indeed, we find some instances of small energy shifts. The most pronounced example is shown in Fig. 3: The molecular and graphite π orbitals about 7 eV below the graphite Fermi energy rehybridize to form bonding and antibonding combinations. From the values of the density isosurfaces in Fig. 3 it is clear, however, that the rehybridization related charge density accumulation between molecule and graphite is extremely small. This is also reflected in the small energy changes of the orbitals. The splitting amounts to 0.3 eV only. Moreover, because both bonding and antibonding combinations are occupied, the rehybridization does not lead to an energy gain. Rather it acts as a repulsive Pauli barrier. This result does not explain the bonding, but it hints at the origin for the specific bonding position: The repulsive interaction between the molecular and graphene π orbitals leads to a molecular position that minimizes the π - π interaction, i.e., close to Bernal's AB stacking.

What causes the attractive molecule-substrate interaction despite a vanishing ionic contribution and a repul-

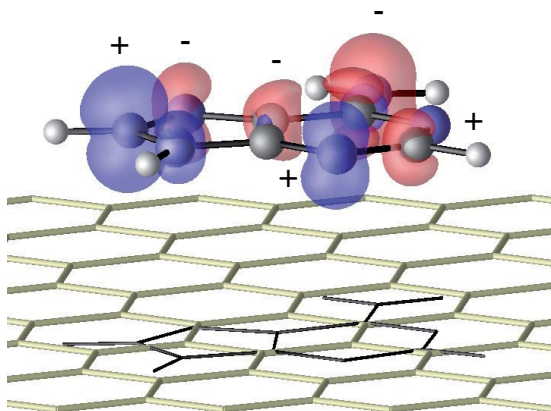


FIG. 2 (color online). Electron density changes upon adenine adsorption on graphite calculated within LDA. Isodensity surfaces for electron accumulation/depletion of $\pm 2 \times 10^{-5} \text{ \AA}^{-3}$ are shown in blue(+)/red(-). The molecule position is projected on the graphene sheet for clarity.

sive Pauli barrier? For adenine adsorbed on Cu, the electron XC effects were found to lower the adsystem energy by nearly 0.4 eV compared to the isolated systems [14]. In that case it was only a minor contribution to the bonding. In order to study the influence of similar effects in the present case, we calculate the XC energy for the isolated and bonded systems for different molecule-graphene distances. Indeed, we find a distinctly stabilizing effect due to the XC energy of the inhomogeneous electron gas within the LDA as well as within GGA and GGA + vdW; see Fig. 4. Moreover, the total bonding energy for distances beyond the equilibrium bonding distance, where the Pauli barrier becomes noticeable, follows remarkably closely the XC energy of the adenine-graphene electron gas, in particular, in the GGA + vdW case.

A close inspection of the XC and total energy curves in Fig. 4 shows, however, that the XC energy is not the only cause of attraction: Somewhat beyond the equilibrium bonding distances, the relative LDA (GGA/GGA + vdW) XC energy is higher than the corresponding relative total energy. Analyzing the remaining contributions to the energy functional shows that the kinetic energy calculated from the single-particle Kohn-Sham orbitals of the adsystem is lower than that of noninteracting adenine and graphene, due to the delocalization of the electronic wave functions. For distances around the respective equilibrium bonding position, however, electron XC effects are clearly responsible for the attraction: The kinetic energy of the valence electrons behaves repulsive.

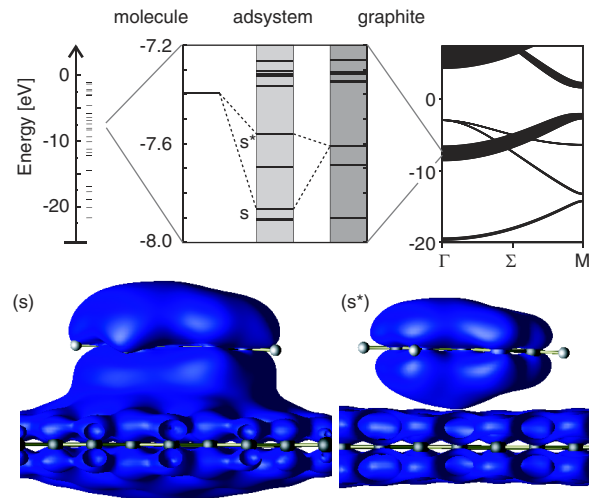


FIG. 3 (color online). Molecular energy levels of gas-phase adenine (top left), the graphite surface projected bulk band structure (top right) and selected energy levels of the adsorbed molecule (top middle) calculated within LDA. The energy alignment has been done with respect to the vacuum potential. The graphite Fermi energy is used as energy zero. Isodensity surfaces (10^{-6} \AA^{-3}) of the bonding and antibonding combinations s and s^* indicated in the energy level diagram are shown below.

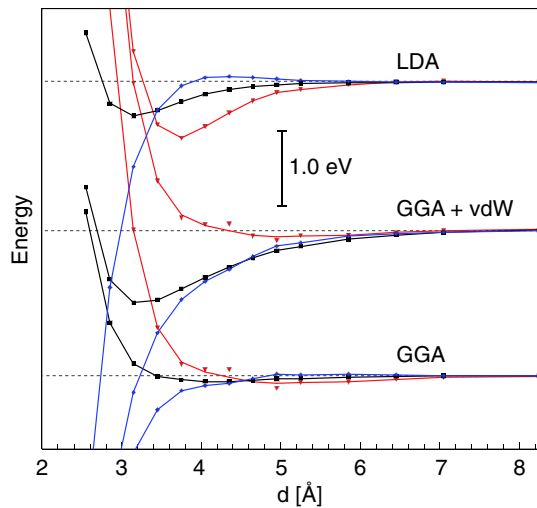


FIG. 4 (color online). Relative total (■, black), XC (◆, blue) and kinetic energy (of the Kohn-Sham particles; ▼, red) of adenine adsorbed on graphene calculated as a function of the molecule-surface distance. Solid lines are guides to the eye.

In conclusion, based on *ab initio* calculations supplemented with a semiempirical term to account for vdW coupling, we analyzed the interaction between adenine and the graphite(0001) surface. In agreement with experiment, we determined for this prototypical system a relatively large adsorption energy of about 1 eV. The bonding is caused by XC effects of the inhomogeneous electron gas: The XC energy either calculated within the LDA or calculated within the GGA but supplemented with dispersion forces overcompensates the Pauli repulsion between the π electron systems. Depending on the direction, energy barriers between 0.03–0.1 eV are predicted to hinder the lateral movement of the molecules. This comes close to the strength of intermolecular hydrogen bonds. The calculations demonstrate that even in cases of chemically inert surfaces there is a noticeable influence of the substrate on the molecular electronic structure and mobility. This needs to be taken into account when one extracts molecular interaction parameters from surface adsorbed species. Dispersion forces may also play an important role in instances of molecular adsorption where chemical interactions dominate: The magnitude of the vdW coupling estimated here is suitable to explain, for example, the discrepancy between the calculated small adsorption energy for adenine adsorbed on Cu(110) and the thermal stability of this adsystem [14,15].

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