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# Physisorption of nucleobases on graphene: Density-functional calculations

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We report the results of our first-principles investigation on the interaction of the nucleobases adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U) with graphene, carried out within the density-functional theory framework, with additional calculations utilizing Hartree-Fock plus second-order Møller-Plesset perturbation theory. The calculated binding energy of the nucleobases shows the following hierarchy: $G > A \approx T \approx C > U$, with the equilibrium configuration being rather similar for all five of them. Our results clearly demonstrate that the nucleobases exhibit significantly different interaction strengths when physisorbed on graphene. The stabilizing factor in the interaction between the base molecule and graphene sheet is dominated by the molecular polarizability that allows a weakly attractive dispersion force to be induced between them. The present study represents a significant step toward a first-principles understanding of how the base sequence of DNA can affect its interaction with carbon nanotubes, as observed experimentally.

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DNA-coated carbon nanotubes represent a hybrid system which unites the biological regime and the nanomaterials world. They possess features which make them attractive for a broad range of applications, e.g., as an efficient method to separate carbon nanotubes (CNTs) according to their electronic properties,[1–3] as highly specific nanosensors, or as an *in vivo* optical detector for ions. Potential applications of single-stranded DNA (ssDNA) covered CNTs range from electronic sensing of various odors[4] to probing conformational changes in DNA triggered by shifts in the surrounding ionic concentration[5] and detection of hybridization between complementary strands of DNA.[6,7] The interaction of DNA with CNT is not limited to the outer surface of the tube; it has also been experimentally demonstrated that ssDNA can be inserted into a CNT,[8] further enhancing the potential applications of this nanobiosystem.

The details of the interaction of DNA with CNTs have not yet been fully understood, though it is generally assumed to be mediated by the $\pi$-electron networks of the base parts of DNA and the graphenelike surface of CNTs. One would like to obtain a better understanding of the binding mechanism and the relative strength of base-CNT binding as it is indicated experimentally from sequence-dependent interactions of DNA with CNTs.[3,4] In this Brief Report, we present the results of our first-principles study of the interaction of nucleobases with a graphene sheet as a significant step toward a deeper understanding of the interaction of ssDNA with CNTs.

Previous theoretical studies focused on the adsorption of the nucleobase adenine on graphite.[9] In the present study, we have considered all five nucleobases of DNA and RNA, namely, the two purine bases adenine (A) and guanine (G) and the three pyrimidine bases cytosine (C), thymine (T), and uracil (U). Our specific interest is to assess the subtle differences in the adsorption strength of these nucleobases on graphene, which, in turn, will allow us to draw conclusions

for the interaction of DNA and RNA with CNTs as well.

Calculations were performed using the plane-wave pseudopotential approach within the local density approximation[10,11] (LDA) of density functional theory,[16] as implemented in the Vienna *ab initio* simulation package (VASP).[17] The cutoff energy was set to 850 eV. For *k*-point sampling of the Brillouin zone, we used the $1 \times 1 \times 1$ Monkhorst-Pack grid,[18] which we found from benchmark calculations to yield identical results as a $3 \times 3 \times 1$ Monkhorst-Pack grid would.

A $5 \times 5$ array of the graphene unit cell in the *x*-*y* plane and a separation of 15 Å between adjacent graphene sheets in the *z* direction were found to be a suitable choice to represent the supercell. The base molecules were terminated at the cut bond to the sugar ring with a methyl group in order to generate an electronic environment in the nucleobase, more closely resembling the situation in DNA and RNA rather than that of just individual isolated bases by themselves. This has the additional benefit that a small magnitude of steric hindrance can be expected from the methyl group, quite similar to the case in which a nucleobase with attached sugar and phosphate group would interact with graphene.

For each of the five nucleobases, an "initial force relaxation" calculation step determined the preferred orientation and optimum height of the planar base molecule relative to the graphene sheet. A slice of the potential energy surface was then explored by translating the relaxed base molecules in a fixed orientation parallel to the graphene plane in steps of 0.246 Å along the lattice vectors of graphene, covering its entire unit cell by a mesh of $10 \times 10$ scan points. The separation between base molecule and graphene sheet was held fixed at the optimum height determined previously. The determination of the minimum total energy configuration was then followed by a 360° rotation of the base molecules in steps of 5° to probe the dependence of the energy on the orientation of the base molecules with respect to the under-
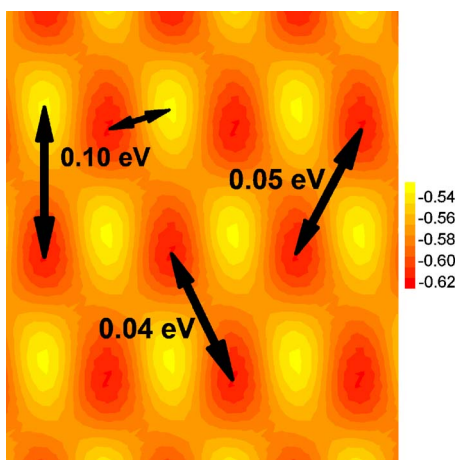
FIG. 1. (Color online) Potential energy surface (PES) plot (in eV) for guanine on graphene. Qualitatively similar PES plots were obtained for the other four nucleobases. Approximately, a $3 \times 3$ repetition of the unit cell is shown. The energy difference between peak and valley is approximately 0.10 eV. The energy barriers separating adjacent global minima have heights of about 0.04–0.05 eV, depending on the direction of translocation.

lying two-dimensional graphene sheet. The configuration yielding the minimum total energy was used in the final optimization step in which all atoms in the system were free to relax. We would like to emphasize here that for all five nucleobases, the eventually determined equilibrium configuration was characterized by a separation between base and graphene sheet that was equal to the optimum height chosen in the previous lateral potential energy surface scan.

An additional set of calculations was performed using the *ab initio* Hartree-Fock approach coupled with second-order Møller-Plesset perturbation theory (MP2) as implemented in the GAUSSIAN 03 suite of programs.[19] Due to the use of localized basis sets (rather than plane wave), the system here consisted of the five nucleobases on top of a patch of nanographene,[20] i.e., a finite sheet containing 28 carbon atoms. The LDA optimized configuration and the 6-311+ +G($d,p$) basis sets for C, H, N, and O atoms were used for the MP2 calculations.

The first optimization step involving the initial force relaxation led to a configuration of all five nucleobases in which their planes are likewise oriented almost exactly parallel to the graphene sheet with a separation of about 3.5 Å, characteristic for $\pi$-$\pi$ stacked systems.[21] The interaction of the attached methyl group with the graphene sheet results in a very small tilt of the molecule, with angles less than 5°.

The base is translated by 2.461 Å along both graphene lattice unit vectors, respectively (maintaining a constant vertical distance of 3.5 Å from the sheet, as determined in the previous step), and rotated by 360° in the equilibrium configuration with respect to the configuration obtained after the initial force relaxation step in the optimization procedure. From the optimization steps involving the translational scan of the energy surface, it is apparent that the energy barriers to lateral movement of a given base can range from 0.04 to 0.10 eV (Fig. 1), thus considerably affecting the mobility of the adsorbed nucleobases on the graphene sheet at
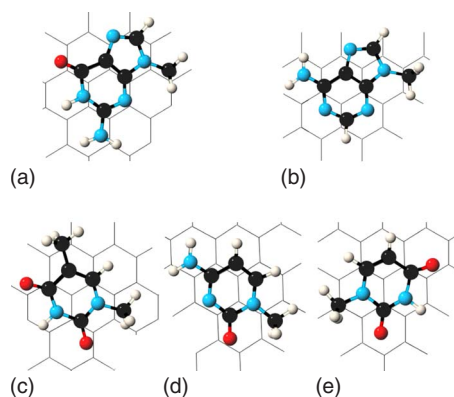


FIG. 2. (Color online) Equilibrium geometry of nucleobases on top of graphene: (a) guanine, (b) adenine, (c) thymine, (d) cytosine, and (e) uracil.

room temperature and constricting their movement to certain directions. The rotational scans carried out by us found energy barriers of up to 0.10 eV, resulting in severe hindrance of changes in the orientation of the adsorbed nucleobase.

In their equilibrium configuration, three of the five bases tend to position themselves on graphene in a configuration reminiscent of the Bernal's *AB* stacking of two adjacent graphene layers in graphite (Fig. 2). Virtually no changes in the interatomic structure of the nucleobases were found in their equilibrium configurations with respect to the corresponding gas-phase geometries, as it could be expected for a weakly interacting system such as the one studied here. This finding is also in agreement with earlier results reported in the literature for the nucleobase adenine.[9] One notable exception is the $R_{\text{C-O}}$ in guanine, which shows a 10% contraction upon physisorption of the molecule on graphene.

The stacking arrangement shown in Fig. 2 can be understood from the tendency of the $\pi$ orbitals of the nucleobases and graphene to minimize their overlap in order to lower the repulsive interaction. The geometry deviates from the perfect *AB* base stacking as, unlike graphene, the six- and five-membered rings of the bases possess a heterogeneous electronic structure due to the presence of both nitrogen and carbon in the ring systems. In addition, there exist different side groups containing $CH_3$, $NH_2$, or O, all of which contribute to the deviation from the perfect *AB* base stacking as well. Adenine, thymine, and uracil display the least deviation from *AB* stacking (Fig. 2) out of the five nucleobases. For guanine and cytosine, on the other hand, there is almost no resemblance to the *AB* stacking configuration recognizable (Fig. 2).

We calculated the binding energy for all five nucleobases. The binding energy of the system consisting of the nucleobase and the graphene sheet is taken as the energy of the equilibrium configuration with reference to the asymptotic limit obtained by varying the distance between the base and the graphene sheet in the $z$ direction (Table I). Within LDA, we found adenine, cytosine, and thymine all to possess nearly identical binding energies of about 0.49 eV, while guanine with 0.61 eV is bound more strongly, and uracil with 0.44 eV somewhat more weakly.

It is somewhat surprising that guanine and adenine would

TABLE I. Binding energies $E_b$ of the five DNA and/or RNA nucleobases with graphene as calculated within LDA are compared with binding energies and polarizabilities $\alpha$ obtained from MP2 calculations.

| Base | LDA $E_b$ (eV) | MP2 $E_b$ (eV) | $\alpha$ ($e^2 a_0^2 E_h^{-1}$) |
|---|---|---|---|
| G | 0.61 | 1.07 | 131.2 |
| A | 0.49 | 0.94 | 123.7 |
| T | 0.49 | 0.83 | 111.4 |
| C | 0.49 | 0.80 | 108.5 |
| U | 0.44 | 0.74 | 97.6 |

possess such different physisorption energies, despite the fact that both contain a five- and a six-membered ring and feature relatively similar molecular structures. A closer analysis of the various contributions to the total energy (Fig. 3) reveals that the Kohn-Sham kinetic energy displays a slightly more pronounced minimum for guanine than for adenine and that the position of that minimum is shifted by about 0.25 Å toward the graphene sheet. The exchange-correlation energy drops off somewhat more rapidly in the case of adenine; however, the difference to the case for guanine is only very small.

For reasons discussed further in the next paragraph, Table I also includes the polarizabilities of the nucleobases calculated at the MP2 level of theory. The polarizability of a given nucleobase,[22] which represents the deformability of the electronic charge distribution, is known to arise from the regions associated with the aromatic rings, lone pairs of nitrogen and oxygen atoms. Accordingly, the purine bases guanine and adenine with their five- and six-membered rings possess the largest polarizabilites, whereas the pyrimidine bases with only one six-membered ring exhibit smaller polarizabilities among the five nucleobases. Furthermore, the purine base guanine with its double-bonded oxygen atom will possess a larger polarizability than the purine base adenine. Our MP2 calculations confirm this trend.

A remarkable correlation is found when the molecular polarizabilities of the base molecules are compared with the binding energies, in particular, when the latter are also determined at the MP2 level of theory (Table I). Clearly, the polarizability of a nucleobase is the key factor which governs the strength of interaction with the graphene sheet. This behavior is expected for a system that draws its stabilization from van der Waals (vdW) dispersion forces, since the vdW energy is proportional to the polarizabilities of the interacting entities. The observed correlation thus strongly suggests that vdW interaction is indeed the dominant source of attraction between graphene and the nucleobases.

The MP2 binding energies are systematically larger than those calculated within the LDA approximation (Table I). This is due to the well established fact that MP2 provides a more accurate treatment of the vdW interaction than LDA. We note that the adsystem consisting of the base and the sheet is not bound at the Hartree-Fock level of theory, which underscores the importance of electron correlation in describing the weak vdW interactions in this system.
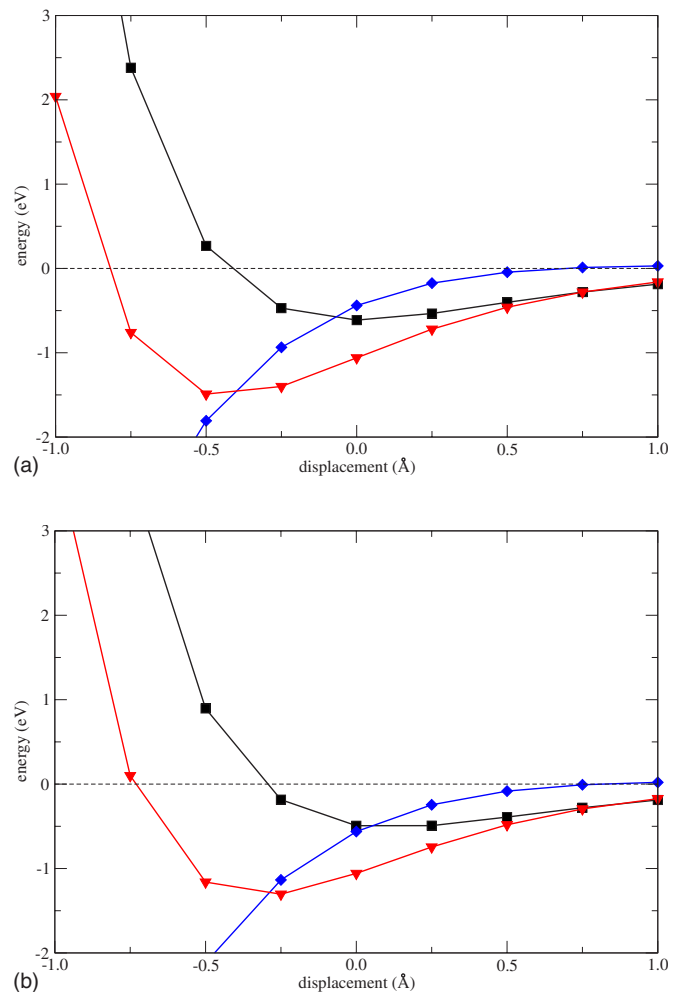


FIG. 3. (Color online) Plot of the relative total energy (black squares), exchange-correlation energy [blue (dark gray) diamonds], and kinetic energy [red (gray) triangles] of guanine (top panel) and adenine (bottom panel) adsorbed on graphene calculated as a function of the displacement from their respective equilibrium position.

In the equilibrium configuration, a redistribution of the total charge density within a given base seems to appear. From an analysis of the Mulliken charges for the MP2 calculations, we also find a negligible charge transfer ($<0.02e$) between any of the five nucleobases and patch of nanographene in the equilibrium configuration. Electrostatic interactions in the adsystem are therefore very unlikely to contribute to the interaction energy.

In summary, we investigated the physisorption of the five DNA and/or RNA nucleobases on a planar sheet of graphene. Our first-principles results clearly demonstrate that the nucleobases exhibit significantly different interaction strengths when physisorbed on graphene. This finding represents an important step toward a better understanding of experimentally observed sequence-dependent interaction of DNA with CNTs.[3,4] The calculated trend in the binding energies strongly suggests that the polarizability of the base molecules determines the interaction strength of the nucleobases with graphene. Since graphene can be regarded as a model system for CNTs with negligible surface curvature, our conclusions should therefore also hold for the physisorp-

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[1] N. Nakashima, S. Okuzono, H. Murakami, T. Nakai, and K. Yoshikawa, Chem. Lett. **2003**, 456.

[2] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. Mclean, S. R. Lustig, R. E. Richardson, and N. G. Tassi, Nat. Mater. **2**, 338 (2003).

[3] M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, and D. J. Walls, Science **302**, 1545 (2003).

[4] C. Staii, A. T. Johnson, Jr., M. Chen, and A. Gelperin, Nano Lett. **5**, 1774 (2005).

[5] D. A. Heller, E. S. Jeng, T.-K. Yeung, B. M. Martinez, A. E. Moll, J. B. Gastala, and M. S. Strano, Science **311**, 508 (2006).

[6] A. Star, E. Tu, J. Niemann, J.-C. P. Gabriel, C. S. Joiner, and C. Valcke, Proc. Natl. Acad. Sci. U.S.A. **103**, 921 (2006).

[7] E. S. Jeng, A. E. Moll, A. C. Roy, J. B. Gastala, and M. S. Strano, Nano Lett. **6**, 371 (2006).

[8] T. Okada, T. Kaneko, R. Hatakeyama, and K. Tohji, Chem. Phys. Lett. **417**, 288 (2006).

[9] F. Ortmann, W. G. Schmidt, and F. Bechstedt, Phys. Rev. Lett. **95**, 186101 (2005).

[10] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[11] LDA appears to give a reliable description of dispersive interactions, unlike the generalized gradient approximation (GGA) (Ref. 12) for which binding is basically nonexistent for van der Waals bound systems (Refs. 13 and 14). The adsorption of adenine on graphite was recently investigated (Ref. 9) using a modified version of the London dispersion formula (Ref. 15) in combination with GGA. The results, however, clearly indicate that LDA, while underbinding the system, does, in fact, yield a potential energy surface for adenine on graphite which is almost indistinguishable in its structure from the one obtained via the GGA+vdW approach [cf. Figs. 1(a) and 1(b) of Ref. 9]. LDA yields almost the same equilibrium distance of adenine to graphene as GGA+vdW. The source of the attraction is identified as the exchange-correlation energy, either calculated within LDA or calculated within GGA+vdW.

[12] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[13] M. Simeonia, C. De Luca, S. Picozzi, S. Santucci, and B. Delley, J. Chem. Phys. **122**, 214710 (2005).

[14] F. Tournus, S. Latil, M. I. Heggie, and J. C. Charlier, Phys. Rev. B **72**, 075431 (2005).

[15] F. London, Z. Phys. **63**, 245 (1930); Z. Phys. Chem. Abt. B **11**, 222 (1930).

[16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[17] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

[20] The dangling bonds at the edge of the nanographene patch have been saturated by hydrogen atoms. For this and other types of nanographene, see Y. Shibayama, H. Sato, T. Enoki, and M. Endo, Phys. Rev. Lett. **84**, 1744 (2000); K. Harigaya and T. Enoki, Chem. Phys. Lett. **351**, 128 (2002).

[21] C. Klein and C. S. Hurlbut, Jr., *Manual of Mineralogy: After Dana*, 20th ed. (Wiley, New York, 1985); J. D. Watson, T. A. Baker, S. P. Bell, A. Gann, M. Levine, and R. Losick, *Molecular Biology of the Gene*, 5th ed. (Benjamin, New York, 2004).

[22] F. Seela, A. M. Jawalekar, and I. Münster, Helv. Chim. Acta **88**, 751 (2005).