First-principles study of physisorption of nucleic acid bases on small-diameter carbon nanotubes

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Abstract

We report the results of our *first-principles* study based on density functional theory on the
interaction of the nucleic acid base molecules adenine (A), cytosine (C), guanine (G), thymine
(T), and uracil (U), with a single-walled carbon nanotube (CNT). Specifically, the focus is on
the physisorption of base molecules on the outer wall of a (5, 0) metallic CNT possessing one of
the smallest diameters possible. Compared to the case for CNTs with large diameters, the
physisorption energy is found to be reduced in the high-curvature case. The base molecules
exhibit significantly different interaction strengths and the calculated binding energies follow
the hierarchy G > A > T > C > U, which appears to be independent of the tube curvature.
The stabilizing factor in the interaction between the base molecule and CNT is dominated by
the molecular polarizability that allows a weakly attractive dispersion force to be induced
between them. The present study provides an improved understanding of the role of the base
sequence in deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) in their interactions with
carbon nanotubes of varying diameters.

1. Introduction

There has been a steady increase in interest over the past four years in the non-covalent interaction of DNA with carbon nanotubes (CNTs). This hybrid system at the junction of the biological regime and the nanomaterials world possesses features which makes it very attractive for a wide range of applications. Initially, the focus rested on a new way to disperse CNT bundles in aqueous solution [1] and the attachment of DNA and RNA onto CNTs has become an important strategy for improving the solubility and bioavailability of nanomaterials in such environments [2]. It was also recognized early that the combination of DNA

and CNTs provides an efficient method to separate the latter according to their electronic properties [3–5]. The nanotube-diameter selectivity in the DNA-wrapping of CNTs [6] may also be exploited to achieve separation according to the band gap of semiconducting nanotubes.

More recently, interest has shifted towards applications aimed at electronic sensing of various odors [7] and in this connection, the conducting properties of DNA and CNT [8] become important. Also, the probing of conformational changes in DNA *in vivo* triggered by a change in the surrounding ionic concentration [9] shows great potential for new detection mechanisms. This and other envisioned applications of CNTs certainly demand a critical understanding of how such nanomaterials can impact biological systems. In

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one recent study [10], it was shown, e.g., that CNTs can reduce and even inhibit polymerase chain reaction and that they may significantly affect the efficiency of biochemical reactions through different action mechanisms.

It has been shown that hybridization between complementary strands of DNA could be detected on the surface of a CNT [11, 12] and can be employed to utilize CNTs as generic nano-biomarkers for the precise detection of a particular gene with very high sensitivity and specificity [13]. Furthermore, DNA may not only interact with the outer surface of CNTs, but can also be inserted inside CNT [14], which may allow for further potential applications of this particular nano-bio system. Finally, while we have concentrated here exclusively on the studies of non-covalent interaction between DNA and CNTs since the year 2003, for the sake of completeness we should also note that there exist many other ways of connecting the two: e.g., amino-terminated DNA strands may functionalize oxidatively prepared single-walled CNTs either at open ends or at defect sites [15] which could serve as a DNA-guided self-assembly process for CNTs.

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 π-electron networks of the base parts of DNA and the graphene-like surface of CNTs [3, 16–18]. It is therefore desirable 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 [4, 7]. Here, we present the results of our *first-principles* study of the interaction of nucleic acid bases with a (5, 0) metallic CNT [19–22] as a significant step towards an understanding of the fundamental physics and the mechanism of this sequence-dependent interaction of single-stranded DNA with CNTs.

In the present study, we have considered all five nucleic acid bases of DNA and RNA: 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 nucleic acid bases on a CNT with a very small diameter. Recently, we investigated the interaction of DNA and RNA base sequences with a planar graphene sheet [23]. The present effort is complementary to the previous study, since the graphene sheet can be seen as a model system for CNTs with a diameter much larger than the dimensions of the bases, and hence a negligible curvature. Comparison of the two sets of results allows us to determine the influence that curvature has on the interaction of DNA and RNA with CNTs.

2. Computational method

We employed a supercell approach in all our calculations. The unit cell of a (5, 0) single-walled carbon nanotube consisting of a ring of 20 carbon atoms with a diameter of 3.92 Å was repeated three times along the tube axis. In the direction perpendicular to the tube axis, a distance of at least 15 Å was kept between repeated units to avoid interactions between adjacent CNTs.

The base molecules were terminated with a methyl group where the bond to the sugar ring had been cut in order to generate an electronic environment in the nucleic acid base more closely resembling the situation in DNA and RNA rather than that of just individual isolated bases by themselves. This has the additional benefit of introducing a small magnitude of steric hindrance due to the methyl group, quite similar to the case in which a nucleic acid base with attached sugar and phosphate group would interact with the surface of the CNT.

Calculations were performed using the plane-wave pseudopotential approach within the local density approximation (LDA) [24] of density functional theory (DFT) [25], as implemented in the Vienna *Ab initio* Simulation Package (VASP) [26]. Results were found to converge for a cutoff energy of 850 eV. We used a $1 \times 1 \times 3$ Monkhorst–Pack grid [27] for k-point sampling of the Brillouin zone. In our previous study on graphene [23], $1 \times 1 \times 1$ was found to yield virtually identical results as that of a $3 \times 3 \times 1$ Monkhorst–Pack grid.

We emphasize that LDA is in principle not the optimal choice for investigations of van der Waals bound systems, since it is known that LDA cannot provide an accurate description of dispersion forces. The use of more reliable methods, such as many-body perturbation theory, would certainly be desirable, but in many cases the high computational cost makes it impossible to apply these methods to systems of larger size. For the particular type of system investigated in our study, it has been reported [28, 29] that the LDA approximation appears to give a good (though perhaps fortuitous) description of the dispersive interactions, unlike the generalized gradient approximation (GGA) [30] for which binding is basically non-existent for van der Waals (vdW) bound systems. In a study of the adsorption of the base molecule A on graphite [16] using LDA and a modified version of the London dispersion formula [31] for vdW interactions in combination with GGA, it was found that LDA, while underbinding the system, does in fact yield a potential energy surface which is almost indistinguishable in its structure from the one obtained via the GGA + vdW approach (cf figures 1a and 1b of [16]). Furthermore, LDA yields almost the same equilibrium distance of A to graphene as GGA + vdW.

Following a similar procedure employed in our previous study with graphene [23], we started by carrying out the optimization process as follows: (i) an initial force relaxation calculation step to determine the preferred orientation and optimum height of the planar base molecule relative to the surface of the CNT; (ii) a curved slice of the potential energy surface was then explored by translating the relaxed base molecules parallel to the CNT surface covering a surface area 4.26 Å in height, 70° in width (figure 1) and containing a mesh of 230 scan points (the separation between base molecule and the surface of the CNT was held fixed at the optimum height determined in the previous step); (iii) it was subsequently followed by a 360° rotation of the base molecules in steps of 5° to probe the energy dependence on the orientation of the base molecules with respect to the underlying CNT surface; (iv) finally, a full optimization was performed in which all atoms were free to relax.

This last step possesses, in principle, no restrictions for the arrangement of the atomic positions, but practically, the only

Figure 2. Rotational energy scan for guanine on top of a (5, 0) CNT.
Zero degree orientation (corresponding to global minimum) and
rotating direction shown in the inset. The blue arrows indicate local
minima for specific rotation angles.
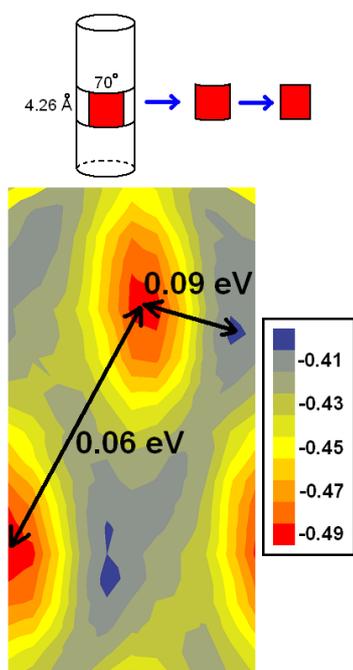
Figure 1. Potential energy surface (PES) plot (in eV) for guanine
with CNT. Qualitatively similar PES plots were obtained for the
other four base molecules. The scanning area is indicated by a red
rectangle. The energy range between peak and valley is
approximately 0.09 eV, while the energy barriers between adjacent
global minima is only 0.06 eV.

way to guarantee that the correct equilibrium configuration
corresponding to the global energy minimum is identified,
would be to start the geometry optimization process from a
large set of plausible trial configurations. In particular, one
could try an explicitly bent structure of the base molecules
to better accommodate the interaction with the curved surface
of the CNT. However, in such a scenario, one should also
consider that the resulting distortion of the geometry would
require the deformation of relatively stiff covalent bonds
which normally keep the base molecule in its native planar
geometry. The expected gain in energy from the increase in the
comparably weak vdW interaction may or may not be sufficient
to compensate for the energy required to bend the molecule.

3. Results and discussion

The initial step in the constrained optimization process resulted
in a configuration of all five nucleic acid bases in which their
planes are oriented almost exactly parallel to the CNT surface.
The base molecule–CNT separation was about 3.2 Å, which
is a little less than the characteristic distance for π–π stacked
systems [32]. The latter does however strictly apply only for
planar entities, the high-curvature surface of a tube such as (5,
0) allows for the π-orbitals of the nucleic acid base to come
closer before the repulsive interaction sets in.

The base was translated both along the CNT axis and
around its circumference respectively, maintaining a constant
separation of approximately 3.2 Å from the CNT surface, as
determined in the previous step. The translational scan of
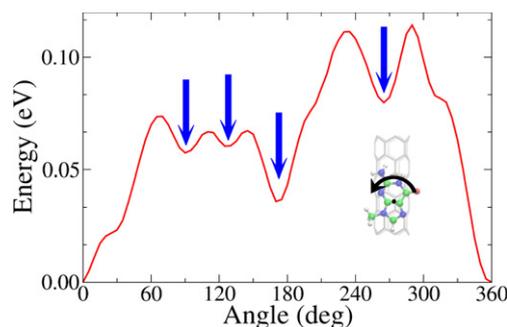
the energy surface, as can be seen from figure 1, gives an
energy barrier of about 0.06 eV for all five molecules. At
room temperature, this barrier is sufficiently large to affect
the mobility of the base molecules physisorbed on the CNT
surface and to constrict their movement to certain directions.
The base was then rotated 360°, in the minimum total energy
configuration obtained from the previous step. We found
energy barriers of up to 0.12 eV (figure 2), resulting in severe
hindrance of changes in the orientation of the physisorbed
nucleic acid base. Interestingly, local minima were found for
special rotations corresponding to 90°, 120°, 180°, and 270°
(figure 2).

We emphasize here that for all five base molecules, the
calculated equilibrium configuration was characterized by a
separation between base and CNT surface that was equal to
the optimum height chosen in the previous lateral potential
energy surface scan. In their equilibrium configuration, the
base molecules A, T and U tend to position themselves
on the CNT in a configuration reminiscent of the Bernal's
AB stacking of two adjacent graphene layers in graphite
(figure 3). The base molecules G and C, on the other hand,
show a lesser degree of resemblance to the AB stacking.
The interatomic structure of the nucleic acid bases in their
equilibrium configurations underwent virtually no changes
when compared to the corresponding gas-phase geometries, as
it could be expected for a weakly interacting system.

The tendency of the π-orbitals of the bases and the
graphene-like surface of a CNT to minimize their overlap, in
order to lower the repulsive interaction, helps us understand
the observed stacking arrangement (figure 3). 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.
Additionally, 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.

The binding energy of the system consisting of the nucleic
acid base and the CNT 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 CNT surface
in the direction perpendicular to both the tube axis and the
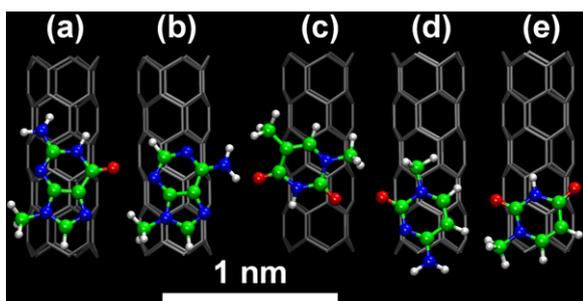
Figure 3. Equilibrium geometry of nucleic acid bases on top of (5, 0) CNT: (a) guanine, (b) adenine, (c) thymine, (d) cytosine, and (e) uracil. The bar indicates the scale in the figure.

Table 1. Binding energy E_b of the DNA/RNA nucleic acid bases with a (5, 0) CNT and with a flat graphene sheet as calculated within LDA. A close correlation with the nucleic acid bases' polarizabilities α from MP2 calculations can be seen.

Base	E_b^{CNT} (eV)	E_b^{graphene} (eV)	α ($e^2 a_0^2 E_h^{-1}$)
G	0.49	0.61	131.2
A	0.39	0.49	123.7
T	0.34	0.49	111.4
C	0.29	0.49	108.5
U	0.28	0.44	97.6

plane of the base molecule (table 1). G is found to bind most strongly, while the binding for U with the CNT surface is the weakest.

Table 1 also includes the polarizabilities of the base molecules calculated using the Hartree–Fock approach coupled with second-order Møller–Plesset perturbation theory (MP2) as implemented in the GAUSSIAN 03 suite of programs [33]. The polarizability of the base molecule [34], 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. The calculated polarizability for the purine base G thus has the largest value, whereas the pyrimidine base U has the smallest value of polarizability among the five bases.

The CNT–molecule binding energies and the molecular polarizabilities of the base molecules calculated using MP2 (table 1) show a remarkable correlation. The polarizability of a nucleic acid base plays a key role in governing the strength of interaction with the CNT. This is an expected behavior for a system that draws its stabilization from 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 the CNT and the nucleic acid bases.

Comparing the present results with those obtained for graphene [23], we clearly see (table 1) that the binding energy of the base molecules is substantially reduced for physisorption on small-diameter CNTs with high curvature. While the curvature allows the nucleic acid base to approach the surface more closely, the majority of the carbon atoms in CNT are actually further removed from the atoms of the bases than in the corresponding case on a graphene sheet (figure 4). Since
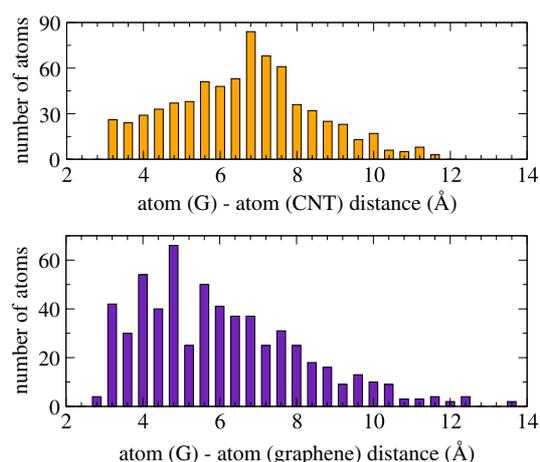
Figure 4. Number of atoms in the physisorbed guanine that lie within a certain distance interval relative to carbon atoms of (top) CNT and (bottom) graphene.

the attractive interaction falls off as the distance between the carbon nanomaterial (either graphene or a CNT) and the base molecule is increased, the overall binding energy is reduced in the case of CNT.

We furthermore calculated the charge transfer between the bases and the CNT. For G, we find from the Bader analysis that the CNT possesses an excess charge of $-0.08e$ and correspondingly a slight depletion of electrons on G by $+0.08e$. For A with CNT, $-0.05e$ were found to have been transferred from the nucleic acid base to the CNT. These results should be compared with our corresponding findings from the interaction of nucleic acid bases with a flat graphene sheet [23], where merely $0.02e$ were transferred in the case of G. Thus, the higher curvature of the (5, 0) CNT leads to an increased electronegativity which manifests itself in the larger amount of charge transferred to it. The different behavior of G and A becomes understandable when one considers that G has a smaller ionization potential than A, and it is thus easier to remove an electron from G than from A. While there are no 'whole elementary charges' transferred in this case, but only fractions, it still shows that the CNT is able to get more charge from G than from A. It appears that the charge transfer originates primarily from the C–C bond that joins the six- and five-membered ring (figure 5). However, the total amount of transferred charge remains relatively small and the resulting contribution to the binding energy from the attractive Coulomb interaction can be estimated to be at or below the 0.01 eV margin of error in our calculations.

Finally, we also analyzed the density of states (DOS) for the combined system of base + CNT and compared with the corresponding DOS for the individual parts, i.e., CNT and nucleic acid base separated (figure 6). We find that the DOS of the combined system is almost exactly the superposition of the DOS of the individual parts, in agreement with a recent tight-binding study of DNA-wrapped CNTs [17]. This finding highlights that the nucleic acid bases and CNT are interacting rather weakly, and that no significant hybridization between the respective orbitals of the two entities takes place.
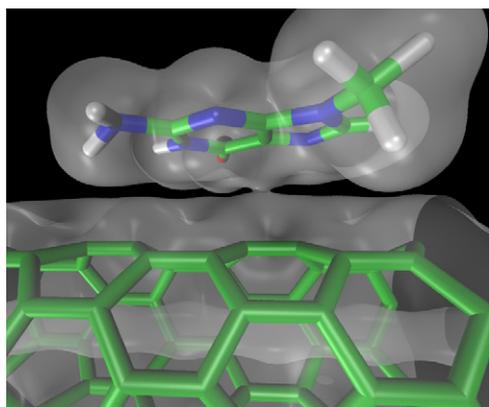
Figure 5. Charge density plot for guanine physisorbed on a (5, 0) CNT. A small funnel is noticeably connecting the two entities near the C–C bond of guanine where the six- and five-membered rings join in the molecule.
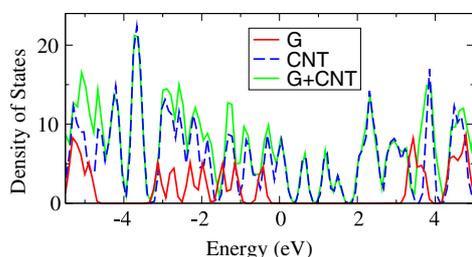
Figure 6. Comparison between the density of states for an isolated guanine molecule (G), an isolated (5, 0) carbon nanotube (CNT), and the combination of the two at equilibrium geometry (G + CNT).

4. Conclusions

In summary, we have investigated the interaction of the five DNA/RNA base molecules with a (5, 0) zigzag CNT of very high curvature by *first-principles* methods. From the calculations, the five nucleic acid bases are found to exhibit significantly different interaction strengths with the CNT. Molecular polarizability of the base molecules is found to play the dominant role in the interaction strength of the base molecules with CNT. This observation should be of importance in understanding the sequence-dependent interaction of DNA with CNTs observed in experiments [4, 7].

When comparing the results obtained here for physisorp-tion on the small-diameter CNT considered with those from the previous study on graphene [23], we see that the interaction strength of nucleic acid bases is smaller for the tube. Thus, it appears that introducing surface curvature reduces the bind-ing energy between the base molecule and the substrate. The binding energies for the two extreme cases of negligible curva-ture (flat graphene sheet) and of very high curvature (the (5, 0) CNT studied here) represent the upper and lower boundaries, and it is expected that the binding energy of bases for CNTs of intermediate curvature is likely to lie in between these two extremes. Based on the results obtained up to this point, the hierarchy of the binding energies of the nucleic acid bases to the graphene-like surfaces of CNTs appears to be universally

valid, as long as the interaction is dominated by vdW forces. Further studies are currently in progress to consider the effect that different chiralities may have on the interaction of nucleic acid bases with high-curvature CNTs.

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