



Nicotine adsorption on single wall carbon nanotubes

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ABSTRACT

This work reports a theoretical study of nicotine molecules interacting with single wall carbon nanotubes (SWCNTs) through *ab initio* calculations within the framework of density functional theory (DFT). Different adsorption sites for nicotine on the surface of pristine and defective (8,0) SWCNTs were analyzed and the total energy curves, as a function of molecular position relative to the SWCNT surface, were evaluated. The nicotine adsorption process is found to be energetically favorable and the molecule–nanotube interaction is intermediated by the tri-coordinated nitrogen atom from the nicotine. It is also predicted the possibility of a chemical bonding between nicotine and SWCNT through the di-coordinated nitrogen.

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1. Introduction

Carbon-based materials have been widely studied in the last decades. The discovery of new carbon forms such as fullerenes, carbon nanotubes and graphene have brought a big interest of the scientific community because these materials exhibit remarkable properties with high potential to be applied in several technological areas [1]. In particular, carbon nanotubes (both multi-walled (MWCNT) and single walled (SWCNT)) are promising materials for several applications such as high performance composites [2–4], components in water filters [5,6], environmental sensors [7], building blocks for electronic nanodevices [8], drug delivers [9], among others.

In the same way, carbon nanotubes curvature presents an additional level of quantum confinement in comparison with graphene, leading to one-dimensional (1D) materials. These 1D systems have a lower strain on their side walls than fullerenes, which make them less reactive and less susceptible to chemical modification than fullerenes. The electronic confinement in the circumferential direction renders to the SWCNTs the metallic or semiconducting behavior depending on how the carbon honeycomb lattice is rolled up to build the tubular structure [1]. The characteristic SWCNTs electronic structure and its selective sensitivity to the interaction with different compounds make SWCNTs suitable for applications as nanosensors and to be used as component materials for toxic compounds filters. The interaction between carbon nanotubes and some of these hazardous molecules is the subject of several exper-

imental and theoretical studies in the literature [10–17]. Recently, it was reported in the literature the experimental realization of using carboxylated carbon nanotubes as an additive in filter tips to increase nicotine and tar sorption [18]. It was pointed out that a greater amount of nicotine and tar were adsorbed on the nanotube surfaces than by traditional materials like activated carbon and zeolites.

Health hazard caused by cigarette smoking is a worldwide discussed issue. Cigarette smoke contains several toxic and carcinogenic compounds including various polycyclic aromatic hydrocarbons (collectively called tar), nicotine, among others [19,20]. The development of systems for removing nicotine and tar is important because the passive smokers are also affected by inhaling the tobacco smoke which dissipates in the environment [21]. Besides its carcinogenic potential, tobacco has a strong capability to induce chemical dependence which is mainly due to nicotine [22]. Hence, the development of filters tips or even air-conditioning filters with improved sorption of those compounds is a desirable task with impact in public health.

The goal of this study is to investigate the interaction process of nicotine with the SWCNT surface and understand the influence of specific structural defects in the adsorption route. The nicotine interaction with pristine and defective SWCNTs was simulated using the DFT framework. Depending on the nicotine molecule interaction with pristine or defective SWCNT it is predicted chemical or physical adsorption.

2. Methodology

The calculations were performed using the SIESTA code [23] which solves self-consistently the Kohn–Sham equations [24] in

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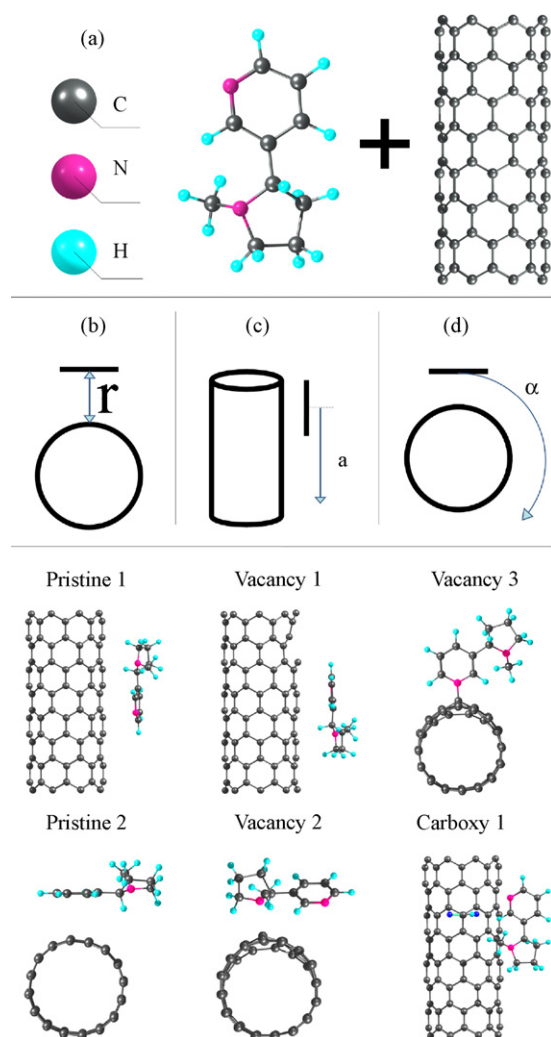


Fig. 1. (a) Nicotine and (8,0) nanotube structures. Cartoon illustrating the procedure used for constructing static energy curves (SECs) in the (b) radial, (c) axial and (d) circumferential directions. In lower panels we show the optimized structures for the studied conformations listed in Table 1.

the DFT framework. Troullier–Martins norm-conserving pseudopotentials [25] were used to represent the core electrons while the valence wave functions were expanded in a series of localized pseudoatomic orbitals as proposed by Sankey et al. [26] within a double- ζ plus a polarization (DZP) scheme with an energy shift of 0.05 eV for all species. The local density approximation (LDA), as parameterized by Perdew and Zunger [27], was used to take into account the exchange and correlation energy. The total energy minimization was performed within a conjugated gradient procedure. The systems were relaxed until the residual forces were below 0.05 eV/Å.

The nicotine molecule and the (8,0) SWCNT structures are shown in Fig. 1a. We previously relaxed these two systems separately. The molecule is then put in a certain conformation in an initial position near to the tube surface and the total energy is calculated without relaxing the structure. Afterwards the radial distance r from the molecule to the tube is varied by steps of 0.1 Å as outlined in Fig. 1b, and at each position the total energy is calculated. We interpolate the data using cubic splines method and construct static energetic curves (SEC) for the total energy as a function of radial distance. We fix the radial position for the lowest energy point of this curve and vary the molecule position a along the tube axis by steps of 0.3 Å, as shown in Fig. 1c, and a new SEC is then constructed for

this axial direction. Once the most stable point is found, we additionally fix the axial position and vary the molecule angular position α along the circumference centered in the SWCNT axis by steps of 5° (Fig. 1d). The lowest energy point from this curve in the circumferential direction is then relaxed and from this calculation we extract the relevant physical properties. It should be pointed out that this procedure does not give us the global minimum energy point for the potential surface. In fact this is done in order to make a less arbitrary choice for the initial point for the geometry optimization. Pristine, vacancy defective and carboxylated (8,0) SWCNTs were used as a model to study the nicotine–SWCNT interaction process. The optimized structures for all arrangements are presented in the lower panel in Fig. 1.

Different conformations were simulated for the pristine SWCNT–nicotine: (i) “Pristine 1” where the nicotine molecule is placed parallel to the tube axis with the hexagonal ring parallel to the SWCNT surface; (ii) “Pristine 2” that is obtained from the previous one (“Pristine 1”) by performing a 90° rotation on the nicotine molecule with respect to an axis perpendicular to the molecular hexagon crossing through its center site.

The SWCNT with a vacancy was approached to the nicotine molecules in different conformations: (i) “Vacancy 1” conformation in which the molecule hexagon is over the vacancy; (ii) “Vacancy 2” where the tri-coordinated nitrogen from nicotine is adsorbed directly over the dangling bond of the SWCNT carbon atom; (iii) “Vacancy 3” conformation with the nicotine position similar to that in “Pristine 2”, but with the nicotine hexagon orthogonal to the tube axis with the nitrogen atom close to the vacancy.

Finally, for the carboxylated SWCNT, we simulate a conformation labeled “Carboxyl” in which the di-coordinate nitrogen from the molecule approaches the oxygen from the OH– group from the carboxyl.

All calculations were performed using four unit cells of (8,0) nanotube. The supercell contains 128 atoms (for the pristine case) and a separation of 30 Å between the tube centers was set in order to make sure that the periodic images do not interact with each other. We also have used a $1 \times 1 \times 8$ Monkhorst–Pack sampling for integration in the reciprocal space. Charge transfer between nicotine and nanotube is estimated by means of Mülliken population.

The binding energies were calculated by the standard equation:

$$E_b = E(\text{SWCNT–Nicotine}) - E(\text{SWCNT–Nicotine}^{\text{Ghost}}) - E(\text{SWCNT}^{\text{Ghost}}\text{–Nicotine}), \quad (1)$$

in which $E(\text{SWCNT–Nicotine})$ is the total energy of the SWCNT–Nicotine interacting system, while $E(\text{SWCNT–Nicotine}^{\text{Ghost}})$ [$E(\text{SWCNT}^{\text{Ghost}}\text{–Nicotine})$] is the total energy of the nanotube [nicotine] alone but including the nicotine [nanotubes] basis functions in its corresponding positions without any atomic potential. This is the so called counterpoise method [16,28] which avoids an artificial lowering in the binding energy due to the smaller basis used in the energy calculation of the isolated nanotube and nicotine. This procedure has little effect on strongly interacting systems but it is fundamental in computing binding energies for weakly interacting systems.

3. Results and discussion

Fig. 2a–c shows the SECs for “Pristine 1” conformation. In these curves the radial distance is defined between the geometrical center of the nicotine hexagon and the SWCNT surface. The axial displacement is relative to the position in which the molecule hexagon is over a nanotube ring. Radial and circumferential SECs show a preferential site (minimum energy) while for axial displacement there is an energy curve with several minimal values. The energy barriers (EBs) for these wells are of the order of 0.1 eV,

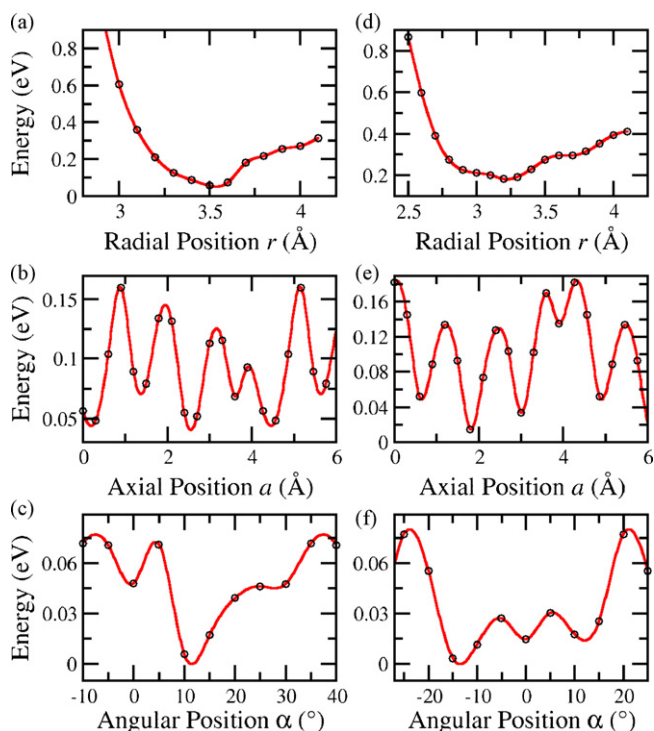


Fig. 2. SEC for radial, axial and circumferential directions for “Pristine 1” (a–c) and “Pristine 2” (d–f) conformations, respectively. The energy values are relative to the minimum value obtained from the interpolation in the circumferential curve for each conformation.

indicating that the nicotine molecule has a limited mobility over the tube surface since these values are significantly higher than the thermal energy ($k_B T$) at room temperature. A similar behavior occurs for “Pristine 2” conformation (Fig. 2d–f) except for the circumferential curve. Nicotine has a larger mobility along this line since this curve presents more than one stable site with EBs of the order of $k_B T$. This larger mobility of nicotine over the tube surface suggests a weak interaction in this conformation.

The smallest distances from one molecule atom to a SWCNT atom (d_{a-a}) and the distance from the classical molecular center of mass (CM) to the SWCNT surface (d_{CM}) are listed in Table 1. Despite d_{a-a} gives us the smallest distance between atoms from the two systems, the d_{CM} value is a more appropriated parameter to evaluate how close the molecule is to the tube surface in this case. The nicotine in “Pristine 1” is overall closer to the SWCNT surface than in “Pristine 2” due to its smaller value for d_{CM} , even though it presents a larger d_{a-a} . These geometrical factors suggest a more stable adsorption in the “Pristine 1” conformation. However, more important aspects related to the interaction, like binding energy and charge transfer, are necessary to confirm this assumption. In fact, the binding energy and charge transfer are more intense in the “Pristine 1” case (Table 1) as compared with “Pristine 2”, revealing

Table 1

Smallest distance between a nicotine atom and a carbon nanotube atom (d_{a-a}), between the classical nicotine center of mass and the tube surface (d_{CM}), binding energy (E_b) and charge transfer (Δq) from the molecule to the SWCNT (positive values indicate that the nanotube is accepting charge).

Conformation	d_{a-a} (Å)	d_{CM} (Å)	E_b (eV)	Δq (e^-)
“Pristine 1”	2.15	3.49	−0.37	−0.09
“Pristine 2”	3.16	3.81	−0.27	−0.02
“Vacancy 1”	2.51	3.48	−0.37	−0.08
“Vacancy 2”	2.50	3.31	−0.63	+0.11
“Vacancy 3”	1.36	4.13	−2.74	+0.39
“Carboxyl”	2.38	4.07	−0.34	+0.05

a more strong interaction of nicotine with pristine nanotube in the former conformation. Moreover, these small binding energy values reveal a physisorption process of the nicotine over the SWCNT surface. Such adsorption is similar to those which occur between several other compounds and SWCNTs [16,17,29,30].

Fig. 3a–c presents the electronic band structure for the pristine SWCNT and the “Pristine 1” and “Pristine 2” conformations, respectively. An electronic level resulting from the interaction between the systems appears about 0.3 eV below the Fermi energy. The local density of states (LDOS) plot confirms that these levels (Fig. 3, lower panel) are localized over a nitrogen atom from the nicotine molecule. These results suggest that this nitrogen atom mediate the interaction process. Since this N atom is closer to the tube surface in “Pristine 1” as compared with “Pristine 2”. This level presents a higher re-hybridization degree in the former conformation, thus strengthening the binding and increasing the charge transfer as listed in Table 1.

By using similar procedure, two nicotine molecules were considered interacting with one carbon nanotube in order to identify the best conformation to adsorb subsequent molecules, considering “Pristine 1” as the start point. The goal is to evaluate if the additional molecule is preferentially adsorbed directly over the SWCNT surface in an opposite site (labeled “Pristine 3”) or through the first one in graphite like conformation (labeled “Pristine 4”). For this last scheme we previously construct a SEC to find the distance between the hexagons which was found to be 3.0 Å. The “Pristine 3” arrangement shows to be the better route since each molecule has little influence on the interaction between the first molecule and the SWCNT. In this case, each molecule interacts with the rest of the structure with a binding energy of −0.32 eV and a charge transfer of about 0.09 e^- from the tube to each nicotine molecule. In the “Pristine 4” scheme, the second molecule presents a binding energy of −0.17 eV to the remaining structure.

The SWCNT surface with structural defects like single vacancies can play an important role in the interaction of several compounds with the nanotubes. Such defects present a high reactivity and can act as active sites for chemical reactions as well as start points in functionalization processes [31,32]. Then, in order to evaluate the importance of the vacancy on the adsorption process, the nicotine interacting with single-vacancy SWCNT were calculated. After optimizing the vacancy-SWCNT structure, two of the di-coordinate carbons, from the defect, combine to form a pentagonal site in a symmetric geometry, thus leaving the third one with a dangling bond. This is already expected for (8,0) SWCNT from theoretical calculations [33,34]. It is pertinent to remember that the presence of vacancies introduces uncoordinated atoms on the SWCNT [30] and this defect can give rise to magnetic properties similar to edge-effects in the graphene nanoribbons [35]. In addition, systems with unpaired electrons require attention to spin-polarization since non-spin-polarized calculations can lead to imprecise binding energies [36,37]. Therefore, we take into account the influence of the spin-polarization effects on the SWCNT with one vacancy and we did not observe changes on the final results for the binding energies and electronic properties compared with the non-polarized system.

In the most stable position from the SECs for “Vacancy 1” (Fig. 4a–c) the nicotine molecule tends to escape from the vacancy, while the minimum for the radial curve (Fig. 4a) occurs at 3.5 Å, similarly to the “Pristine 1” case. In fact, for the lowest SEC point, the axial displacement from the initial position is about 3.0 Å far from the defect (Fig. 4b) and, consequently, the molecule is adsorbed out of the defect. This is reflected in binding energy (−0.37 eV) and charge transfer (0.08 e^-) which are very similar to the “Pristine 1” case as well as in the presence of a slightly dispersed nicotine level around 0.3 eV below the Fermi energy (Fig. 3e) in comparison to the isolated defective nanotube (Fig. 3d).

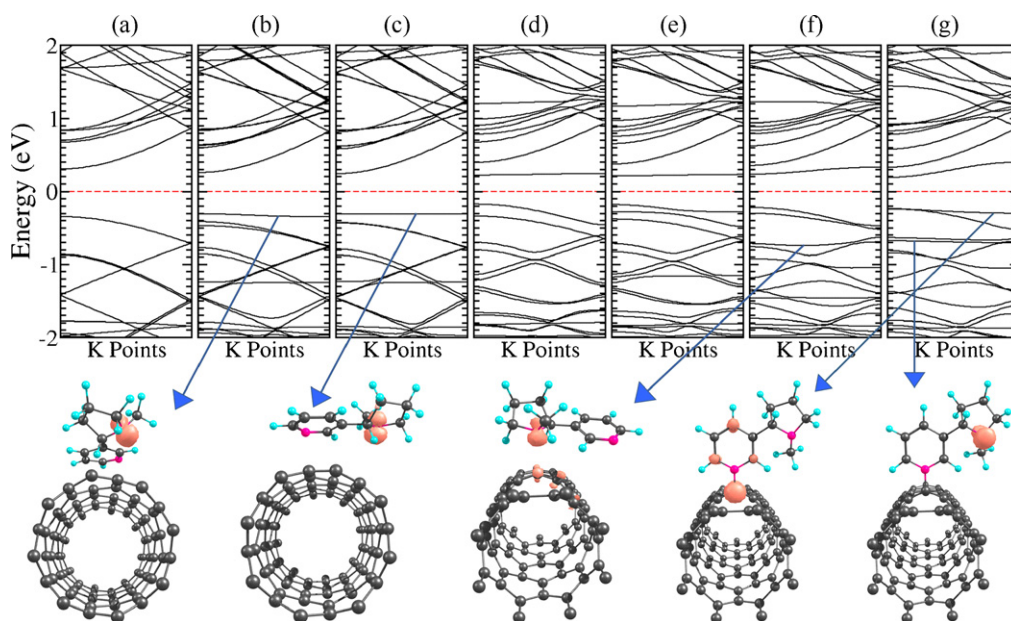


Fig. 3. (Upper panel) Electronic band structure for the (a) pristine (8,0) tube, (b) “Pristine 1”, (c) “Pristine 2”, (d) (8,0) tube with a vacancy, (e) “Vacancy 1”, (f) “Vacancy 2” and (g) “Vacancy 3” conformations close to the Fermi level (at 0.0 eV). (Lower panel) Local density of electronic states (LDOS) for some nicotine related levels near the Fermi level. The contour isosurfaces are $0.01e^-/\text{Bohr}^3$ for the pristine cases and $0.005e^-/\text{Bohr}^3$ for the single-vacancy cases.

For the “Vacancy 2” system the SECs (Fig. 4d–f) indicate that the molecule has a reduced freedom over the tube surface in comparison to the pristine tube cases. Besides the radial curve (Fig. 4d), the circumferential one (Fig. 4f) also presents an unique and well defined minimum, while the axial equilibrium (Fig. 4e) is limited by only two minima which are separated by $\sim 0.7 \text{ \AA}$. This higher stability can be viewed as a consequence of the significantly stronger interaction revealed by a more intense binding energy (-0.63 eV) between tube and the molecule and by the transfer of $0.11e^-$ from nicotine to the tube. This is expected since the molecule approaches to the tube through the tri-coordinated nitrogen, which was shown to be the interaction channel by the calculations involving pristine

tubes. The electronic structure of the defective nanotube also shows significant changes due to the interaction with nicotine (Fig. 3d and f). The dispersion of the vacancy level above the Fermi energy is raised from 0.02 eV to nearly 0.1 eV , while the bands, around -1 eV , are strongly perturbed. The LDOS for the level around -0.7 eV (Fig. 3) is mainly localized on the tri-coordinate nitrogen but it also spreads over the nanotube atoms near the adsorption site, revealing re-hybridization between nicotine and SWCNT levels.

In the “Vacancy 3” scheme the system presents a well defined and very stable adsorption site revealed by a global minimum in all SECs, as shown in Fig. 4g–i. All EBs are about 1 eV and the $N_{\text{Nicotine}}-C_{\text{Nanotube}}$ distance is only 1.36 \AA . This last distance is com-

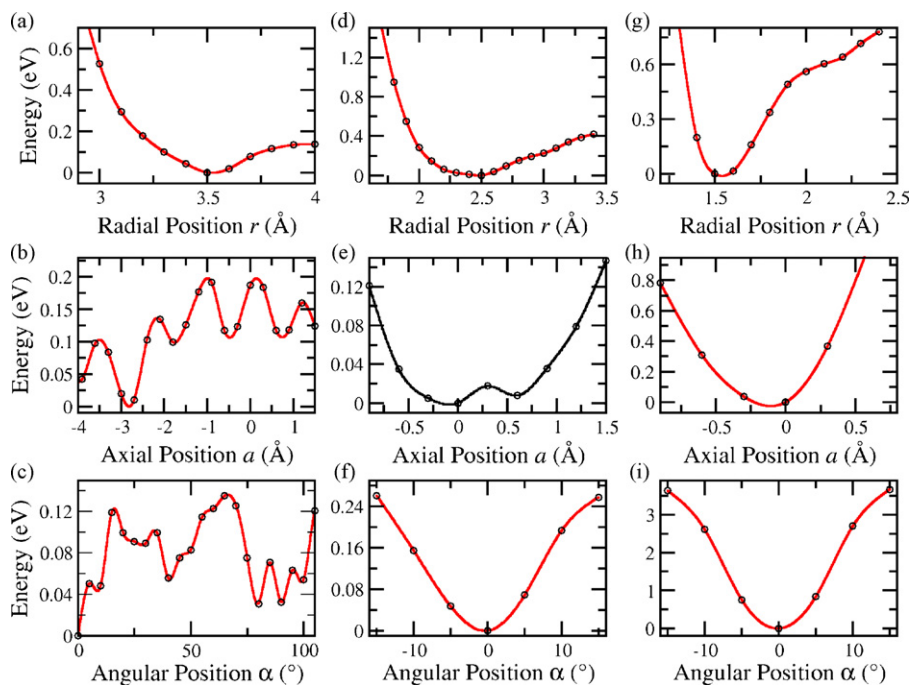


Fig. 4. SEC curves for radial, axial and circumferential directions for “Vacancy 1” (a–c), “Vacancy 2” (d–f) and “Vacancy 3” (g–i) conformations, respectively.

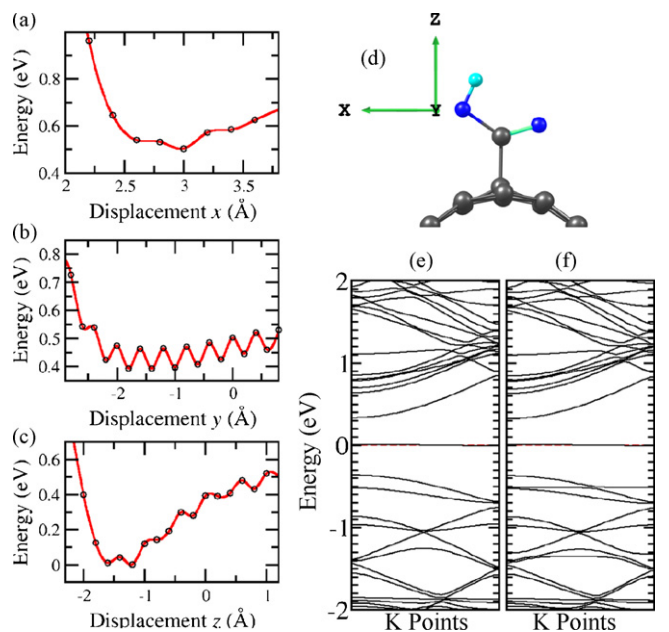


Fig. 5. SEC curves (a–c) for “Carboxyl” conformation along three mutually orthogonal axes (d) and electronic band structures for the carboxylated (8,0) SWCNT (e) and for the “Carboxyl” conformation (f), respectively.

comparable to the others C–N bond length involving this nitrogen in the isolated molecule, which are 1.34 Å. The binding energy between tube and molecule is -2.74 eV while nicotine presents a strong donor character transferring $0.39e^-$ to the tube, characterizing a chemisorption process. The electronic structure shows that the double degeneracy from the nicotine valence band is broken and a large charge transfer to the tube shifts down by about 0.4 eV (Fig. 3g). The nicotine molecule interaction increases to 0.2 eV the dispersion of the original vacancy level. Below the Fermi energy a localized level is observed, mainly, on the dangling bonds SWCNT atom, as can be seen in the LDOS (Fig. 3g).

Carboxylated SWCNTs have been used as sorbents for nicotine and tar [18]. In order to see how a carboxylated SWCNT influences the interaction with nicotine molecule we simulate the conformation labeled as “Carboxyl”. For this case the three SECs (Fig. 5a–c) were constructed with steps of 0.2 Å along of the three coordinate axes for the nicotine displacement from the O atom of the carboxyl group (Fig. 5d). In the preferential interaction site, the d_{CM} value was 4.07 Å, while the d_{a-a} distance (between the O from carboxyl and an H atom from nicotine) was 2.38 Å. The d_{CM} value is significantly greater than the corresponding values in the “Pristine 1,2” and “Vacancy 1,2” cases (Table 1), where there is no chemical bond.

The binding energy was found to be -0.34 eV and an amount of $+0.05e^-$ was transferred from the molecule to the tube (Table 1). These values reveal a slightly less intense interaction compared to the “Pristine 1” conformation and notably weaker than the “Vacancy 1,2” cases. The effect of nicotine on the electronic band structure of the carboxylated SWCNT is the introduction of a flat level around -0.5 eV (Fig. 5e and f).

4. Conclusions

The calculations predict that nicotine presents a more strong interaction with SWCNTs containing a single vacancy rather than with pristine or carboxylated tubes. Nicotine adsorbs over the perfect SWCNT surface through a physisorption process and the simulations indicate that this interaction is mediated by the tri-coordinated nitrogen atom from the molecule. For the SWCNTs containing a single vacancy the interaction depends on the

molecule arrangement over the tube surface resulting in either physisorption or chemisorption regimes. This conclusion is based on the considerable values for binding energies and reduced freedom of movement for nicotine over nanotube surface. The resulting systems suggest that SWCNT, in pristine or defective form, can be used as nicotine sensors due to the sensitivity of the electronic levels around the Fermi energy.

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