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Carbon Dioxide Adsorption on Doped Boron Nitride Nanotubes

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Abstract

Boron nitride nanotubes are promising structures as far as gas adsorption process is concerned. Electronic and vibrational properties of pristine and cobalt doped single walled boron nitride nanotubes of different chiralities interacting with a carbon dioxide molecule are investigated through the use of the Density Functional Theory and the Discrete Variable Representation method. When compared to similar simulations concerning carbon nanotubes, a stronger interaction is observed between the carbon dioxide molecule and the functionalized BN nanotube. Density of state investigation suggests that the doping induces major changes in the electronic structure pattern in the sense of critically reducing the original gap. From the vibrational point of view, we note that the zig-zag chirality tends to present higher values of vibrational frequencies for most of the states considered regardless of the nanotubes being doped or not. Our results suggest that doped zig-zag BN nanotubes are among the best possible candidates for adsorption purposes.

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I. INTRODUCTION

Due to the current dependence of the global community on fossil fuel as a source of energy, a constant rise on the carbon dioxide (CO_2) level measured on the atmosphere is observed. This behavior has greatly contributed to the greenhouse effect, that in turn implies on sudden and undesired climate and environmental changes in our planet.[1] In order to overcome, or at least to minimize this deleterious effect, an urgent need to develop efficient and low cost carbon sequestration systems is in course.

Currently, the scientific community agrees that such systems must have, among other properties, high surface to volume ratio, chemical and mechanic stability, high electronic conductivity as well as a good catalytic performance. Taking these properties into account, carbon nanotubes (CNTs) stand out as natural gas sensors candidates[2] to be then used as carbon sequestration systems. In this sense, some success has been obtained in detecting and arresting several molecular species (CO_2 included) through the use of this kind of system.[2–9] As a matter of fact, we have recently performed a thorough investigation of the CO_2 adsorption mechanism on cobalt functionalized CNTs.[10] It is shown that, from the theoretical point of view, functionalized CNT are indeed good candidates to be used as CO_2 gas sensors, but we also noticed that their sensibility depends on the chirality and the diameter of the system. This feature agrees with the experimental observation that CNTs synthesized by different means may present completely different electronic properties depending on geometrical characteristics.[11] Since controlling these properties is still a challenge for the industry, obtaining suitable CNTs to be used as carbon arresting systems in large scale is currently an unresolved issue. As an alternative route, boron nitride nanotubes (BNNTs) have recently received great attention from the scientific community. As a nanostructure representative, BNNTs also presents a good surface to volume ratio but unlike CNTs, they tend to exhibit uniform electronic properties regardless of the diameter, chirality and number of layers considered. Add that to the high oxidation and thermal resistances observed,[12] greater chemical stability when compared to CNT,[13] and fair temperature conductivity[14] and one has an interesting class of system to nanotechnology applications particularly in harmful and oxidative environments in which CNT would not be so efficient.[4] Despite all these favorable properties presented, several studies have established that the doping of BNNTs with transition metals further improve their performance of detecting and adsorbing molecular species. Recent works have shown that the ability of gallium and aluminum doped BNNTs to chemically adsorb CO , NH_3 and SCN molecules is greatly increased in relation to that of the pristine nanotube.[15–17] In the same fashion, other study proposed that platinum doped BNNTs might increase the capacity of adsorbing hydrogen molecules.[18] As far as the CO_2 adsorption in BNNTs is concerned, a recent theoretical investigation conducted by Mousavi and co-workers has proposed that, depending on the adsorption site, the system would turn into either a donor or an acceptor type semiconductor with reduced gap.[19] This study applied a random tight-binding hamiltonian model together with the Green Function methodology to perform a systematic investigation of the adsorption effects of a CO_2 specie over the density of states of a zig-zag BNNT (9,0). Their results are expected to hold valid for other systems. Concerning the effects of functionalization, it has been reported that by doping a BNNT with Boron atoms, [20] a chemisorption energy higher than that of free molecules at room temperature is achieved. According to this work, it is thus, theoretically possible to arrest CO_2 at ambient conditions. Similarly, Sun *et al.* studied the CO_2 adsorption on platinum doped armchair BNNT. Regardless the substitutional site for the platinum atom being of a nitrogen or boron, once again a reduction of the band gap was observed together with a considerable charge transfer between the doped BNNT and the CO_2 molecule.

Considering those works as a background, one can see that the CO_2 adsorption on BNNTs is not fully described, and thus a complete understanding on the influence of many properties over the adsorption mechanism is desired. Therefore, the motivation of this study was due to the fact that there is little information in the literature regarding the effects of chirality in the CO_2 adsorption on functionalized BN nanotubes. It is our goal to perform a detailed study, not only on the effects of functionalization over the carbon dioxide adsorption, but also on the role played by chirality and the influence of the active site of adsorption. In order to do so, we performed a systematical investigation on the electronic structure (in the scope of the Density Functional Theory — DFT — within the Generalized Gradient Approximation) and on the rovibrational spectra (solving the nuclear Schrödinger equation by means of the Discrete Variable Representation) of pristine and doped BNNTs interacting with a CO_2 molecule in different sites. Our goal is to investigate how the adsorption mechanism differs from that of CNNTs previously studied. We also seek to investigate whether there is a difference on the adsorption properties depending on the considered active site.

This work is organized as follows: in section II we describe the main computational features together with the methods used; section III presents the main results and the description of our calculations; we outline the conclusions in section IV.

II. METHODOLOGY

Our density functional theory calculations consist on CO₂ adsorption on boron nitride nanotubes of infinite length on a 1D periodic box using the DMol³ code.[21, 22] The goal is to compute equilibrium geometries, total energies, charge and electronic density analysis for these complex systems. Electronic exchange correlation was treated using generalized gradient approximation (GGA) [23] with the PW91 functional.[24] The positions of all the atoms were fully relaxed until the following convergence criterions are achieved: 10⁻⁶ Ha for total energy, 0.001 Ha/Å for the force and 0.003 Å for the displacement. The electronic wave functions were expanded in a 4.4 version double numerical plus polarization basis set (DNP) truncated at a real space cut-off of 4.1 Å.

Due to the presence of boron and nitrogen atoms in the models, all calculations were spin unrestricted. A 0.005 Ha smearing[25] and 6 Pulay direct inversion of the iterative subspace (DIIS)[26] was applied to the system to ease the convergence of the electronic structures. 3D periodic boundary conditions were applied to the whole system in order to simulate infinitely large BNNTs. The size of the vacuum space in-between two adjacent tubes was set to be 20 Å to prevent the interaction of atoms with their periodic images. The Brillouin zone for a single cell was sampled by 1 × 1 × 11 special k-points.

In order to compute the adsorption energy of the CO₂ molecules onto the BNNTs from the quantities obtained through our simulations we adopted the following expression:

$$E_b = E_{BNNT+CO_2} - E_{BNNT} - E_{CO_2}, \quad (1)$$

where $E_{BNNT+CO_2}$, E_{BNNT} , and E_{CO_2} are the total energies of the complex, the pristine nanotube and the free CO₂ molecule, respectively. To analyze the adsorption energies we need similar diameters to study only the substitutional effects. The charge distribution of the system was analyzed by the Mulliken method.[27]

In this work we performed several single point DFT calculations for varying distances between the CO₂ molecule and each considered BNNT. We thus obtained a set of points consisting of our potential energy curve — PEC — that we fit in an analytical expression through the use of a Extended Rydberg[28] function of the type:

$$V(R) = -D_e \left[1 + \sum_{k=1}^{n=10} c_k (R - R_e)^k \right] e^{-c_1(R-R_e)}, \quad (2)$$

where D_e stands for dissociation energy, R_e for equilibrium distance — both of which were fixed prior to the fittings to happen — and c_k are the coefficients to be determined (in this work, they were obtained by Powell's method[29]). It is important to note that, for R_e to be used, we have to establish different definitions for this equilibrium distance, depending on the system to be doped or not. In this sense, R_e refers to the equilibrium distance between the carbon atom of the CO₂ molecule and the nitrogen atom for the pristine BNNT (5,5). Similarly, this equilibrium distance is defined from the same carbon atom of the CO₂ and the center of the hexagon for the pristine BNNT (10,0). When doped BNNTs are considered, R_e stands for the distance between the carbon dioxide molecule and the substitutional cobalt atom. The CO₂ molecule interacting with the nanotube is treated as a body of reduced mass, thus the treatment of vibration and rotation in this case refers only to the internal modes.

By fitting our electronic energy results with Extended Rydberg functions (Equation 2), we were able to obtain novel analytical expressions for the several considered systems to be used in the solution of Schrödinger nuclear equation through the application of the DVR methodology[30] and, in this fashion, to obtain rovibrational energies $\mathcal{E}(v, J)$, where v and J respectively denote the vibrational and the rotational quantum numbers. From these energies one can obtain rovibrational spectroscopic constants using the following equations[31]

$$\begin{aligned} \omega_e &= \frac{1}{24} [14(\mathcal{E}_{1,0} - \mathcal{E}_{0,0}) - 93(\mathcal{E}_{2,0} - \mathcal{E}_{0,0}) + 23(\mathcal{E}_{3,0} - \mathcal{E}_{1,0})] \\ \omega_e x_e &= \frac{1}{4} [13(\mathcal{E}_{1,0} - \mathcal{E}_{0,0}) - 11(\mathcal{E}_{2,0} - \mathcal{E}_{0,0}) + 3(\mathcal{E}_{3,0} - \mathcal{E}_{1,0})] \\ \omega_e y_e &= \frac{1}{6} [3(\mathcal{E}_{1,0} - \mathcal{E}_{0,0}) - 3(\mathcal{E}_{2,0} - \mathcal{E}_{0,0}) + (\mathcal{E}_{3,0} - \mathcal{E}_{1,0})] \\ \alpha_e &= \frac{1}{8} [-12(\mathcal{E}_{1,1} - \mathcal{E}_{0,1}) + 4(\mathcal{E}_{2,1} - \mathcal{E}_{0,1}) + 4\omega_e - 23\omega_e y_e] \\ \gamma_e &= \frac{1}{4} [-2(\mathcal{E}_{1,1} - \mathcal{E}_{0,1}) + (\mathcal{E}_{2,1} - \mathcal{E}_{0,1}) + 2\omega_e x_e - 9\omega_e y_e]. \end{aligned} \quad (3)$$

III. RESULTS AND DISCUSSION

In this work, we investigate the interaction process between pristine and functionalized BNNTs and a carbon dioxide molecule. We used single walled armchair (5,5) and zig-zag (10,0) nanotubes to carry out a comparison between the effects of chirality over the adsorption mechanism. Also, we investigated properties such as adsorption energy and rovibrational spectra, between the gas molecule and the pristine or cobalt doped nanotube. The goal is to provide an understanding of how the functionalization affects the interaction process.

In order to better present our results we organized the present section into three subsections, each one dealing with one set of simulations. Subsection III A regards the adsorption mechanism of the CO₂ molecule in pristine BNNTs. In subsection III B we investigate the very effect of the functionalization of the BNNTs with cobalt. Finally, subsection III C is devoted to investigate the adsorption of CO₂ molecules in functionalized BNNTs.

A. Pristine BNNTs interacting with a CO₂ molecule

In this subsection we discuss the adsorption phenomenon of CO₂ molecule in pristine BNNTs of different chiralities, namely armchair (5,5) and zig-zag (10,0). The first step on accomplishing this task was to perform the optimization of the CO₂ molecule separately from that of the BNNT (5,5) with its 60 atoms and of BNNT (10,0) with its 80 atoms.

The geometry optimization yielded a C · · · O bonding length of 1.166 Å for the carbon dioxide molecule, which is in good accordance with previous results.[32] Similarly, geometric results concerning solely the nanotubes reached excellent agreement with previously published results.[33, 34] By using the Mulliken method, the charge analysis performed on the armchair nanotube indicated that roughly 0.61e of charge was transferred from the boron atom in the nanotube to the nearby nitrogen sites. As for the zig-zag system, this ratio was observed to be of smaller magnitude as 0.54e of charge was transferred between the B and the N centers. This fact emphasizes the quasi-ionic nature of the B—N bonding in BNNTs. From the density of states (DOS) point of view together with the band structure analysis, we observed an indirect gap of 4.45eV for the (5,5) system and a 4.03eV direct gap for the (10,0), values that present good agreement with data from the literature.[33, 34]

The next step on tackling the adsorption mechanism was to perform the geometry optimization of the complex system composed of CO₂ molecule together with the nanotubes. Figure 1 presents frontal and side view for the equilibrium configuration

of the two different systems studied in this work, namely CO₂ + BNNT (5,5) (1 a and b) and CO₂ + BNNT (10,0) (1c and d). It is important to note that, for both cases, neither the CO₂ nor the nanotube present structural/geometrical variations when compared to their original equilibrium configuration reached when the optimization was performed separately.

From Figure 1 the most energetically favorable relative configuration of CO₂ + BNNT (5,5) system is the gas molecule aligned parallel to the nanotube axes with the carbon atom of the CO₂ molecule standing directly over the nitrogen atom of the nanotube. This configuration can be explained in terms of the polar character of the B—N bonding, that results in a higher electron concentration over nitrogen atoms when compared to boron. Naturally, these facts directly follows from electronegativity considerations between the atomic species. Thus, one might expect the carbon atom from the gas molecule that, incidentally, presents low electron concentration, to approach the nitrogen center. In the case of the CO₂ + BNNT (10,0) system, the configuration is with the carbon atom of CO₂ directly over the center of the hexagon in the nanotube wall. The CO₂ molecule has a rotation of 38° from its original orientation around its symmetry axis. After this rotation one of the oxygen atoms stands right above a boron atom. In this case, the curvature of the B—N binding in the zig-zag BNNTs plays an important role in the orientation of the molecule relative to the axis of the nanotube, as observed in previous work.[35] Taking the optimized geometry of complex systems, the PEC calculations were carried out. The procedure was to systematically approach the CO₂ molecule to the nanotube and to compute the corresponding energies, as well as other properties, but always maintaining the subsystems (CO₂ and nanotube) geometrically frozen. The main purpose of this work is to analyze the nanotube-CO₂ interaction by applying Equation 1 to obtain the adsorption energy. Table I presents the equilibrium distances between the closest atom of BNNT and carbon of CO₂ (D), adsorption energies (E_{ads}), energy gap (E_g) and charge transfer ratio (Q_T) for the BNNT-CO₂ complex system in the two different chiralities considered. One can readily see that the optimized configurations present small binding energies, indicating a poor process of CO₂ adsorption in BNNTs, that can be characterized as a physical adsorption that takes place through the mediation of Van der Waals type interactions. It is important to remark that the results obtained in this subsection are indeed in good agreement with the well known fact that BNNTs are structures with a high level of stability, thus being chemically inert in the absence of dopants.[10]

The comparison between the values obtained for E_{ads} and Q_T between armchair and zig-zag BNNTs present a subtle difference of, respectively 0.02 eV and 0.002 e favoring the former. From Table I, no difference between the gap energy is achieved when solely considering the adsorption mechanism, which indicates that the presence of the adsorbed molecule does not affect the electronic properties of pristine BNNTs.

B. Functionalizing BNNTs with Cobalt

We have seen that the interaction between the carbon dioxide molecule and the pristine BNNTs is of a very weak nature, corresponding to a physical adsorption. Since our goal is to provide a good candidate to carbon arresting system, this interaction must be strengthened. In order to do so, we functionalized the nanotube through a substitutional doping with a cobalt atom. Because of the very nature of BNNTs, one should expect a different behavior depending on which is the substituted atom on the nanotube lattice, i.e., boron or nitrogen.

Considering n and m the indexes that take chirality into account, when a cobalt atom substitutes a boron atom, we used the notation $\text{BNNT}(n,m)\text{Co}_B$. Alternatively, when the substituted atom is nitrogen, used the notation $\text{BNNT}(n,m)\text{Co}_N$. A new complete geometry optimization was performed for the system composed of BNNT with the substitutional Co atom. The optimized geometries for doped BNNTs are presented in Figure 2, in which the geometric configuration for the cobalt atom related to the adjacent boron and nitrogen species are highlighted for both chiralities. One can readily see that the geometrical structure of doped BNNTs is modified. Particularly, the cobalt atom is projected outside the nanotubes wall, due to its great size related to the rest of the chain.

One can see that for both $\text{BNNT}(5,5)$ and $(10,0)$, substituting a nitrogen atom causes a larger geometric deformation on the nanotubes in relation to the boron substitution. This fact is confirmed by noting that the average length of the Co—N bondings around 1.70 Å, which is smaller than the Co—B length of roughly 1.90 Å. Therefore, substituting a boron atom yields a smaller difference on the binding length related to typical B—N of 1.45 Å for the pristine nanotube. It is important to note that these geometrical deformations lead to important changes in the electronic properties for the nanotubes.

Figure 3 is a density of states (DOS) for calculated nanotubes that show how the addition of a cobalt atom affects the electronic distribution of BNNTs. Adding a cobalt atom to the BNNTs induces the appearing of some impurity states near the Fermi level, thus resulting in a gap decrease (Figure 3). Particularly, for $\text{BNNT}(5,5)\text{Co}_B$ the appearing of a state at the end of the valence band reduces the original gap to 2.57eV. In the case of $\text{BNNT}(5,5)\text{Co}_N$ we should stress the appearing of three states, two of those on the end of the valence band and the other on top of the conduction band. In this case, the energy gap is even further decreased to 1.63 eV. $\text{BNNT}(10,0)\text{Co}_B$ shows a similar pattern as $\text{BNNT}(5,5)\text{Co}_B$, thus presenting a final gap of 2.13 eV. However, for the zig-zag nanotube it is observed an electronic state much closer to the valence band. $\text{BNNT}(10,0)\text{Co}_N$, on the other hand, presents a whole different behavior when it comes to the functionalization induced change of density of states. In this case, states next to the conduction band together with a gap reduction to 2.13eV were obtained. The partial DOS reveals that these impurities states are mainly due to the electrons of the cobalt atom and the π electrons of the three cobalt neighbors in the BNNTs.

The Mulliken charge analysis indicate that a certain amount of electrons is transferred from the cobalt center to the BNNT. It is important to note that, for both chiralities, the amount of charge transferred in the case of $\text{BNNT}(n,m)\text{Co}_N$ is smaller than in the case of $\text{BNNT}(n,m)\text{Co}_B$. This can be explained by remembering that the electronegativity of nitrogen is larger than that of boron, therefore leading the former to attract cobalt.

C. Cobalt Doped BNNTs Interacting with CO₂ Molecule

The equilibrium configurations for the optimized geometries of different simulations are depicted in Figure 4. We have found a difference compared to the non-doped structure: the optimized geometry yields a symmetry breaking of the CO₂ molecule for all the cases, i.e., the gas molecule changes from a linear to a bent configuration. This trend is related to a chemical adsorption process because the bent structure is expected in the case of highest binding energy.

Table II presents a comparison between E_{ads} , D , E_g and Q_T values for the cobalt doped BNNTs interacting with CO₂. The first interesting feature to be noted is that the presence of cobalt atoms significantly raises the adsorption energy for all complexes.

Either for the $\text{BNNT}(5,5)$ or for $\text{BNNT}(10,0)$ the substitution of a nitrogen for a cobalt atom yields larger values for the adsorption energy than the correspondent substitution of a boron atom. The 1.02eV energy obtained for $\text{BNNT}(5,5)\text{Co}_N\text{-CO}_2$ is 0.86eV larger than the $\text{BNNT}(5,5)\text{-CO}_2$ case, indicating that the interaction of the carbon

dioxide molecule with this functionalized armchair tube is far superior than that of the pristine system. The equilibrium distance between the carbon and cobalt atom was observed to be of 1.90 Å, which, together with the energy values, suggest a strong chemical interaction between the species. Table II also shows that the charge transfer between BNNT(5,5)Co_N to the CO₂ molecule is of 0.156 e and that the energy gap is reduced from 1.63 eV to 0.87 eV, indicating that the electronic properties of free BNNT(5,5)Co_N are drastically changed after the adsorption process takes place. The BNNT(5,5)Co_B-CO₂ configuration presented an interaction distance of 2.0 Å and a charge transfer ratio of 0.057, thus consisting in a much poorer candidate to adsorbing system. Note that this configuration yielded smaller values of adsorption energy than the previous case of BNNT(5,5)Co_N.

An even more interesting result is observed when considering the simulations for BNNT (10,0). Considering the functionalized BNNT(10,0)Co_N both the carbon and the oxygen atoms of the molecule simultaneously interact with the cobalt atom in the nanotube. The C—Co distance was of around 1.95 Å whereas the O—Co was 1.87 Å. The obtained adsorption energy was of 2.54 eV, which is 1.52 eV larger than the one for BNNT(5,5)Co_N-CO₂, indicating that for this dopant, the zig-zag chirality is more efficient than the armchair in the capture of CO₂ molecule. It is important to note that this values for adsorbing energy is far superior than those for single walled carbon nanotube similarly doped.[15] This remarkable results indicate that BN nanotubes are better suitable candidates for CO₂ arresting when compared to carbon nanotubes, which gives 0.12 eV of adsorption energy.[10] The charge transfer between the molecule and the nanotube was of 0.247e, demonstrating the chemical bonding character obtained in these cases. Due to the reduction from 4.03 eV to 1.00 eV of the gap, we can see that substituting nitrogen by cobalt provides the nanotube with electronic transport properties that were absents in the previous case. For the case of BNNT(10,0)Co_B-CO₂ a 0.67 eV value is achieved for the adsorption energy, and 0.065 e for the charge transfer. These values are superior to those presented for the BNNT(5,5)Co_B-CO₂ system, what confirms our previous statement about the the zig-zag chirality being more effective than the armchair in the present case. These results are in accordance to the recent study of carbon nanotubes showing that the zigzag chirality present high adsorption energies than the armchair.[10]

In order to full understand the electronic properties of the complex systems composed of functionalized BNNTs interacting with the carbon dioxide molecule, we make use of the total charge density and the density of electronic states. Figure 5 presents an isosurface calculation for the total density of the most stable geometrical configuration of each chirality. As shown, for the pristine BNNTs, the electronic density of the tube is isolated to that of the molecule. In this case, no considerable charge overlap is perceived, thus confirming the weak interaction between these species. This situation is in striking contrast to the one observed when the tubes are functionalized. In this case, a considerable overlap of the electronic density between the nanotube and the molecule is observed, indicating a strong interaction between the correspondent orbitals and a clear electronic flux from the tube to the molecule. Focusing on BNNT(5,5)Co_B, the charge superposition involves only the carbon atom and presents itself as a carbon coordination.[36] In the case of BNNT(10,0)Co_N, the charge overlap also involves the oxygen atom, thus consisting on a side-on coordination. We believe that the coordination of CO₂ on Co is stabilized mainly due to electrostatic interactions and back-bonding process, in the same fashion as reported by Morokuma *et. al* for N₂ complexes.[36]

We present, in Figure 6, the DOS comparison for all the configurations considered in this work. The DOS for pristine BNNTs interacting with the CO₂ molecule did not present any considerable change when compared to the case in which the nanotubes are isolated (Figure 3). This means that the electronic properties of BNNTs are not influenced by the presence of the CO₂ molecule, which is another manner to state the poor interaction between the species in this case. BNNT(5,5)Co_N-CO₂ shows an electronic state at the end of the valence band along with another one on the top of the conduction band. For the BNNT(10,0)Co_N-CO₂, the same tendency was observed. Figure 6 shows a decrease of DOS intensity after CO₂ interaction compared to Figure 3 without CO₂, for all cases. Furthermore, we found a shift of bands near the Fermi level towards lower energies. This behavior is probably due to the interaction of empty Co "d" originated from the cobalt atom and of the π electrons from the CO₂ molecule in the gap region of the nanotubes. This new configuration positively affects the chemisorption capacity of the nanotubes, thus improving their reactiveness with the gas molecule.

An interesting feature of the DOS plots is the Fermi level shifting towards lower energies caused by the Co doping found in the BNNT (5,5). This shifting is a direct consequence of cobalt substitution in the nanotube. This is probably due to the charge transfer from the cobalt atom to the neighbor atoms of the nanotube. However, this shift occurs differently for both substitutions: 0.90eV and 0.35eV for BNNT(5,5)Co_B and BNNT(5,5)Co_N, respectively. In this case a charge transfer of 0.016a.u. for BNNT(5,5)Co_B and 0.019a.u for BNNT(5,5)Co_N was observed. The same trend was also verified in the BNNT(10,0)Co_B and BNNT(10,0)Co_N, in which the values were of 1.02eV and 0.40eV, respectively. A charge transfer of 0.40a.u. for BNNT(10,0)Co_B and 0.34a.u for BNNT(10,0)Co_N took place. For the nanotubes interacting with CO₂ molecule, the Fermi level was shifted towards lower energies, considering that there is a charge transfer from the nanotube to the CO₂ molecule. The shift was of 0.38 eV for BNNT(5,5)Co_B, 0.66 eV for BNNT(5,5)Co_N, 0.39 eV for BNNT(10,0)Co_B and 0.90 eV for BNNT(10,0)Co_N.

Figure 7 presents the adsorption energy curve as a function of the equilibrium distance for the complex

BNNT(*n,m*)Co-CO₂. Through all the cases, the curves are constructed taking the cobalt to carbon distance into account. The considered distances were taken from the strong repulsion to the asymptotic region of the potential. It is important to note that the PEC was carried out using frozen structures. These curves were used in determining the vibrational spectrum of all the considered tubes. We should also remark that the high energy of the wall obtained for BNNT(10,0)+Co_N-CO₂, also demonstrates that this is a system with great potential of applicability in a chemisorption process.

van der Waals corrections were carried out for all studied systems. We have found a contribution of van der Waals correction (Table I) for the physical adsorption. In the other hand, chemical adsorption energies shows a small contribution of vdW correction (Table II). Furthermore, the difference of pristine and doped BNNTs adsorption energies, showed the same trend with or without vdW correction (Table III).

The Nuclear Schrödinger Equation was solved using the analytical form of the potential obtained using the data of Table IV. Through this formalism we investigate the vibrational spectra of the system and, as a consequence, the spectroscopic constants.

Table V presents the results of the 11 first vibrational states for the pristine and cobalt doped complexes. It was found higher values of the vibrational energies for the doped systems when compared with the pristine BNNTs. We can also see that, typically, substituting the cobalt in the nitrogen site yields an even greater vibrational energy for all the cases when compared to the boron, regardless the chirality considered. Also, the zig-zag chirality presented greater values of vibrational frequency when compared with armchair. This result is consistent with this chirality presenting a potential well of greater depth than that of the armchair, as already mentioned. The electron transfer of backbonding strengthens the Co-CO₂ bonding and should be related to the increase of this bonding vibration.

By taking the differences between the rows of Table V for a given column, one can get the shift on the spectrum for each system. We thus obtain energy redshifts concerning transitions from the states listed in Table V. By carrying out this analysis one can note that the redshifts are accompanied by a shortening of the BNNTCo-CO₂ equilibrium distances. These result mean that pristine BNNT-CO₂ intermolecular interaction energies are weaker than that of BNNTCo-CO₂, due to the interaction of CO₂ molecule with Co and the nanotube. The redshifts obtained belong to far and mid-infrared portions of the electromagnetic spectrum, as expected for intermolecular interactions.

The first strikingly evidence to be observed is that the doping strongly affects the shifts in the sense of increasing their energies. This fact is expected from the deepening of the potential well, due to this doping, as previously observed in the PECs analysis. Another clear feature is that the transitions on the zig-zag chirality are more energetic than those of armchair. This happens to be true when we compare the same kind of functionalization. As far as functionalization is concerned, we can see that, for both chiralities, when the cobalt dopant substitutes the nitrogen atom, a higher energy shift pattern is observed. This fact is consistent with the other results.

Finally, by applying equations 3, we obtain the spectroscopic values for all the BNNT-CO₂ complexes in Table VI. From this table, it is possible to note that the BNNTCo-CO₂ vibrational frequency constants, ω_e , are greater than ω_e for the pristine BNNT-CO₂. This feature shows that in the BNNTCo-CO₂ complex, the frequencies are more harmonic than for the pristine BNNT-CO₂ complex. The BNNT-CO₂ and BNNTCo-CO₂ intermolecular rotation-vibration interaction constants (α_e and γ_e) are very small, which means the rotational and vibrational modes are little coupled. This is expected as the mass of CO₂ is negligible compared to the nanotube. We can also see that when cobalt substitutes a nitrogen in the nanotube, the frequency tends to be enhanced, a fact that, again, is consistent to our other results. These results are of major importance for future spectroscopic works, and are to be used for comparison whenever experimental and theoretical studies on carbon dioxide adsorption on carbon nanotubes are considered.

IV. CONCLUSIONS

In this work, we carried out DFT *ab initio* calculations within GGA to study the interaction of a CO₂ molecule with two different sites on the surface of pristine and doped BNNTs. Both the armchair (5,5) and the zig-zag (10,0) chiralities were investigated. We found that the CO₂ molecule interacts weakly with pristine

BNNTs through van der Waals like interaction. By carrying out the doping with a cobalt atom, a considerable increase on the binding energy between the CO₂ and the nanotube was noted. We developed a set of simulations to draw comparisons between the adsorption energy for the cobalt atom substituting either the nitrogen or the boron atom for both nanotubes chiralities. It was concluded that the most suitable system as far as adsorption energy is concerned is the doped zig-zag system in which the a nitrogen was substituted by the cobalt dopant. We noted that the BNNT(10,0)Co_N-CO₂ complex presented chemisorption states far superior than those observed for carbon nanotubes, whose data is present in literature[10]. The better quality of BNNTs when compared to carbon nanotubes, as potential candidates as gas adsorbants, were confirmed through DOS investigations, Mulliken charge analysis and also from the vibrational spectrum. As for this latter analysis, we noted vibrational frequencies of systematically

higher values than those for carbon nanotubes. These fact, together with advantages such as great chemical stability and ease of synthesis control that BNNTs present, leads to consider doped BNNTs as promising structures for the detection, capture and arresting of CO₂ molecules in different media. Therefore, we have shown that these systems are tools of significant importance on the challenge of developing an environmentally desired mechanism of carbon arresting.

V. ACKNOWLEDGEMENTS

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TABLE I: Binding energies, with and without vdW correction, E_g , equilibrium distances, and Q_T for pristine BNNT-CO₂ complexes.

System	E_{ads} (eV)	$E_{ads,vdW}$ (eV)	E_g (eV)	D (Å)	Q_T (e)
BNNT (5,5)-CO ₂	0.17	0.37	4.45	3.00	-0.003
BNNT (10,0)-CO ₂	0.18	0.42	4.03	2.95	-0.005

TABLE II: Binding energies, with and without vdW correction, gap energies, equilibrium distances and charge transfer for BNNTs—CO₂ complexes.

System	E_{ads} (eV)	$E_{ads,vdW}$ (eV)	E_g (eV)	D (Å)	Q_T (e)
BNNT(5,5)Co _B -CO ₂	0.61	0.79	1.63	2.00	-0.086
BNNT(5,5)Co _N -CO ₂	1.02	1.12	0.89	1.90	-0.180
BNNT(10,0)Co _B -CO ₂	0.67	0.87	1.50	2.10	-0.102
BNNT(10,0)Co _N -CO ₂	2.54	2.79	1.00	1.95	-0.247

TABLE III: Difference of pristine and doped BNNTs adsorption energies for BNNTs—CO₂ complexes.

System	ΔE_{ads} (eV)	$\Delta E_{ads,vdW}$ (eV)
BNNT(5,5)Co _B -CO ₂	0.42	0.44
BNNT(5,5)Co _N -CO ₂	0.76	0.85
BNNT(10,0)Co _B -CO ₂	0.44	0.49
BNNT(10,0)Co _N -CO ₂	2.37	2.36

TABLE IV: Fitting coefficients for the BNNTs—CO₂ potential energy curves.

Coefficients (\AA^{-k})	BNNT(5,5)	BNNT(5,5)Co _B	BNNT(5,5)Co _N	BNNT(10,0)	BNNT(10,0)Co _B	BNNT(10,0)Co _N
C ₁	0.4010528.10 ¹	0.5232746.10 ¹	0.4600582.10 ¹	0.4567201.10 ¹	0.6115366.10 ¹	0.7040093.10 ¹
C ₂	0.5030727.10 ¹	0.9369224.10 ¹	0.5677401.10 ¹	0.7005336.10 ¹	0.1441551.10 ²	0.1816739.10 ²
C ₃	0.1732614.10 ¹	0.1411859.10 ²	0.6954038.10 ¹	0.1063563.10 ²	0.1539079.10 ²	0.2356444.10 ²
C ₄	0.3538602.10 ¹	0.1262842.10 ²	0.6161214.10 ¹	0.1408899.10 ²	0.1261757.10 ²	0.2091481.10 ²
C ₅	0.1570261.10 ²	-0.1994591.10 ²	-0.1954557.10 ²	-0.1239502.10 ²	0.5521242.10 ²	0.1418446.10 ³
C ₆	-0.6353567.10 ¹	0.1075792.10 ²	-0.1865900	-0.5775726.10 ¹	0.3535850.10 ²	0.3083373.10 ²
C ₇	-0.2287133.10 ²	0.6586673.10 ²	0.5043954.10 ²	0.3746132.10 ²	-0.8246642.10 ²	-0.4739153.10 ³
C ₈	0.2267056.10 ²	-0.9270648.10 ²	-0.5766459.10 ²	-0.3842283.10 ²	0.7531488.10 ²	0.8008445.10 ³
C ₉	-0.7336704.10 ¹	0.4957445.10 ²	0.2504332.10 ²	0.1522006.10 ²	-0.2135814.10 ²	-0.4811759.10 ³
C ₁₀	0.7945204	-0.9315078.10 ¹	-0.3925971.10 ¹	-0.1905156.10 ¹	0.7613046.10 ¹	0.1169292.10 ³

TABLE V: Vibrational energies (cm^{-1}) for the BNNT(n,m)-CO₂ and BNNT(n,m)Co-CO₂ complexes.

ν	BNNT(5,5)-CO ₂	BNNT(5,5)Co _B -CO ₂	BNNT(5,5)Co _N -CO ₂	BNNT(10,0)-CO ₂	BNNT(10,0)Co _B -CO ₂	BNNT(10,0)Co _N -CO ₂
0	39.09	92.09	127.29	43.99	95.25	231.77
1	115.42	272.05	377.76	127.05	283.54	692.39
2	188.44	447.47	623.17	204.96	467.85	1148.42
3	258.23	618.96	863.90	279.28	648.51	1599.78
4	324.83	786.90	1100.29	350.96	825.74	2046.32
5	388.36	951.54	1332.61	420.49	999.62	2487.83
6	449.03	1113.02	1561.10	488.12	1170.11	2924.08
7	507.15	1271.39	1785.93	553.97	1337.08	3354.86
8	563.08	1426.68	2007.23	618.07	1500.38	3779.94
9	617.18	1578.86	2225.12	680.42	1659.85	4199.10
10	669.71	1727.90	2439.65	741.02	1815.35	4612.17

TABLE VI: Spectroscopic constants for the BNNT-CO₂ complexes.

Spectroscopic constants	BNNT(5,5)	BNNT(5,5)Co _B	BNNT(5,5)Co _N	BNNT(10,0)	BNNT(10,0)Co _B	BNNT(10,0)Co _N
$\omega_e (cm^{-1})$	79.6765	185.0764	255.9174	89.7255	192.6107	465.111
$\omega_e x_e (cm^{-1})$	1.6922	2.7222	2.8298	3.7563	2.2535	2.2221
$\omega_e y_e (cm^{-1})$	0.00965	0.10067	0.06572	0.26174	0.05768	-.01526
$\alpha_e (cm^{-1})$	0.0003	0.00163	0.0004	0.0012	0.0002	0.0003
$\gamma_e (cm^{-1})$	-5.2063.10 ⁻⁵	5.3221.10 ⁻⁵	1.8543.10 ⁻⁵	5.6580.10 ⁻⁵	-5.2871.10 ⁻⁵	-2.3347.10 ⁻⁵

FIGURE CAPTIONS

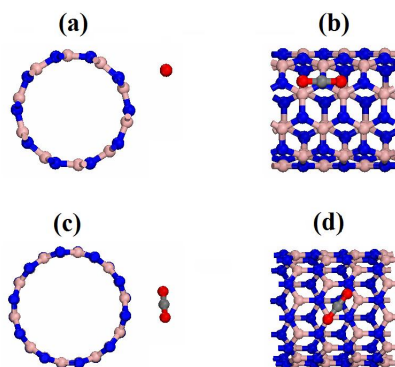


FIG. 1: Frontal and side view of the equilibrium distance for the BNNT—CO₂ complexes. (a) and (b) armchair BNNT(5,5). (c) and (d) zig-zag BNNT(10,0).

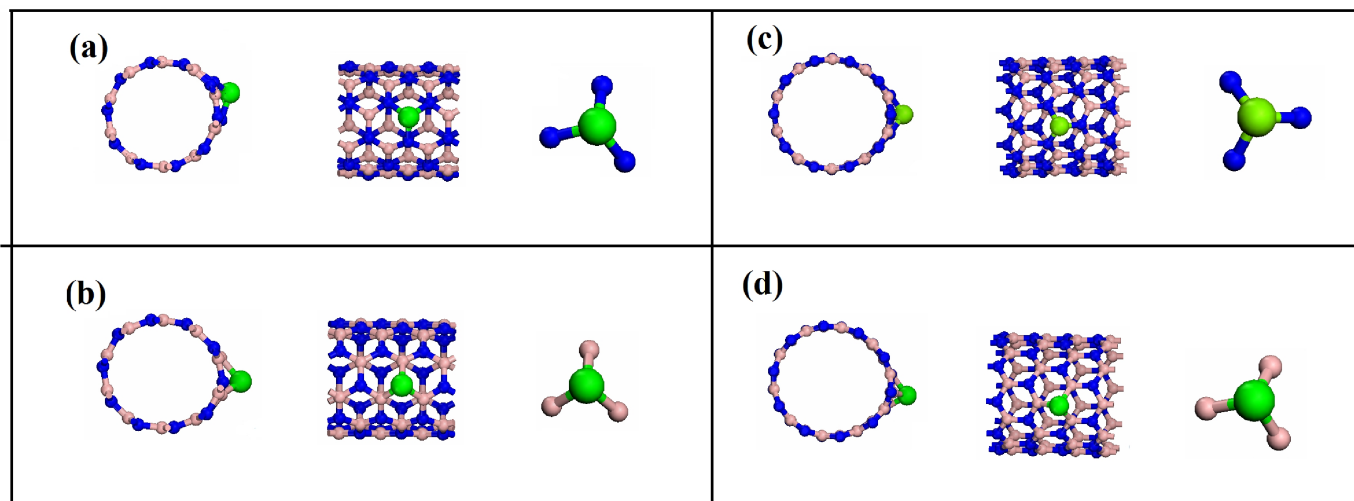


FIG. 2: Frontal and side view of the optimized geometries for cobalt doped BNNTs (a) BNNT(5,5)Co_B, (b) BNNT(5,5)Co_N, (c) BNNT(10,0)Co_B, (d) BNNT(10,0)Co_N. Geometric configuration for the cobalt atom is highlighted.

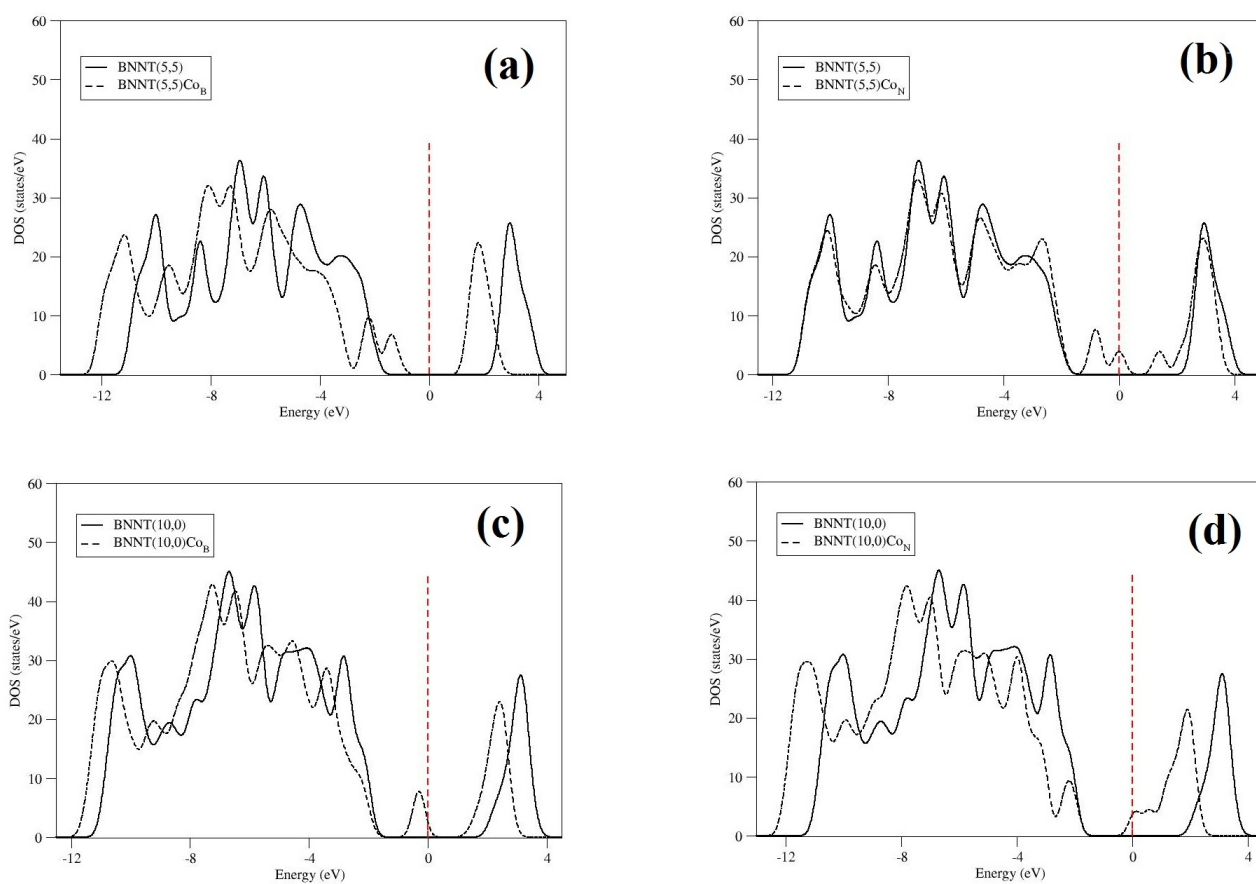


FIG. 3: DOS for pristine (solid line) and doped (dashed line) BNNTs. (a) BNNT(5,5)Co_B, (b) BNNT(5,5)Co_N, (c) BNNT(10,0)Co_B, (d) BNNT(10,0)Co_N.

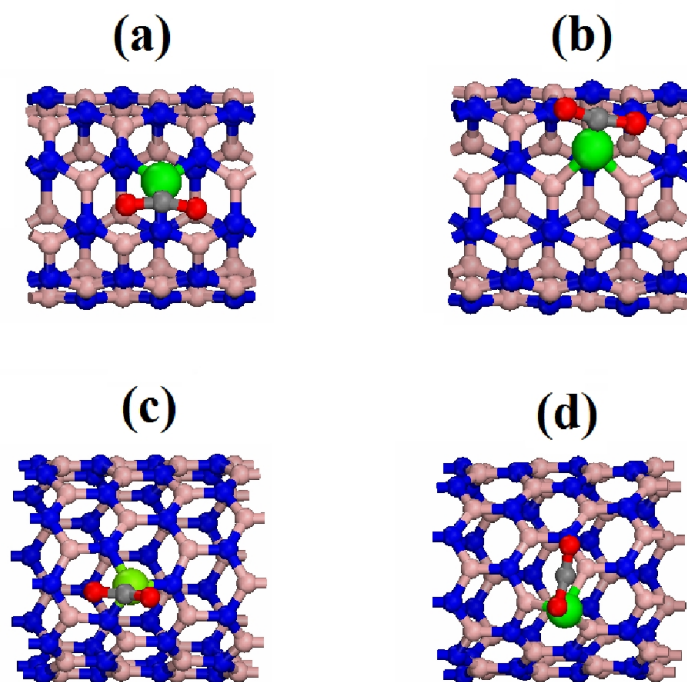


FIG. 4: Frontal and side view of the equilibrium configuration of the CO_2 related to cobalt doped BN nanotubes (a) $\text{BNNT}(5,5)\text{Co}_B$, (b) $\text{BNNT}(5,5)\text{Co}_N$, (c) $\text{BNNT}(10,0)\text{Co}_B$, (d) $\text{BNNT}(10,0)\text{Co}_N$.

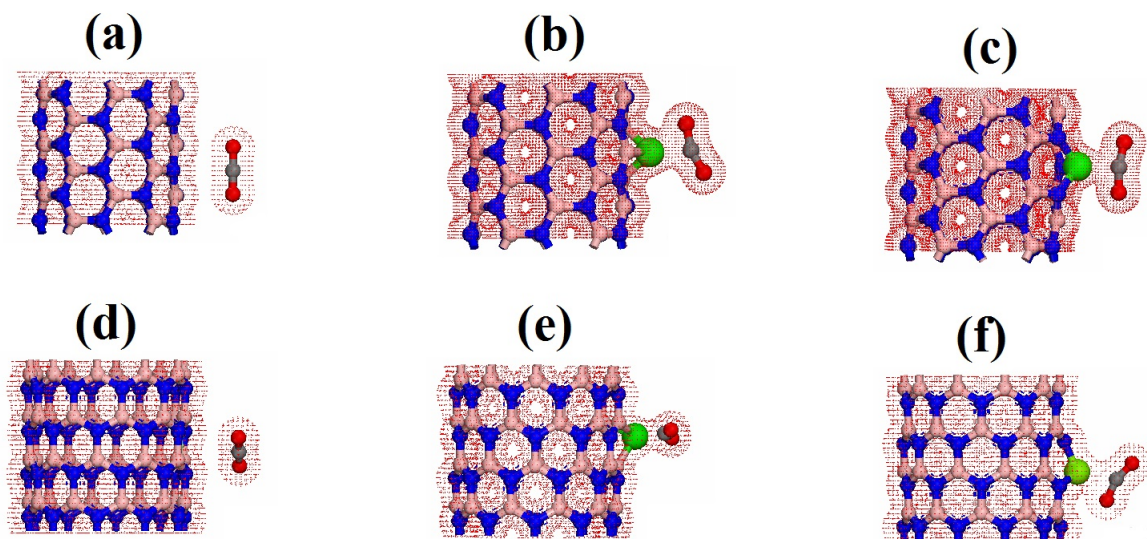


FIG. 5: Charge density for pristine and cobalt doped BNNT interacting with the CO_2 (a) $\text{BNNT}(5,5)$, (b) $\text{BNNT}(5,5)\text{Co}_N$, (c) $\text{BNNT}(5,5)\text{Co}_B$, (d) $\text{BNNT}(10,0)$, (e) $\text{BNNT}(10,0)\text{Co}_N$, (f) $\text{BNNT}(10,0)\text{Co}_B$.

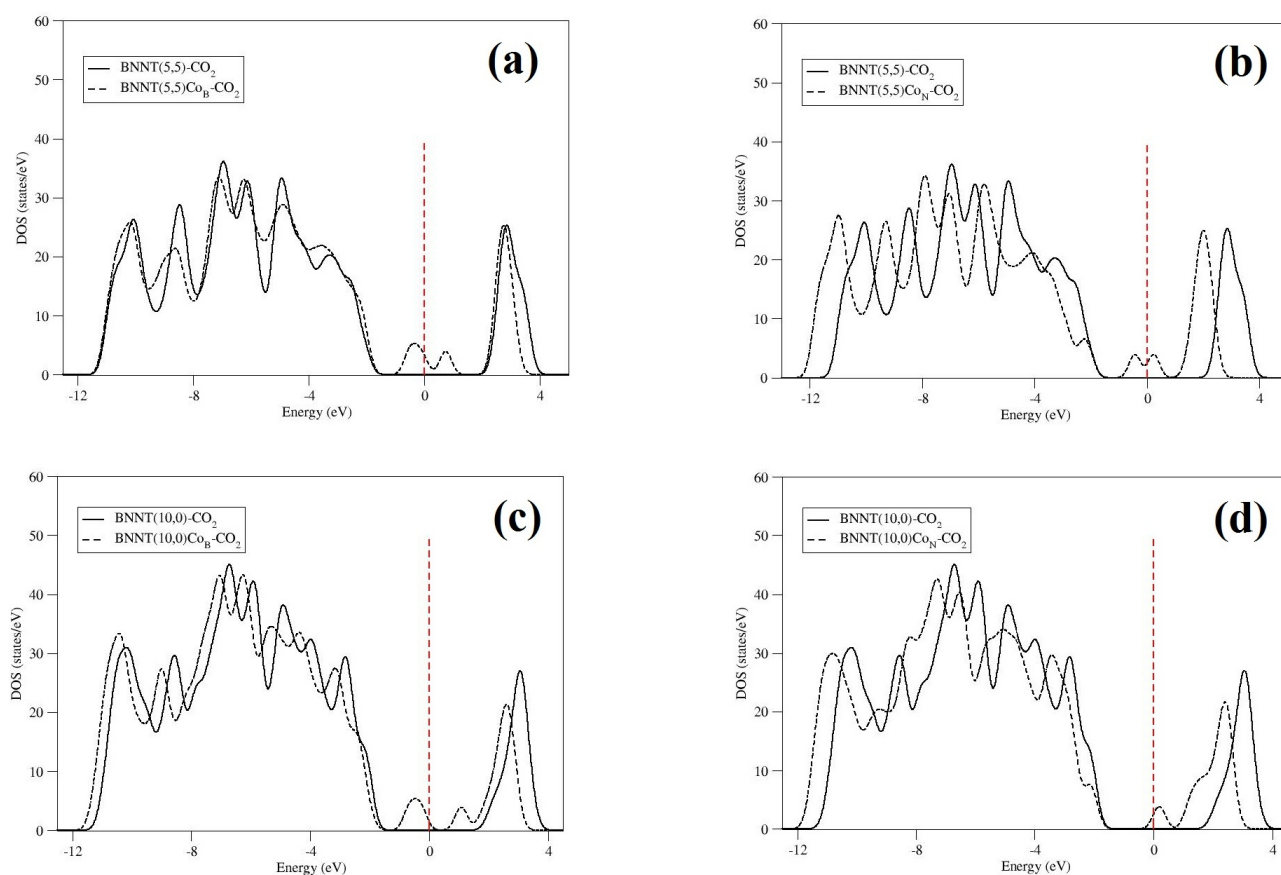


FIG. 6: DOS comparison for pristine (solid line) and doped (dashed line) BNNTs interacting with CO_2 . (a) $\text{BNNT}(5,5)\text{Co}_B$, (b) $\text{BNNT}(5,5)\text{Co}_N$, (c) $\text{BNNT}(10,0)\text{Co}_B$, (d) $\text{BNNT}(10,0)\text{Co}_N$.

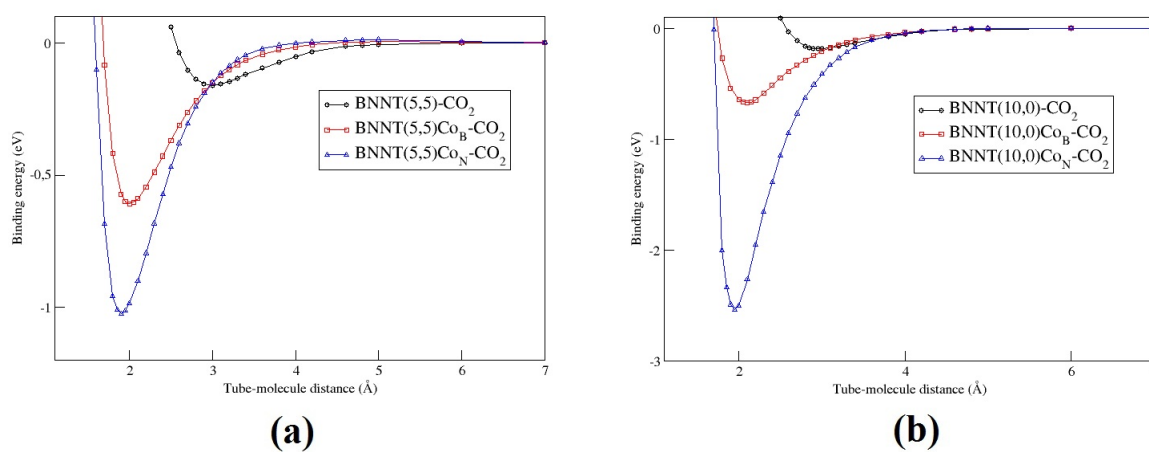


FIG. 7: Comparison between the PECs for pristine and doped BNNTs interacting with the CO_2 molecule. (a) $\text{BNNT}(5,5)$ e (b) $\text{BNNT}(10,0)$.