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Interaction of narrow carbon nanotubes with nitronium tetrafluoroborate salts

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(Received 24 January 2008; accepted 26 April 2008; published online 6 June 2008)

Density functional calculations have been performed to investigate the destruction of narrow carbon nanotubes (CNTs) under the attack of nitronium tetrafluoroborate salts. The dissociation of these salts in a solvent produces nitronium and tetrafluoroborate ions which coadsorb on the external surface of the tubes. It is shown that the ions bind strongly to both metallic and semiconducting narrow nanotubes, although stronger to the metallic ones. The nitronium cations bind to the CNTs through a charge transfer mechanism, whereas the tetrafluoroborate anions remain negatively charged upon adsorption on the nanotubes. The surface of the nanotubes gets substantially deformed around the adsorption site of the nitronium ion, but it is hardly changed around the adsorption site of the tetrafluoroborate ion. These results are the theoretical basis to explain the destruction of the narrow CNTs found in the experiments and also to unravel, in agreement with the experimental interpretation, the distinct role played by the nitronium and the tetrafluoroborate ions. The tetrafluoroborate ions contribute to separate the CNTs from the bundles into individual tubes, without affecting the tubes. The nitronium ions, in contrast, modify the electronic and geometrical structures of the narrow tubes leading eventually to their destruction. The implications for the selective removal of intermediate diameter metallic CNTs found in the experiments are also discussed. The adsorption of the neutral nitrogen dioxide molecule is also studied, and the results show that the weak interactions of this molecule with both metallic and semiconducting tubes cannot be used as a model for the strong attack of the nitronium ions to the narrow tubes. The sensor effect of the nanotubes toward adsorption of nitrogen dioxide is also discussed. © 2008 American Institute of Physics. [DOI: [10.1063/1.2931455](https://doi.org/10.1063/1.2931455)]

I. INTRODUCTION

Nowadays, most of the production techniques of carbon nanotubes (CNTs) yield bundles of tubes of mixed radii and chiralities and, therefore, of mixed metallic and semiconducting characters. However, samples of CNTs of well defined characteristics, specific radius, and either metallic or semiconducting character are required to exploit the extraordinary electronic properties of the tubes. There are several options to overcome this problem. One is to develop new techniques for the selective production of CNTs of specific characteristics. Other possibility is to use functionalization methods that change the electronic structure of the nanotubes. Hydrogenation^{1–3} and fluorination^{4–6} of the nanotube surface turns the metallic nanotubes into semiconducting nanotubes. However, these methods sometimes deteriorate and disintegrate the nanotubes. Probably the most promising option up to date is the separation and sorting of the tubes after production. Several materials and methods have been proposed to separate metallic from semiconducting nanotubes: dielectrophoresis,^{7–9} octadecylamine,^{10,11} bromination,¹² DNA,^{13–15} diazonium,^{16,17} and solution-phase osmylation.¹⁸ Some researchers have reported diameter-selective removal of nanotubes by using chemical

oxidation,^{19–21} ozonation,²² and light-assisted oxidation,²³ but these are not metallicity-dependent separation methods.

Recently, new techniques have been introduced which lead to the selective removal of the intermediate diameter (in the range of 0.85–1.1 nm) metallic CNTs from the semiconducting ones in the presence of nitronium ions NO_2^+ . The narrow tubes (with diameters smaller than 0.85 nm) are all disintegrated independently of their metallic or semiconducting character and the large diameter (larger than 1.1 nm) tubes are all preserved also independently of their electronic character. These techniques consist either in the dispersion of the tubes in tetramethylene sulfone/chloroform solution with nitronium hexafluoroantimonate (NO_2SbF_6) or nitronium tetrafluoroborate (NO_2BF_4),²⁴ or in the acid treatment of the tubes with a $\text{HNO}_3/\text{H}_2\text{SO}_4$ mixture.²⁵ The ionization of the salts or acids in the solvent produces nitronium ions NO_2^+ and the corresponding negative counterions, SbF_6^- , BF_4^- , or HSO_4^- , respectively. Since these techniques have in common the presence of the nitronium ions, the picture that emerges from the experiments is that the nitronium ions attach strongly to the walls of all narrow tubes and selectively to the walls of the intermediate diameter metallic tubes, leading to their disintegration. The attachment of the corresponding negative ions to the tubes helps in the dispersion of the tubes from the bundles. However, the basic mechanisms of (a) the attack of nitronium ions to the narrow nanotubes, (b) the selectivity of the attack to the intermediate diameter metallic

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tubes, and (c) the role played by the negative ions remain unexplored from a fundamental viewpoint. There has been an attempt (by the same authors of the experimental papers) of explaining the selective removal of the metallic tubes through the weak (and in some cases even repulsive) interactions of neutral nitrogen dioxide molecules NO_2 with the nanotubes.²⁶ Clearly, the weak adsorption of neutral NO_2 molecules on either metallic or semiconducting CNTs cannot simulate the strong attack of the nitronium ions to the tubes, leading to the disintegration of the narrow tubes and to the selective removal of the intermediate diameter metallic tubes.

In this paper, we have focused on the study of the destruction of narrow CNTs and leave the investigation of the selective removal of the intermediate diameter metallic tubes for a further work. Therefore, to unravel the basic mechanisms of the attack of the dissolved nitronium tetrafluoroborate salts to the narrow tubes and the distinct role played by the nitronium and the tetrafluoroborate ions BF_4^- , we have performed density functional theory (DFT) calculations of the coadsorption of these two ions on both metallic and semiconducting narrow (diameter of 5.5 Å) CNTs, (4,4) and (7,0), respectively.

The structure of the paper is as follows. In Sec. II, we describe the type of simulations performed in this paper and give some details of the calculations. In Secs. III and IV, we present the results for the coadsorption of NO_2^+ and BF_4^- ions, and the adsorption of the NO_2 molecule, respectively, and discuss the relevance of these results to understand the attack to the narrow nanotubes. A possible sensor effect of the tubes toward NO_2 is also discussed. We end with a brief summary in Sec. V.

II. METHOD

We have performed DFT calculations to investigate the coadsorption of the nitronium NO_2^+ and the tetrafluoroborate BF_4^- ions, and the adsorption of the nitrogen dioxide NO_2 neutral molecule on metallic and semiconducting narrow CNTs. The nitronium, tetrafluoroborate, and nitrogen dioxide belong to the $D_{\infty h}$, T_d , and C_{2v} groups and their ground electronic states are $^1\Sigma_g^+$, 1A_1 , and 2A_1 , respectively. We have selected two nanotubes, (4,4) and (7,0), that have approximately the same diameter, about 5.5 Å, and different electronic characters, metallic and semiconducting, respectively. Therefore, the differences in the adsorption behavior of these two tubes, if any, should be attributed to their different electronic characters.

The DFT calculations, as implemented in the DACAPO code,^{27,28} have been performed using the generalized gradient approximation (GGA)-PW91 exchange-correlation functional²⁹ and ultrasoft pseudopotentials³⁰ to represent the ionic cores of the atoms. The NO_2 molecule has one unpaired electron and, therefore, all the calculations with this molecule have been performed using the spin-density approach within the DFT-GGA formalism. The rest of the calculations are nonspin polarized. A tetragonal supercell with $a=b=18$ Å has been used to minimize the interactions between cells. The c parameter is taken along the main axis of

the tubes. To guarantee an accuracy of 0.1 eV in the binding energies, we have considered a cutoff of 270 eV for the plane waves and a [1,1,2] Monkhorst–Pack κ -point sampling. The calculation of the electronic charge density differences and the densities of states requires, however, a larger κ Monkhorst–Pack set, [1,1,32] to obtain good converged results, e.g., the plateau at the Fermi level of the density of states (DOS) of the metallic (4,4) nanotube.

A full optimization of the structure of the pristine isolated tubes has been first performed by relaxing the positions of the C atoms and the c parameter of the supercell. The supercell contains four tube cells in the axial direction of the tube (64 C atoms) in the case of the (4,4) tube and two cells (56 C atoms) in the case of the (7,0) tube. The corresponding optimized values of the c parameter are 9.91 and 8.59 Å. The relaxed structures of the tubes have been used in the adsorption simulations. The positions, orientations, and structures of the adsorbed NO_2^+ and BF_4^- ions or the adsorbed NO_2 neutral molecule and the C atoms at the adsorption sites are then fully relaxed.

III. COADSORPTION OF NITRONIUM AND TETRAFLUOROBORATE IONS ON CARBON NANOTUBES

We have performed DFT calculations of the coadsorption of a nitronium ion and a tetrafluoroborate ion on the external surface of the (4,4) and the (7,0) CNTs. The two ions were positioned on opposite sides of the nanotube. Table I summarizes the results, including binding energies, structural data, and Mulliken electronic charges. The optimized geometries of the coadsorbed systems on the (4,4) and the (7,0) CNTs, for one orientation (A) of the nitronium ion, are shown in Fig. 1. Several orientations of the nitronium ion with respect to the nanotube surface have been considered, which can be easily identified in Figs. 2 and 3 through the labels given in Table I.

The structural optimizations began with the optimized structures of the free ions. The free NO_2^+ ion is a linear molecule with an optimized $d_{\text{N-O}}$ distance of 1.144 Å, which agrees with the experimental value of 1.148 Å.³¹ The free BF_4^- ion has a tetrahedral structure with an optimized $d_{\text{B-F}}$ distance of 1.43 Å, also in good agreement with the experimental value of 1.45 Å.³² After relaxation, the structure of the NO_2^+ adsorbed on the CNT surface changed and acquired a geometry very close to that of the free neutral NO_2 molecule, which has a bent structure ($\theta_{\text{O-N-O}}=133.6^\circ$ and $d_{\text{N-O}}=1.22$ Å, see next section), as can be seen in Figs. 1–3 and in Table I. The Mulliken charges of nitrogen and the two oxygen atoms add up to give a value of the net charge Q_{NO_2} close to zero (see Table I). These results suggest a charge transfer mechanism for the adsorption of the nitronium ions on both metallic and semiconducting tubes, such that the nanotube transfers charge to the nitronium ion, and this extra charge turns the ion into a neutral molecule and prompts a change in the structure, from linear to bent. In contrast, the relaxed geometry of the BF_4 group of atoms changes very little, upon adsorption on CNTs, with respect to the geometry of the free BF_4^- ion, as it is shown in Fig. 1 and in Table I. The Mulliken charges of the boron and the four fluorine at-

TABLE I. Binding energy E_b (in eV) and structural parameters of the coadsorbed nitronium and tetrafluoroborate ions on the (4,4) and the (7,0) CNTs for several optimized structures (see Figs. 2 and 3). d_{C-N} and d_{C-O} are the equilibrium distances of the N and the closest O atom, respectively, to the closest C atom; $\Delta r_C(N)$ is the relaxation in the radial direction of the tube of this C atom; Δd_{C-C} is the averaged change in the C–C bond lengths between this C atom at the adsorption site and its three first neighbors; and d_{N-O} and θ_{O-N-O} are the structural parameters of the adsorbed NO_2^+ ion. d_{C-B} is the equilibrium distance of the B atom to the closest C atom, $\Delta r_C(B)$ is the relaxation in the radial direction of the tube of this C atom, and d_{B-F} and θ_{F-B-F} are the structural parameters of the adsorbed BF_4^- ion. All distances are in Å and the angles in degrees. Q_{NO_2} and Q_{BF_4} are the sums of the Mulliken charges over the atoms of the NO_2 and the BF_4 groups, respectively.

CNT	Site	E_b	d_{C-N}	d_{C-O}	$\Delta r_C(N)$	Δd_{C-C}	d_{N-O}	θ_{O-N-O}	Q_{NO_2}	d_{C-B}	$\Delta r_C(B)$	d_{B-F}	θ_{F-B-F}	Q_{BF_4}
(4,4)	A	5.6	1.73	...	+0.24	+0.05	1.23	127.8	−0.12	3.07	−0.01	1.43	109.5	−0.84
(4,4)	C	5.6	1.82	...	+0.23	+0.05	1.23	127.0	−0.12	3.08	−0.01	1.43	109.5	−0.85
(4,4)	D	5.3	4.28	3.18	+0.00	+0.00	1.23	127.9	−0.22	3.07	−0.01	1.43	109.5	−0.84
(7,0)	A	4.2	1.85	...	+0.18	+0.03	1.22	130.2	−0.02	3.25	−0.01	1.43	109.5	−0.80
(7,0)	C	4.1	2.04	...	+0.14	+0.02	1.22	130.8	+0.00	3.30	−0.00	1.43	109.5	−0.81
(7,0)	D3	4.0	4.12	2.98	+0.00	+0.00	1.22	132.1	−0.07	3.26	−0.01	1.43	109.5	−0.79

oms add up to give a value of the net charge Q_{BF_4} close to -1 (see Table I) that indicates a small transfer of charge from the BF_4^- ion to the nanotube. These results suggest that the tetrafluoroborate ion largely preserves its identity upon adsorption on the nanotubes.

It is interesting to notice that the structure of the tubes gets substantially deformed around the adsorption site of the nitronium ion. The position of the C atom nearest to the nitrogen atom relaxes radially outwards the tube wall by about 0.24 Å and there is a 3% increase in the length of the three C–C bonds around the adsorption site (see Δr_C and Δd_{C-C} in Table I). The consequence is that the C–C bonds near the adsorbed nitronium ion become strained and weakened in the narrow nanotubes. The structure of the tubes near the adsorbed BF_4^- ion, however, is not affected by the ion.

The binding energy E_b of the coadsorbed nitronium and the tetrafluoroborate ions to the nanotube surface given in Table I is defined as

$$E_b = E(\text{CNT}) + E(\text{NO}_2^+) + E(\text{BF}_4^-) - E(\text{NO}_2^+\text{BF}_4^- @ \text{CNT}), \quad (1)$$

where $E(\text{NO}_2^+\text{BF}_4^- @ \text{CNT})$ is the energy of the nanotube with the adsorbed ions, $E(\text{CNT})$ is the energy of the isolated nanotube, and $E(\text{NO}_2^+)$ and $E(\text{BF}_4^-)$ are the energies of the

NO_2^+ and BF_4^- free ions, respectively. The ions are strongly adsorbed on both metallic and semiconducting tubes, with total binding energies of 5.6 and 4.2 eV, respectively. The binding energy on the metallic tubes is substantially larger (by about 1.4 eV) than on the semiconducting ones. This higher binding energy of the coadsorbed ions on the metallic nanotubes correlates with their smaller distance to the tube surface. Notice that the two ions are placed closer (by about 0.1–0.2 Å) to the surface of the metallic nanotubes than to the surface of the semiconducting ones. The distance ($d_{C-N} \sim 1.7$ –2.0 Å) of the nitronium ions to the nanotube surface, although it is large compared with the C–N distance (1.172 Å) in the CN, cyano radical,³³ it is much smaller than the distance ($d_{C-B} \sim 3.1$ –3.3 Å) of the BF_4^- ions to the tube surface. Therefore, one would expect a stronger interaction of the nitronium ions than the BF_4^- ions with the nanotubes. The contribution of the nitronium ions to the strong coadsorption on both metallic and semiconducting tubes arises from the charge transfer mechanism explained above. The binding mechanism of the BF_4^- , in contrast, involves little transfer of charge between the ion and the tube and also little redistribution of the electronic density (see below), what supports the idea of a much weaker interaction of this ion with the tubes.

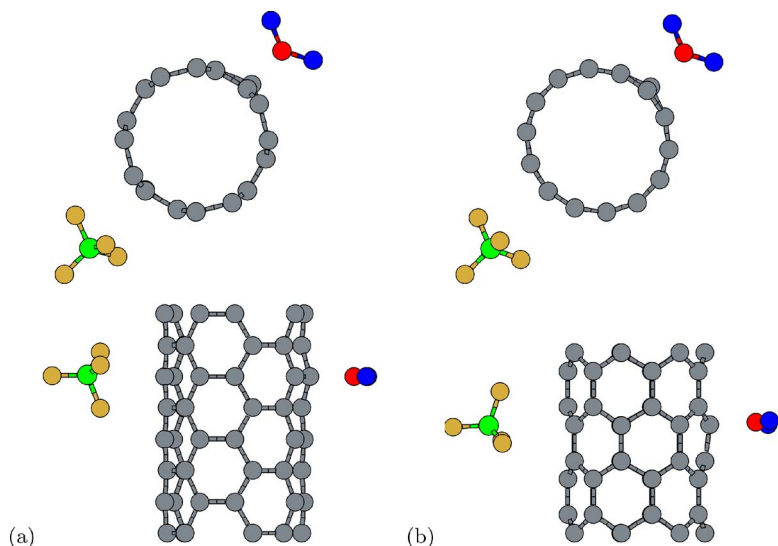


FIG. 1. (Color online) Optimized geometry of the NO_2^+ and BF_4^- ions on configuration A on the external surface of the (4,4) and (7,0) nanotubes, (a) and (b) panels, respectively. Top and front views are shown for each structure. The length of the nanotubes shown in the figure is that of the supercell used in the calculations. Notice that the adsorbed nitronium ion acquires the same bent structure of the neutral NO_2 molecule (see text).

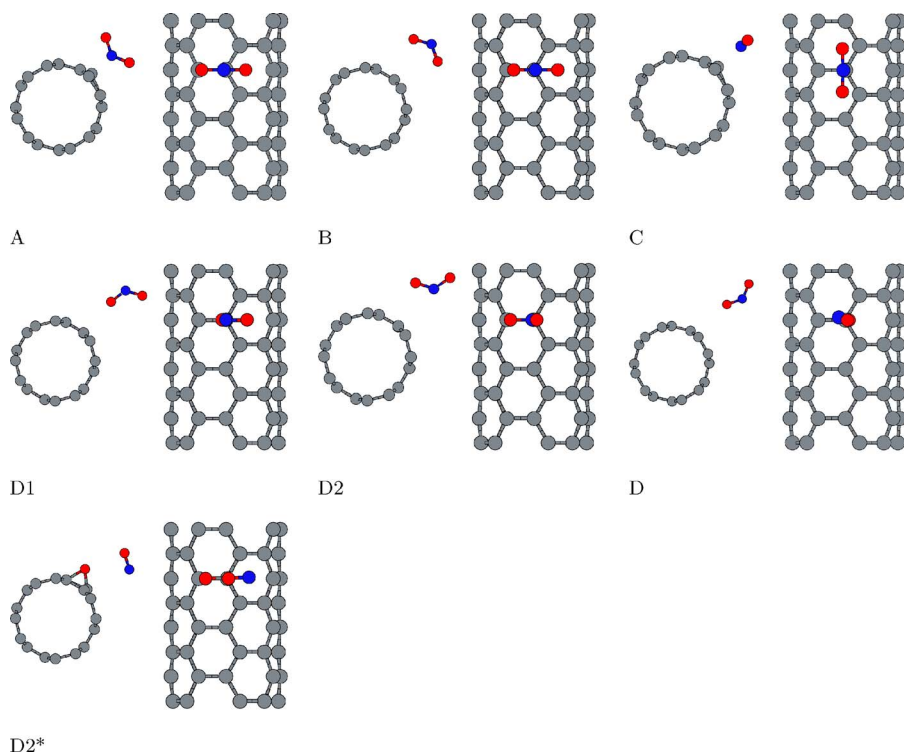


FIG. 2. (Color online) Several optimized structures of the neutral NO_2 molecule adsorbed on the surface of the metallic (4,4) carbon nanotube. Top and front views are shown for each structure. The length of the nanotubes shown in the figure is that of the supercell used in the calculations. These same structures were obtained for the adsorption of the NO_2^+ cation that acquires, upon adsorption, the same bent structure of the neutral NO_2 molecule (see text).

The nature of the bonding of the nitronium and the BF_4^- ions to the metallic and the semiconducting tubes can be examined through the redistribution of electronic density upon adsorption of the ions. Figure 4 shows the density difference

$$\Delta\rho = \rho(\text{NO}_2^+\text{BF}_4^-\text{@CNT}) - \rho(\text{CNT}) - \rho(\text{NO}_2^+) - \rho(\text{BF}_4^-) \quad (2)$$

between the adsorbed system $\{\text{NO}_2^+\text{BF}_4^-\text{@CNT}\}$ and the separated CNT, NO_2^+ , and BF_4^- subsystems with the same geometries as in the adsorbed case. The density difference around the NO_2 group of atoms has a shape similar to the highest occupied molecular orbital of the neutral NO_2 molecule, showing that charge (about one electron) is transferred from the tube to the nitronium ion. This gives further support to the charge transfer binding mechanism of the nitronium ions suggested by the zero value of the Mulliken charge and the bent structure of the NO_2 group of atoms (see above).

The density difference around the BF_4^- ion is very small in agreement with its Mulliken charge (close to -1). The bonding between BF_4^- and the tube arises mainly from a relatively small charge density redistribution in the nanotube around the adsorption site of BF_4^- . Therefore, one would expect a weaker interaction of the BF_4^- ions with the CNTs than that of the nitronium ions. It has been shown¹⁷ that water-soluble diazonium salts can extract electrons from the nanotubes. The speculation was that the extent of that electron transfer depends on the DOS near the Fermi level and, therefore, the interaction with metallic nanotubes would be more intense than with the semiconducting ones. In contrast to that interpretation, we have found that the extent of charge transfer from narrow CNTs to the nitronium ions is similar for both metallic and semiconducting tubes, although the interaction between the nitronium tetrafluoroborate salt and the CNTs is stronger for the metallic tubes.

Figure 5 shows the total DOS of the $\{\text{NO}_2^+\text{BF}_4^-\text{@}(4,4)\}$

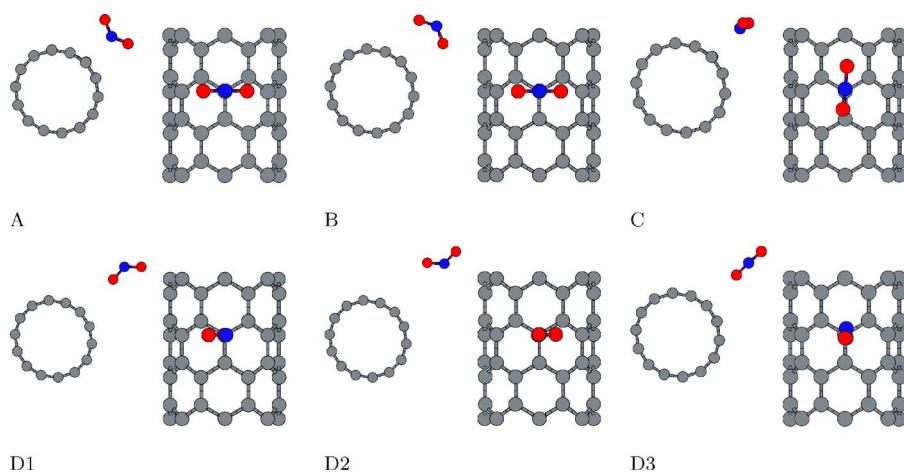


FIG. 3. (Color online) Same as Fig. 2 for the semiconducting (7,0) CNT.

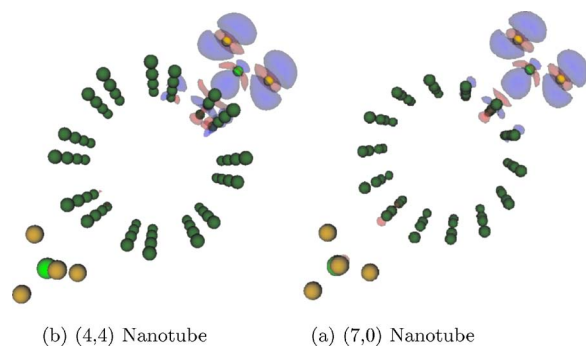


FIG. 4. (Color online) Isosurfaces of the electronic density difference $\Delta\rho$ between the adsorbed system $\{\text{NO}_2^+\text{BF}_4^-\text{@CNT}\}$ and the separated CNT, NO_2^+ , and BF_4^- subsystems having the same structure as in the adsorbed one. (a) and (b) panels correspond to the adsorption of nitronium on the (4,4) and (7,0) nanotubes, respectively. The blue and red surfaces correspond to $\Delta\rho = +0.04$ and -0.04 $\text{e}/\text{\AA}^3$, respectively.

and the $\{\text{NO}_2^+\text{BF}_4^-\text{@(7,0)}\}$ adsorbed systems for the most stable (A) configuration of the adsorbed nitronium ion. The DOSs of the corresponding (4,4) and (7,0) isolated tubes are also shown for comparison. We can observe that upon adsorption of the nitronium ion, the (4,4) metallic tube remains metallic, whereas the gap of the (7,0) semiconducting tube is closed and some molecular levels appear just above the Fermi energy.

From the previous results, the picture that emerges on the attack of nitronium tetrafluoroborate salts in solution to narrow CNTs and on the role played by the nitronium and the tetrafluoroborate ions is as follows. Despite the strong coadsorption of the nitronium and the BF_4^- ions on the narrow tubes, the two ions play a very different role. The electronic and geometrical structures of the adsorbed BF_4^- ion are similar to those of the free ion. The CNT, around the adsorption site, is hardly affected, both from the structural and the electronic points of view, which reflects a relatively weak interaction between the BF_4^- ion and the CNT. This indicates, in agreement with the experiments,²⁴ that the BF_4^- ions are not involved in the actual destruction of the tubes but that their role is to help in the dispersion of the tubes from the bundles. The much stronger interaction of the nitronium ions with the tubes, which arises from the charge transfer mechanism, together with the significant deformation experienced by the CNTs around the nitronium adsorption site, indicate that the nitronium ion plays the active role in the destruction of the narrow nanotubes. Under the experimental conditions, many nitronium ions could adsorb on the walls of the tubes and would produce deformations of the tubes. Preliminary calculations on the effect of increasing the coverage of the

nanotubes with nitronium ions indicate a moderate reduction in the binding energy per molecular ion but a larger distortion of the nanotube surface. These deformations debilitate the C–C bonds and eventually would lead to the structural breaking of the narrow tubes, irrespective of their electronic character, in agreement with the experiments.^{24,25} One could speculate on the dependence of the attack of the nitronium ions on the diameter and electronic character of the tubes. A decrease can be expected in the strength of the interaction between the nitronium ions and the tubes with a decrease in the curvature of the tube surface, that is, with increasing tube diameter. As a consequence, it is plausible that only the metallic tubes will be removed in the intermediate size range due to the stronger adsorption of nitronium ions on the metallic tubes. Finally, the attack of nitronium to larger diameter tubes would be less effective and the tubes will not be destroyed. This gives some hints to understand the selective removal of intermediate size metallic tubes found in the experiments.^{24,25} For a more complete understanding of the experiments, it would be useful to investigate the actual dependence of the coadsorption of NO_2^+ and BF_4^- on the size of the tubes.

IV. INTERACTION OF THE NEUTRAL NO_2 MOLECULE WITH CARBON NANOTUBES

As we have explained in Sec. II, the NO_2 molecule has one unpaired electron. Therefore, the calculations related to this molecule are spin polarized (although the nonspin polarized calculations lead to the correct geometry of the NO_2 molecule, they produce incorrect electronic densities and energies; see below). The optimized structure of the isolated NO_2 molecule has a bent geometry with an angle $\theta_{\text{O–N–O}} = 133.6^\circ$ and a bond length $d_{\text{N–O}} = 1.216$ \AA , in good agreement with the experimental values³³ of 134.1° and 1.193 \AA , respectively. Its electronic ground state is 2A_1 . We have considered several orientations of the adsorbed molecule with respect to the CNT surface. The optimized structures are shown in Figs. 2 and 3 for adsorption on the metallic (4,4) and the semiconducting (7,0) tubes, respectively. The results of the spin polarized DFT–GGA calculations are summarized in Table II.

The binding energy E_b of the molecule to a nanotube is given by

$$E_b = E(\text{CNT}) + E(\text{NO}_2) - E(\text{NO}_2\text{@CNT}). \quad (3)$$

The binding energies are small for both types of nanotubes. One can see, nevertheless, that E_b values are larger for the (4,4) nanotube due to its metallic character. Our results are in

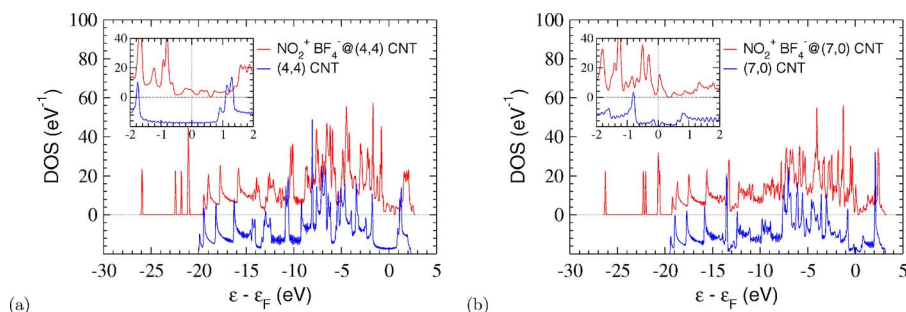


FIG. 5. (Color online) Total density of states (in eV^{-1}) of (a) $\{\text{NO}_2^+\text{BF}_4^-\text{@(4,4)}\}$ and (b) $\{\text{NO}_2^+\text{BF}_4^-\text{@(7,0)}\}$. For comparison the DOS of the corresponding isolated (4,4) and (7,0) tubes are also shown.

TABLE II. Same as Table I for the adsorption of the nitrogen dioxide neutral molecule. For comparison, the calculated geometrical parameters of the free NO₂ molecule are also included.

CNT	Site	E_b	d_{C-N}	d_{C-O_A}	Δr_C	d_{N-O_A}	d_{N-O_B}	θ_{O-N-O}	Q_{NO_2}
	Free NO ₂					1.22	1.22	133.6	
(4,4)	A	0.20	2.77	...	0.01	1.23	1.23	128.0	-0.28
(4,4)	B	0.22	3.43	...	0.00	1.24	1.24	126.3	-0.36
(4,4)	C	0.19	2.65	...	0.01	1.23	1.23	127.6	-0.28
(4,4)	D1	0.18	4.09	2.87	-0.01	1.24	1.23	127.1	-0.31
(4,4)	D2	0.14	3.28	2.98	-0.01	1.24	1.23	127.0	-0.29
(4,4)	D2*	-0.71	3.21	1.41	0.18	3.05	1.17	85.0	-0.38
(7,0)	A	0.04	2.79	...	0.00	1.23	1.22	130.6	-0.15
(7,0)	B	0.05	3.33	...	0.00	1.23	1.23	128.6	-0.21
(7,0)	C	0.04	2.80	...	0.00	1.22	1.23	130.3	-0.14
(7,0)	D1	0.03	4.57	3.35	0.00	1.23	1.22	129.9	-0.13
(7,0)	D2	0.01	4.98	4.24	0.00	1.22	1.23	130.5	-0.11

agreement with previous DFT-GGA calculations³⁴ and lead to lower binding energies than the low density approximation.³⁵ The molecule is adsorbed on the tube surface at relatively large distances and its structure does not change upon adsorption (see Table II). We have noticed that nonspin polarized calculations lead to wrong binding energies; for instance, they produce repulsive energies ($E_b = -0.14$ eV) between the NO₂ molecule and the (7,0) tube.

The sum of the Mulliken charges of atoms in the NO₂ group Q_{NO_2} adds up to about 0.1–0.3 e , which indicates that there is a small charge transfer from the tube to the molecule. The redistribution of the electronic density upon adsorption is given by the difference

$$\Delta\rho = \rho(\text{NO}_2@\text{CNT}) - \rho(\text{CNT}) - \rho(\text{NO}_2), \quad (4)$$

between the electronic density of the adsorbed system $\rho(\text{NO}_2@\text{CNT})$ and that of the separated CNT and NO₂ subsystems with the geometries as in the adsorbed case. Figure 6 shows $\Delta\rho$ for the adsorption on the (4,4) (left panel) and the (7,0) (right panel) tubes. In both cases, a small increase in the electronic density is observed around the NO₂ molecule, which corresponds to the small charge transfer given by the Mulliken charges. Notice that the isosurfaces shown in the figure correspond to very small values, 0.001 $e/\text{\AA}^3$, of the density difference and that there is no formation of covalent bonds, which correlates with the small binding energies found in both cases.

The DOS of the adsorbed NO₂@(4,4) and NO₂@(7,0) systems are shown in Fig. 7. The DOS of the corresponding (4,4) and (7,0) clean tubes are shown for comparison. The (4,4) metallic CNT remains metallic upon adsorption of NO₂ molecules. The molecules introduce a partially filled band at the Fermi energy. On the other hand, the adsorption of NO₂ on the (7,0) semiconducting tube introduces a molecular level in the band gap. There is a little charge transfer of about 0.1–0.3 e from the nanotube to that molecular level, giving rise to some holes in the valence band of the tube. As a result, one would expect an increase in the p -conductivity of semiconducting tubes upon adsorption of NO₂ molecules, in agreement with the experimental observation.³⁶ Therefore, semiconducting CNTs could be used as chemical sensors for detection of NO₂ gas.

One could try to force a stronger interaction between the CNT and NO₂ by pushing the molecule toward the nanotube surface. As the initial structure for one of the optimizations, we have considered the NO₂ molecule in the D2 configuration on the surface of the (4,4) nanotube (see Fig. 2) at a short distance from the tube, $d_{C-N} = 1.8$ Å. The final optimized geometry is the D2* configuration of Fig. 2. That is, the molecule dissociated into an oxygen atom and the NO molecule. The oxygen atom is bound to a C–C bond, whereas the NO molecule is at a larger distance from both the tube and the dissociated oxygen atom. The binding energy of this configuration is negative (see Table II), which

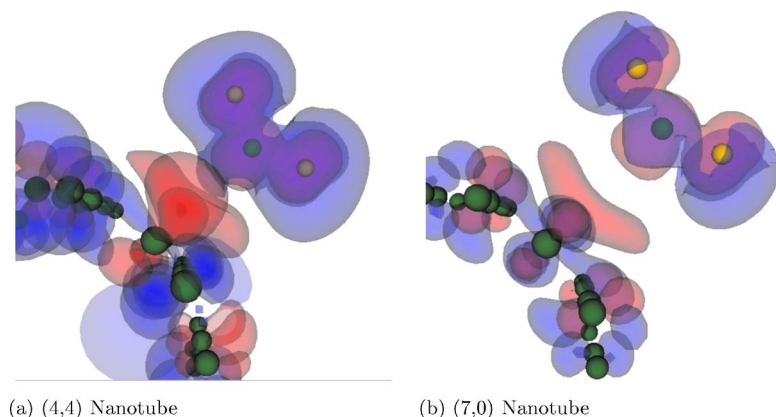


FIG. 6. (Color online) Isosurfaces of $\Delta\rho$, the density difference between the adsorbed system NO₂@CNT and the separated CNT and NO₂ subsystems having the same structure as in the adsorbed case. (a) and (b) panels correspond to the adsorption of NO₂ on the (4,4) and on the (7,0) nanotubes, respectively, for configuration A. Blue and red surfaces correspond to $\Delta\rho = +0.001$ and -0.001 $e/\text{\AA}^3$, respectively.

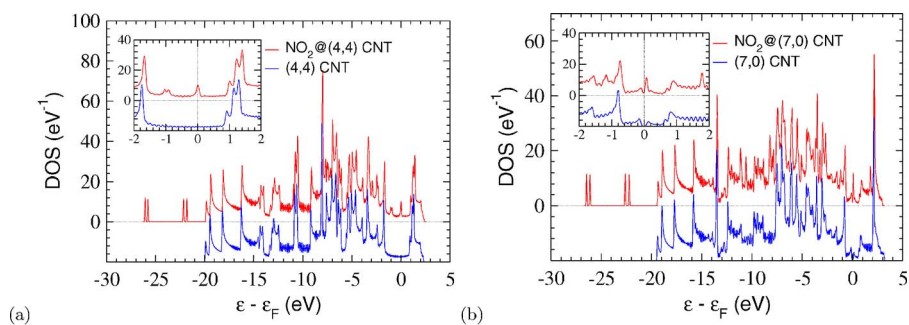


FIG. 7. (Color online) Total density of states (in eV^{-1}) of (a) NO_2 @(4,4) CNT and (b) NO_2 @(7,0) CNT. The inset shows the DOS around the Fermi energy. The DOS of the corresponding isolated (4,4) and (7,0) tubes are given for comparison.

means that the dissociation of the NO_2 molecule on the surface of a CNT is an endothermic process. From these results it becomes clear that the weak interactions of neutral NO_2 molecules with CNTs cannot explain the disintegration of narrow nanotubes, neither the selective removal of metallic CNTs of intermediate diameter. The actual, strong, interactions of the nitronium ions with the CNTs have to be considered, instead.

V. CONCLUSIONS

We have performed DFT-GGA calculations of the interaction of nitronium and BF_4^- ions and of the neutral nitrogen dioxide molecule with metallic and semiconducting narrow CNTs to investigate the destruction of these tubes under the attack of nitronium tetrafluoroborate salts in solution found in the experiments, and to unravel the distinct roles played by the nitronium and the BF_4^- ions in this attack. We have found a strong coadsorption of the nitronium and the BF_4^- ions on the surface of both metallic and semiconducting narrow CNTs. The nitronium ions bind strongly to the nanotubes through a charge transfer mechanism. The tube transfers about one electron to the nitronium ion which turns into a neutral NO_2 molecule. The linear structure of the free nitronium ion changes upon adsorption on a CNT to a bent structure almost identical to that of the neutral molecule. Moreover, the geometrical structure of the nanotube deforms substantially, relaxes outwards the tube surface, in the vicinity of the adsorbed nitronium ion. The BF_4^- ions preserve their structural and electronic characteristics upon adsorption on CNTs. A weaker bonding than in the case of the nitronium ions is expected from the relatively small charge density redistribution around the adsorption site. Moreover, the structure of the tubes is not affected by the adsorption of BF_4^- .

Our results indicate that the BF_4^- ions do not play an active role in the disintegration of the narrow CNTs but that their adsorption contributes to the dispersion of the tubes from the bundles. In our point of view, it is the strong adsorption of nitronium ions on the narrow CNTs together with the structural changes taking place in the tubes upon adsorption of these ions that provides the basis to explain the destruction of the narrow tubes found in the experiments. For a substantial concentration of nitronium ions, the additive effect of the structural destabilization of the nanotube will produce its disintegration. For larger diameter tubes, one would expect a reduction in the strength of the interaction between the nitronium ions and the tubes. Since the metallic tubes interact stronger with the nitronium ions than the semicon-

ducting ones, the weakening of the binding with increasing tube diameter would lead to the selective removal of the metallic tubes of intermediate size found in the experiments. However, a complete explanation of the experiments will require the study of the coadsorption of NO_2^+ and BF_4^- in metallic and semiconducting tubes as a function of the diameter of the tubes and concentration of the reactants.

The binding mechanism of neutral NO_2 to CNTs is completely different to that of the nitronium ion. The NO_2 molecules bind weakly to the tubes and the structure of both metallic and semiconducting narrow nanotubes remains unaffected upon adsorption of these neutral molecules. Clearly, the weak interaction of NO_2 with the CNTs cannot be used to explain the destruction of the tubes under the attack of nitronium tetrafluoroborate salts in solution found in the experiments. On the other hand, we have found, in agreement with the previous works, that the semiconducting tubes change their electronic character upon adsorption of NO_2 . There is a little charge transfer from the nanotube to a molecular level introduced in the gap by the NO_2 molecules. This charge transfer leaves some holes in the valence band of the tube that justifies the increase in the p -type conductivity of the tubes observed in the experiments. Therefore, semiconducting CNTs could be used as chemical sensors for NO_2 .

ACKNOWLEDGMENTS

This work was supported by MEC of Spain and FEDER-FSE 2000/2006 (Grant No. MAT2005-06544-C03-01), Junta de Castilla y León (Grant No. VA039A05), and the University of Valladolid. I. C. acknowledges support from MEC-FSE through the Ramón y Cajal Program.

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