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A Computational NMR Study of Chemisorption of Nitrogen-Doped on the Surface of Single-Walled Carbon Nanotubes

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ABSTRACT

In this paper a computational nuclear magnetic resonance (NMR) study and chemisorption energies ΔE_{ads} *are performed to investigate the electronic structure properties of arm-chair (4,4) single -wall carbon nanotube (*N_2*-SWCNTs). In summary, the optimized chemisorption rates are calculated. The study performed by using density function theory (DFT) and hartree-fock (HF) methods. The untidy nature of these "chemical shift" interactions caused most physicists to lose interest, leaving the field to be developed by chemists. Chemisorption is treated within the Anderson–Newns model, which takes account of Coulomb interaction between adsorbate electrons. The structural forms are firstly optimized and then the calculated* σ *tensors in the optimized structures are converted to chemical shielding isotropic (*σ_{iso}*) and chemical-shielding anisotropic (*$\Delta\sigma$*) and asymmetric (*μ_j*) parameters. The computations were fully implemented by Gaussian 98 Software package.*

Key words: DFT, HF, chemisorption, NMR, nitrogen-doped, carbon nanotube.

INTRODUCTION

Since their discovery by Iijima in 1991 [1], carbon nanotubes have been the subject of intensive research interest based on pioneering explorations [2,3], carbon nano-tubes (CNTs) are proposed as chemical sensors to detect toxic gases and other species, such as NH_3, NO_2, $O_2$and N_2 [4]–[8]. There have been several reports on Nitrogen-doping into CNTs [9]–[14]. Even at low concentration, gas chemisorption can change the conductance of CNTs due to the charge transfer between gases and tubes. When a foreign atom is inserted in the nano tube lattice, the nano tube symmetry is altered structure and properties consequently change [15]. This was first confirmed experimentally by Stephan et al. [16] nitrogen [17]–[23] atoms are the most conveniently used dopants, because of their small atomic size; they have a reasonable probability to enter the nanotubes lattice. Nitrogen- doped CNTs appear significantly more reactive than their undoped counterparts [24]. The nitrogen in the nanotubes can be seen as regular defects which change the chemical behavior of the tubes.

Only one single report deals with the changed reactivity and fictionalization of nitrogen doped SWNTs. Holzinger *et al* [25]. It is well known that the doping of CNTs with various elements such as nitrogen (N), potassium, and boron is a significant and effective method to tailor both chemical and electronic properties of CNTs [26]–[28]. In particular, Nitrogen -doping in CNTs has been studied intensely because it can induce a transformation of the (C) atomic network of carbon [29, 30]. Also, the Nitrogen-doping process is effective way to promise diverse carbon nanostructures. In a semiconducting (8, 0) nanotube, the state associated with the nitrogen was localized to within 30 Å for 90% of the spin density, leading to a chemically and electronically active defect [31].

All armchair nanotube (4,4) and zig-zag (5,0) nanotube are semiconductors. As we observe on figure 1, the total number of carbon atoms in a single wall nanotube is many much causes long calculations even for one small filament of nanotube. For resolve this used based method and standard basis set and adequate calculations. Problem we have in this computational study, the electronic structure properties of SWCNTs are investigated by calculations of the σ tensors at the sites of various ^{15}N nuclei for the first time. As representative models, two forms of a 7.1 A$^{\circ}$ and 4.8 A$^{\circ}$ length (5, 0) and (4,4) single-wall nanotube including nitrogen-doped (N-doped), respectively. (Figs. 1–2) forms are considered in the calculations (Tables 1–4).

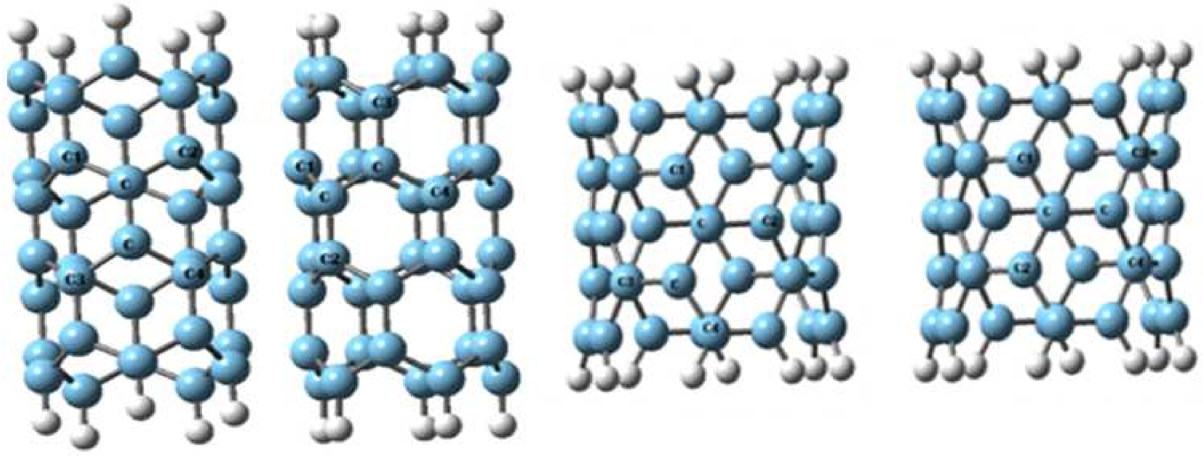

CNT(5,0)(A_1) CNT(5,0)(A_2) CNT(4,4)(A_1) CNT(4,4)(A_2)

Fig.1. (A_1&A_2), (5,0) and (4,4) SWCNT

METHODS AND COMPUTATIONAL DETAILS

In present work, all computations are carried out via Gaussian98 package [32] at the level of (DFT) and HF [31] using the hybrid exchange-functional B3LYP method [31, 32]. According to prior calculations [33], 6-311G* standard basis set is sufficient for structural optimization of nanotubes. calculations based on the density function theory (DFT) were performed in this investigation with the generalized gradient approximation (GGA) by Perdew et al. [34]Therefore, structures of SWCNTs are allowed to fully relax during the B3LYP/6-311G* optimization process and Properties of the structures considered models of SWCNTs is (4,4) armchair and (5,0) zigzag types (table1&2). Then, the optimized structures were used to obtain shielding tensors at the sites of ^{15}N nuclei is calculated based on the gauge included atomic orbital (GIAO) method via B3LYP/6-311G* level of theory [35]. London [36] initially suggested local gauge origins to define the vector potential of the external magnetic field in the study of molecular diamagnetism. The doping atoms are substituted for two nitrogen atoms.

Table1: Calculated structural parameters and Chemisorption energies of N_2 adsorbed on the (4,4) SWCNT [a]

Model	**$r_{C\text{-}C}$**	**$r_{C\text{-}N}$**	**$r_{N\text{-}N}$**	**ΔE_{ads}-DFT**	**ΔE_{ads}-HF**
CNT(4,4)(A_1)	(C-C)$_1$=1.421 (C-C)$_2$=1.422 (C-C)$_3$=1.421 (C-C)$_4$=1.422	-	-	-	-
CNT(4,4)(A_2)	(C-C)$_1$=1.451 (C-C)$_2$=1.419 (C-C)$_3$=1.422 (C-C)$_4$=1.452				
CNT(4,4)-N_2(A_3)	-	(C-N)$_1$=1.334 (C-N)$_2$=1.334 (C-N)$_3$=1.334 (C-N)$_4$=1.334	2.52	-42650.00	-42374.00
CNT(4,4)-N_2(A_4)	-	(C-N)$_1$=1.433 (C-N)$_2$=1.439 (C-N)$_3$=1.443 (C-N)$_4$=1.416	1.454	-42648.00	-42377.00

[a] All calculated distances in A°. All calculated binding energies in electron volt (eV).

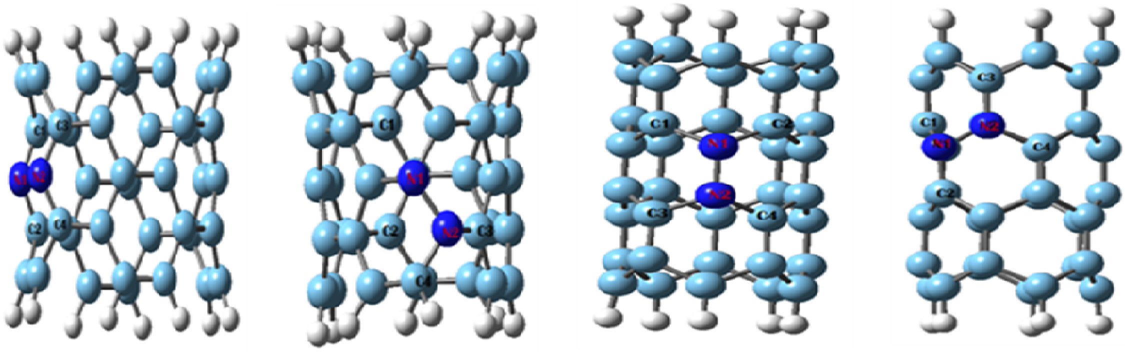
Table2: Calculated structural parameters and Chemisorption energies of N_2 adsorbed on the (5,0) SWCNT [a]

Model	**$r_{C\text{-}C}$**	**$r_{C\text{-}N}$**	**$r_{N\text{-}N}$**	**ΔE_{ads}-DFT**	**ΔE_{ads}-HF**
CNT(5,0)(A_1)	(C-C)$_1$=1.437 (C-C)$_2$=1.451 (C-C)$_3$=1.437 (C-C)$_4$=1.451	-	-	-	-
CNT(5,0)(A_2)	(C-C)$_1$=1.426 (C-C)$_2$=1.451 (C-C)$_3$=1.408 (C-C)$_4$=1.437	-	-	-	-
CNT(5,0)-N_2(A_3)	-	(C-N)$_1$=1.467 (C-N)$_2$=1.454 (C-N)$_3$=1.467 (C-N)$_4$=1.454	1.475	-42538.00	-42265.00
CNT(5,0)-N_2(A_4)	-	(C-N)$_1$=1.383 (C-N)$_2$=1.427 (C-N)$_3$=1.435 (C-N)$_4$=1.388	1.538	-42539.00	-42375.00

[a] All calculated distances in A°. All calculated binding energies in electron volt (eV).

Following Ditchfield's [37] work in which each atomic orbital has its own local gauge origin placed on its center, A. Jerschow [38] and Fukui et al. [39] implemented the GIAO method. The evaluated NMR parameters at the sites of ^{15}N nuclei in the N-doped model are presented in (Table 3&4).

A (4,4) and (5,0) CNT containing 40 carbon atoms with length of 4.8A°and 7.1 A° is chosen for the purpose, fig.1, respectively. Due to the absence of periodic boundary conditions in molecular calculations, it is necessary to saturate the carbon dangling bonds with hydrogen atoms. Curvature of small tubes is a crucial feature responsible for intense interaction of atoms in tubes. (4, 4) CNTs had shown very unique properties due to their large curvature effects [40]. Small CNTs have also stronger interactions between their species. they serve as ideal basis models to study NMR parameters and curvature effects[41,42].(table3 and table4) They are N_2-CNTs (A_1,A_2,A_3,A_4) models for (5,0), (4,4), Fig. 2, respectively.



CNT(4,4)-N_2(A_3) CNT(4,4)-N_2(A_4) CNT(5,0)-N_2(A_3) CNT(5,0)-N_2(A_4)

Fig.2 chemisorption configurations of an N_2 molecule (sites (A_3,A_4) The(4,4)and(5,0) SWCNT-N_2, respectively)

In closed-shell molecules, this leads to a second-order change in the molecular energy:

$$E = E_0 + B_0 \chi B_0 + \sum_{i=1}^{N} \mu_i \sigma B_0 + \cdots$$

Where the summation is take over the N nuclei in the system. Here, we are not interested in the magnetic susceptibility, χ, but only in the bilinear response property, σii.

Components of σ tensor of nucleus are defined by following relation [43].

$$\sigma_{\alpha\beta_i} = \left(\frac{\partial^2 E}{\partial B_\beta \partial \mu_{\alpha_i}}\right)_{\mu_i B \to 0} \quad \alpha,\beta = \text{x,y,z}$$

Where E is energy of system and $\mu_{\alpha i}$ and B_β are components of magnetic moment and external magnetic field, respectively.

σ tensor in the principal axes system (PAS), the σii tensor is converted to a diagonal matrix with σ11, σ22 and σ33 components. Where ($\sigma_{11} \le \sigma_{22} \le \sigma_{33}$) and thus, principal values for specification of shielding are defined by this coordinate system as following:

$$\sigma_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3} \qquad , \qquad \Delta\sigma = \frac{3}{2}(\sigma_{33} - \sigma_{iso})$$

$$\eta_\sigma = \frac{3}{2}\left(\frac{\sigma_{22} - \sigma_{11}}{\Delta\sigma}\right)$$

Table 3: Calculated ^{15}N NMR parameters for CNT, N_2–CNT (4,4) systems ^{a}

Model	^{15}N	atoms	σii(σ11; σ22; σ33)^b	σ_{iso}	$\Delta\sigma$	η_σ
CNT(4,4) (A_1)	-	C_1	(-1.16; -1.16; 163.87)	53.8495	165.0308	0.0000
		C_2	(-1.16; -1.16; 163.87)	53.8495	165.0308	0.0000
		C_3	(-0. 73; -0. 73; 163.79)	54.1090	164.5215	0.0000
		C_4	(-0. 75; -0. 75; 163.74)	54.0800	164.4900	0.0000
CNT(4,4) (A_2)	-	C_1	(-0.71; -0.71; 163.77)	54.1157	164.4815	0.0000
		C_2	(-40.9778; 52.7796; 159.7877)	57.1965	153.8868	2.4588
		C_3	(-35.3100; 13.8404; 175.9600)	51.4968	186.6948	1.4317
		C_4	(-1.17; -1.17; 163.85)	53.8354	165.0219	0.0000
CNT(4,4)-N_2(A_3)	N_1	C_1	(-65.7148; 14.9561; 129.4085)	129.4085	154.7878	4.6156
		C_2	(-65.6491; 14.9320; 129.3856)	26.2228	154.7442	4.6094
	N_2	C_3	(-65.6564; 14.9540; 129.4354)	26.2443	154.7866	4.6073
		C_4	(-65.6518; 14.9639; 129.4032)	26.2384	154.7472	4.6086
CNT(4,4)-N_2(A_4)	N_1	C_1	(-34.9738; 44.0376; 117.5517)	42.2052	113.0197	2.8081
		C_2	(-76.9772; -39.0220;120.5170)	1.5059	178.5167	37.8064
	N_2	C_3	(-76.2848; -20.9271; 30.6033)	11.1305	179.2092	7.4603
		C_4	(-55.4982; 63.6156; 121.5112)	43.2095	117.4526	4.1350

Where, σ_{iso} , $\Delta\sigma$ and η_σ are isotropic, anisotropic and asymmetric parts of σ tensor, respectively and in certain cases vanishes.

^{a} Calculated σ ii, σ iso, Δ σ values in ppm

^{b} In each raw, the first number is for σ_{11}, the second number is for σ_{22}, and the third number is for σ_{33}.

Table 4: Calculated ^{15}N NMR parameters for CNT, N_2–CNT (5,0) systems ^{a}

Model	^{15}N	atoms	σii(σ11; σ22; σ33)^b	σ_{iso}	$\Delta\sigma$	η_σ
CNT(5,0) (A_1)	-	C_1	(-118.0860; 12.8629; 163.87)	18.0597	212.0138	10.8763
		C_2	(-116.9704; 13.8079; 159.2077)	18.6817	210.7890	10.5005
		C_3	(-118.1198; 12.8584; 159.4017)	18.0467	212.0325	10.8866
		C_4	(-116.9332; 13.8073; 159.2050)	18.6930	210.7680	10.4911
CNT(5,0) (A_2)	-	C_1	(-45.2746; 155.1751; 325.7105)	145.2037	270.7602	2.0707
		C_2	(-118.1198; 12.8584; 159.4017)	18.0467	212.0325	10.8866
		C_3	(-27.4737; 155.3875; 319.5851)	149.1663	255.6282	1.8388
		C_4	(-0.0454; 120.08; 120.08)	78.5398	62.3103	0.0000
CNT(5,0)- N_2(A_3)	N_1	C_1	(-1342.5; 102.2; 129. 155.8)	-361.4607	775.8911	2.7930
		C_2	(-3.3789; 96.89; 96.89)	-48.0324	217.3836	0.0000
	N_2	C_3	(-1327.4; 103.5; 157.3)	-355.5204	769.2306	-6.0372
		C_4	(-321.77; 98.39; 98.39)	-41.6679	210.0869	0.0000
CNT(5,0)- N_2(A_4)	N_1	C_1	(6.4895; 82.2362; 165.4940)	84.7399	121.1311	1.3408
		C_2	(-129.8251; 49.2138; 113.8990)	11.0959	154.2047	24.2034
	N_2	C_3	(-120.3952; -27.0594; 96.9833)	-16.8238	170.7106	-8.3218
		C_4	(7.2977; 42.7656; 150.6444)	66.9026	125.6127	-0.7952

^{a}Calculated σ ii, σ iso, Δ σ values in ppm.

^{b}In each raw, the first number is for σ_{11}, the second number is for σ_{22}, and the third number is for σ_{33}.

RESULTS AND DISCUSSION

In this work, geometries and binding energies, ^{15}N NMR chemical shielding of N-doped (4,4) and (5,0) SWCNT interacted with molecular N_2 are taken in to consideration. The calculated geometry parameter sand binding energies, ^{15}N chemical shielding their relative orientation are presented in (Table1&2 and 3&4) in the following sections, molecular geometries and binding energies, NMR chemical shielding resulted from molecular N_2 chemisorption sari discussed, separately.

Molecular geometries and binding energies

When two carbon atom substituted by one N_2 molecular in a super cell, we find the geometric structures of the N-doped (4,4) and (5,0) SWNTs present dramatic changes, as schematically displayed in fig. 2 and Table 1&2, before and after the doping of N atoms, the bond length of in SWNT-A_1(4,4) from $(C\text{-}C)_{1,3}$=1.421 A˚ and $(C\text{-}C)_{2,4}$=1.422 A˚ decreased to 1.334A˚ and bond length of in SWNT-A_2(4,4)) from $(C\text{-}C)_1$=1.451A˚ , $(C\text{-}C)_2$=1.419A˚ , $(C\text{-}C)_3$=1.422A˚ and $(C\text{-}C)_4$=1.452A˚ decreased to 1.433 -1.443 before and after the doping of N atoms, the bond length of in SWNT-A_1(5,0) from $(C\text{-}C)_{1,3}$=1.437A˚ and $(C\text{-}C)_{2,4}$=1.451A˚ increased to 1.467 A˚ and 1.454 A˚ bond length of in SWNT-A_2(5,0)) from $(C\text{-}C)_1$=1.426 A˚, $(C\text{-}C)_2$=1.451A˚ , $(C\text{-}C)_3$=1.408A˚ and $(C\text{-}C)_4$=1.437A˚ decreased to 1.383-1.435 Density functional calculations of SWNT tips with substituted nitrogen show the nitrogen related donor levels reduce the work function of the tip and significantly enhance the localized density of states [46]. Nitrogen doping can also sensitize nano-tubes for gas chemisorption, which may suggest another way to improve field emission properties of N - doped nano-tubes.

More recent DFT calculations by Nevidomskyy *et al.* [31] in much larger super cells confirm the presence of a donor state associated with substituted nitrogen at around 0.2 eV below the conduction band in zig-zag (8,0) nanotubes[44], and around the same energy in armchair (5,5) nanotubes. Whether these will be electron-donor or electron acceptor state or none of these two, depends crucially on the way the hetero atoms are substituted into the lattice. In the following, we will focus on the electronics most relevant case of CNTs substitution of nitrogen atoms into the carbon lattice of a SWNT. For nitrogen atoms we have considered distinct chemisorption sites, marked as CNT (A, A_1, A_2, A_3 and A_4 (Table1&2)). Performed calculation on the values of nitrogen molecule chemisorption energy over zig-zag (5,0) and armchair, (4,4) nanotubes with determined length and diameter, by DFT and HF methods show the difference amounts twice grater. Although (4, 4) carbon nano-tubes have more Chemisorption energies of nitrogen, compared to N_2-CNTs-A_3 (-42650 eV) and N_2-CNTs-A_4 (-42648 eV) to (5, 0) carbon nano-tubes have Chemisorption energies of nitrogen, compared to N_2-CNTs-A_3(-42538 eV) and N_2-CNTs-A_4 (-42539 eV) for a nanotube with a diameter of 0. 6 nm and 0.4 nm depending on the nano-tube and nitrogen molecules, also HF method has proven this fact (table 1&2) respectively) [45]. The nature of stationary points are confirmed by vibrational frequency calculations at the B3LYP/6-311G* level. CNT, CNT–N_2 binding energies, ΔE_{ad} , are calculated using

$$E_{ad} = E_{tot}(\text{molecule}N_2 + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{molecule}N_2)$$

Where, E_{tot}(CNT), E_{tot} (N2) and E_{tot} (CNT+N_2) are the energies of the optimized tubes, that are adsorbate and tube–adsorbate systems, respectively. Armchair (4,4) and zig-zag (5, 0) tube has different C–C bonds thus offers two distinct chemisorption sites (table 1&2). Such a structure has also been chemisorption for other SWCNTs [46, 47, 48].

The calculation was performed for a zig-zag (5,0) nano-tube of 7.10 A˚ length and 2.26A˚diameter for arm-chair(4,4) nano-tube of 4.18 A˚ length and 5.67 A˚ diameter. For carbon bond saturation, 10 hydrogen atoms model (5,0) and 16 hydrogen atoms model (4,4) were added to the end links of nano-tubes, for filament. Using density approximation and gradient-corrected approximation (DFT-GCA) methods, Jordan et al. [49]. The nitrogen molecules almost formed a chemical binding with the carbon nano-tube. The electron configuration of N_2 is KK $(\sigma_{2s})^2$

$(\sigma_{2s}*)^2$ $(\pi_{2px})^2$ $(\pi_{2py})^2$ $(\pi_{2pz})^2$, this is due to decreased sp_2 character in the carbon or a filling of the $\pi*$ state by excess nitrogen electrons [50]. The binding orbital of N_2 molecule is filled so that electron can't fill in the binding orbital. The N_2-tube equilibrium distances for chemisorption sites (A1, A_2, A_3 and A4) clarify the interaction of N_2 with CNT belongs to chemisorption. It was found that N_2 binding energy decreases as the diameter of (5, 0) CNT increases. In addition, all these energies are negative which show the reaction is regulated. Based on these results we can conclude that the chemisorption on the surface area of nanotable occurs difficultly and so this is a suitable case.

^{15}N NMR chemical shielding

Table 3&4 shows the calculated NMR parameters for the nitrogen nuclei in the two models (4,4) and(5,0) of the CNTs, N_2 molecule chemisorption of the SWCNTs has markable influence on ^{15}N NMR tensors, which is in complete accordance with the facts mentioned above . Previously, it has been indicated that for the H-capped SWCNTs, the calculated ^{15}N chemical shielding values at the ends are smaller than in the tube's center if the carbon is directly bound to a hydrogen; otherwise it is larger [51]. It is also depicted that chemical shielding components converge in a way similar to that of the chemical shifts when increasing the tube length albeit not as smoothly as the isotropic shielding. Chemical shielding tensors and chemical shifts are efficient parameters for characterization of carbon nano-tubes. Calculation of these shielding tensors for nitrogen nuclei reveals that increasing length and diameter of SWCNTs –A_1 (5, 0) chemical shielding will cause N nuclei converge on the nano tube surface; Results are consistent with strong interaction between the tube and N_2 molecule in SWCNTs –A_1 (5, 0). This is consistent with previous results derived from band structure calculations [52, 53]. On the other hand, the calculated ^{15}N chemical shielding values in the middle of the CNT (4,4) and CNT (5,0) seem to approach values 53.8495 ppm , 54.1090ppm and 78.5398 ppm, 149.1663 ppm, respectively (Table 3&4). The NMR chemical shielding of finite SWCNTs were found to converge very slowly, if at all, to the infinite limit, indicating that hydrogen capped tube fragments are not necessarily good models of infinite systems. As the length of the fragment increases, these orbitals do not yield a contribution to the electron density along the tube (except at the ends) and must therefore be regarded as artifacts due to treating the finite-sized systems. More recently, this group indicated that [54] Also, the introduction of nitrogen atoms is theoretically predicted to give rise to chiral current flow along the nano-tube due to symmetry breaking [55, 56]. Due to N_2 chemisorption the calculated ^{15}N NMR parameters of those interacted carbon atoms are also modified. As understood by comparison of sites (A_1, A_2, A_3 and A_4), the carbon atoms included in N_2 chemisorption become more shielded. Among the four NMR principal components, intermediate shielding component, σ_{22}, shows more change from nano-tube to the N_2–CNT system. The discrepancy between the ^{15}N chemical shielding tensor for the sites (A_1, A_2, A_3 and A_4) systems must be attributed to the different nature of the frontier orbitals which will have an influence on the ^{15}N chemical shielding.

However, this theoretical considerations and predictions are undermined by recent experimentally investigations where chiral currents have been observed in undoped single-walled carbon nano-tubes [57]. The interest in nitrogen-doped CNTs in terms of application is the control of the type of charge carriers within the carbon nano-tubes. This control is one key-issue for a successful implementation of CNTs in nano- and molecular-electronics. N_2-CNTs should show significant advantages over nano-tubes for gas sensor applications, due to their reactive tube surfaces, and the sensitivity of their transport characteristics to the presence, distribution and chemistry of nitrogen. Peng and Cho first suggested N_2-CNT for use in gas sensors, due to the ability of nitrogen dopants to bind to incoming gas species [58]. The nitrogen in the nano-tubes can be seen as regular defects which change the chemical behavior of the tubes.

CONCLUSION

According to DFT and HF calculations, adsorption of, N_2 Molecules extremely influenced geometrical and electronic structure properties of (4, 4) and (5,0) SWCNT. For nitrogen molecule adsorption, the binding energy at the Table 1&2 is found to be -42650.00 eV, which is more stable than nitrogen molecule adsorption. It is found that ^{15}N chemical shielding is appropriate parameters to investigate the nature of interactions in (4,4) and (5,0) SWCNT. The ^{15}N chemical shielding isotropy and anisotropy values vary remarkably from CNT to CNT–N_2 systems, for adsorption sites.

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