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Carbon Dioxide Adsorption on Single Walled Bamboo-Like Carbon Nanotubes (SWBCNT): A Computational Study

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ABSTRACT: Adsorption of CO_2 on single walled (12,0) and (5,5) bamboo-like carbon nanotubes (SWBCNT) has been investigated theoretically. Adsorption of CO_2 at 12 different sites is calculated on the surface of these tubes. The advantage of using BCNT's is the multiple number of potential binding sites available near the partition wall. On them, CO_2 can get adsorbed and the number is greater as compared to normal SWCNTs. It has been observed in BCNTs, that the CO_2 molecule gets absorbed via chemisorption at most of the sites. The mechanism is that the molecule breaks and the oxygen atom binds to the carbon atom of BCNT surface, changing sp2 to sp3 hybrization. The adsorption has been interpreted with reference to change in structural and electronic properties e.g. length, diameter, bond length, charge transfer and energy band gap of tubes. Our findings show that the molecule is adsorbed more strongly with larger adsorption energy on (12,0) surface than on the (5,5). The calculated value of adsorption energy in the present work is greater than the values reported previously on SWCNTs. For the first time the adsorption of any gas has been carried out on SWBCNTs.
Keywords: Bamboo-like carbon nanotubes, CO_2 , adsorption, physisorption, chemisorption.

I. INTRODUCTION

Carbon dioxide (CO_2) is of course well known as being responsible for green house effect. Burning fossil fuel releases CO_2 stored over several millions of years. Fossil fuel is extensively used worldwide to power vehicles, generate electricity (in coal based power stations), power factories and heat interiors. In addition, deforestation releases CO_2 stored in plants. Several gases including CO_2 act like a blanket and their increasing concentration restricts the rate at which the earth's surface can radiate heat to space. This in turn further contributes to global warming. Once released, green house gases remain in the atmosphere till they are absorbed by plants or animals, degraded by sunlight or by chemical reaction with other molecules. CO_2 remains in the atmosphere for approximately 100 years, hence it is extremely hard to reverse global warming, once it sets in. Therefore it is essential to restrict and control the release of CO_2 into atmosphere.

Emission of CO_2 can be controlled either by making it react with other molecules or by adsorbing it on some substrate before its being pumped into atmosphere. A lot of research has been done in this direction both theoretically and experimentally. The motive is to search for a suitable material for adsorbing and storing CO_2. Metal-organic framework (MOFs) and related compounds have received preferential attention till now. Based on computational studies, Torrisi et al. [1] proposed new metal-organic framework material (MOFs) intended to improve CO_2 adsorption capacity. Valenzano et al. [2] carried out computational and experimental investigation of Mg-MOF-74 in order to verify the adsorption capacity of CO2 along with CO and N_2. Millward et al. [3] examined nine crystal structures of MOFs for CO_2 storage capacity at room temperature and concluded that they were excellent candidates for CO_2 storage. Walton et. al [4] presented experimental adsorption isotherms for CO_2 in MOF-5 over a wide range of temperatures. Bastin et al. [5] examined MOF Zn (BDC) for separation and removal of CO_2 from its binary and ternary mixtures. The high concentration of open metal sites in MOFs has been suggested [6] as a measure for methane and CO_2 storage and for separation chambers at different temperature and pressure range.

Carbon nanotubes (CNTs) have demonstrated the scope of their wide applicability in emerging technologies. Hence they seem to be plausible candidates for absorbing gases on account of their several exceptional features. As compared with the MOFs, CNTs have large surface to volume ratio, high thermal and electrical conductivity, remarkably high chemical stability at high temperature and other useful features [7,8]. Thus they are ideal candidates for various functional materials. Having high surface to volume ratio, the tubular structure of CNTs leads to unique surface chemistry. Another advantage of CNTs in the context of surface chemistry is high reactivity at nano dimensions as compared to bulk state. The potential of these tubes towards affinity of adsorbing various gases on CNTs has been largely explored during recent years [9-18]. The hollow structure of CNTs makes them suitable material for nanoscale chemical sensing devices [19]. Kong et al. [20] observed a change in resistance of semiconductor SWNTs on exposure to NH_3 and NO_2 and thus serve as the basis of molecular sensors which exhibits fast response and high sensitivity over solid state sensors. CNTs for

effective CO_2 adsorbent have been studied by a number of worker from different perspectives. Hsu et al. [21] used CNTs for studying thermodynamics and regeneration of CO2 capture from gas streams. Cinke et al. [22] studied adsorption of CO_2 experimentally in the temperature range 0-200 ºC as well as did theoretical investigation. They concluded that CO_2 is physisorbed side-on to the nanotube, the value of adsorption energy obtained by them is 0.024 eV experimentally, which is consistent with their calculated value. Feng et al. [23] reported CO_2 adsorption binding energy 1.18 eV on functionalization with metal oxide i.e. MgO (metal oxide) decorated carbon nanotube. Du et al.[17] investigated Fe doped carbon nanotubes as host for CO_2/N2 absorption.

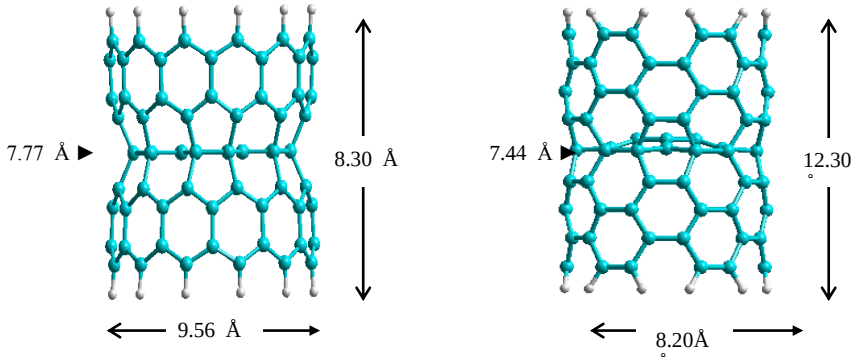
In the present work, we investigate the performance of bamboo-like carbon nanotubes (BCNT) for CO_2 absorption using semi empirical PM3 method. The structural and electronic properties of bamboo-like nanostructures have been studied [24] theoretically by semi empirical (PM3) method. Results show that these structures are stable and endothermic. Using molecular dynamics simulation Malcioğlu et al. [25] showed that single wall bamboo-like nanotubes are thermodynamically and energetically stable. To the best of our knowledge, adsorption of any gas on bamboo-like nanotube has not been investigated so far. For the first time we are presenting here the study of adsorption of any gas on bamboo-like carbon nanotubes. In this study, (12,0) and (5,5) bamboo-like carbon nanotubes (BCNTs) are used for adsorbing CO_2 molecule. Bamboo-like shape is due to corenene-spacers which make the tube compartmented. The geometrical aberrations in vicinity of spacer are due to the curvature induced by the pentagons [26]. The motivation for using bamboo-like instead of normal SWNTs is that the outer surface of BCNTs is not smooth and the geometrical aberration forms grooves between two pentagons and two hexagons on either side of the coronene partition wall that may serve as ideal site for gas absorption.

II. COMPUTATIONAL DETAILS

Initially the bamboo-like carbon nanotubes (BCNTs) (12, 0) and (5,5) were constructed. These structures are primarily optimized classically using molecular mechanics method [27] with (mm+) force field [25], so as to get equilibrium geometry with the lowest possible strain energy. The classically optimized geometrical structures are further optimized by applying PM3 (Modified Neglect of Differential Overlap Parametric Method Number 3) semiempirical method [28] with in Restricted Hartee-Fock (RHF) formulation [29], sufficient to study carbon systems. Semi empirical methods serve as sufficient computational tools which can yield fast quantitative estimates for a number of properties [30]. Compared with ab initio or density functional methods, semi empirical calculations are much faster, typically by several order of magnitude [31]. All the structures were then subjected to conjugate gradient geometry optimization (Polak-Ribiere method [32], setting convergence limit 0.001 kcal-mol^{-1} and rms gradient 0.001 kcal (Å-mol)$^{-1}$. The optimized calculations were performed using Hyperchem 7.5 molecular modeling program [33]. The electron density difference has been calculated by semiemperical module [34] of the Quantumwise Atomix Toolkit 12.8.0, program [35].

III. RESULTS AND DISCUSSION

Fig. 1(a) and (b) show the optimized structures of side and top view (below them) of (12, 0), (5, 5) bamboo-like carbon nanotubes (BCNTs). Due to the absence of periodic boundary conditions in molecular calculations, the end carbon atom (which is not bonded) is saturated by hydrogen atoms. The length and diameter of (12,0) and (5,5) BCNTs are 8.30, 9.56 and 12.30, 8.20 Å respectively. There are 144 atoms in both these zigzag and armchair configurations. These tubes are squeezed at the partition wall and the diameter there becomes less than that at the ends. The decrease in diameter due to squeezing is more pronounced in (12, 0) as compared to (5, 5) BCNT. The values of diameter these two cases at partition wall are 7.44 and 7.77 Å. However the fractional change ($\Delta D / D$) in diameter is 18.7% in (12,0) and 9.3% in (5,5) BCNT The pristine hydrogenated (12,0) and (5,5) have 144 atoms.



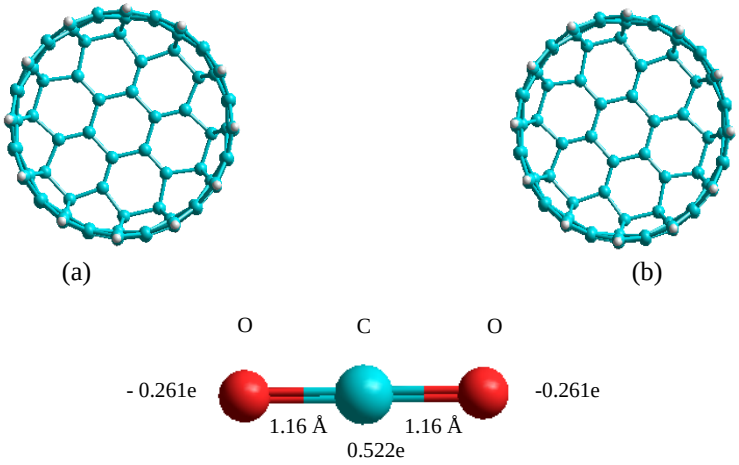
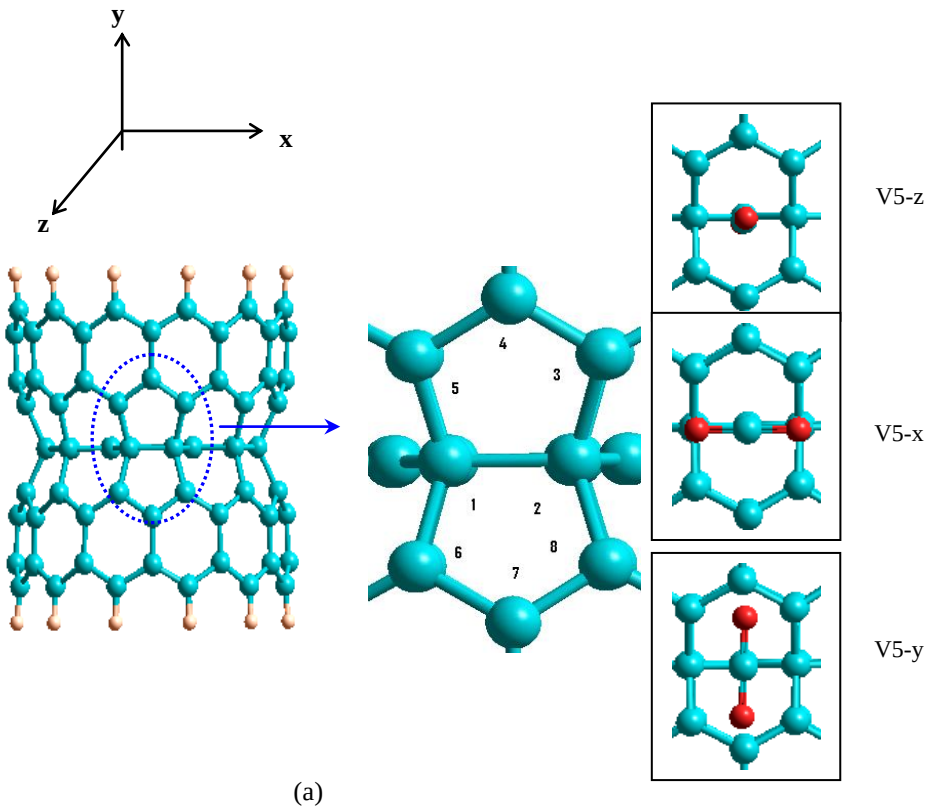
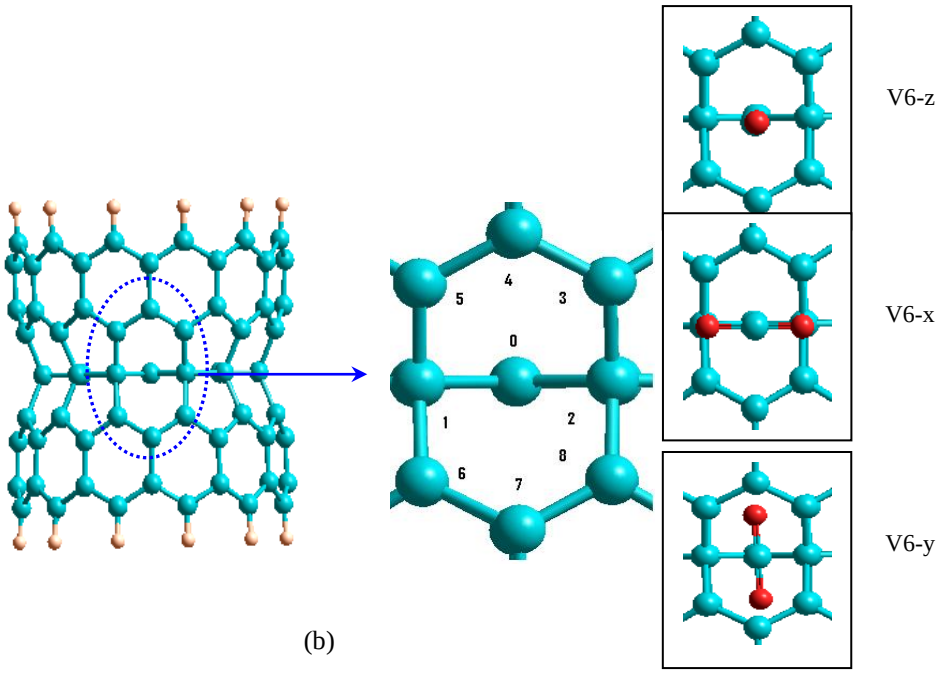


Fig 1: Optimized structures of (a) (12,0) and (b) (5,5) bamboo-like nano tubes (BCNT). Shown below each tube are corenene spacers which make them compartmented (top view) (c) CO_2 molecule.

Fig. 1 (c) shows the optimized structure of CO_2 molecule, where the C–O distance is 1.16 Å. A 0.522e charge develops on C and -0.261e charge on two oxygen atoms there by making the molecule neutral. As mentioned earlier the interaction of CO_2 molecule on the exterior walls of (12,0) and (5,5) BCNTs was studied by performing PM3 calculations for two different sites termed as V5 and V6 site. i) The V5 is the site at a point on partition wall with two carbon pentagons on either side, as shown in Fig. 2(a) and Fig. 3(a) in case of (12,0) and (5,5) BCNTs respectively, similarly ii) V6 is the site at a point on partition wall with two carbon hexagons on either side as shown in Fig. 2(b) and 3(b) in case of (12,0) and (5,5) BCNTs respectively.

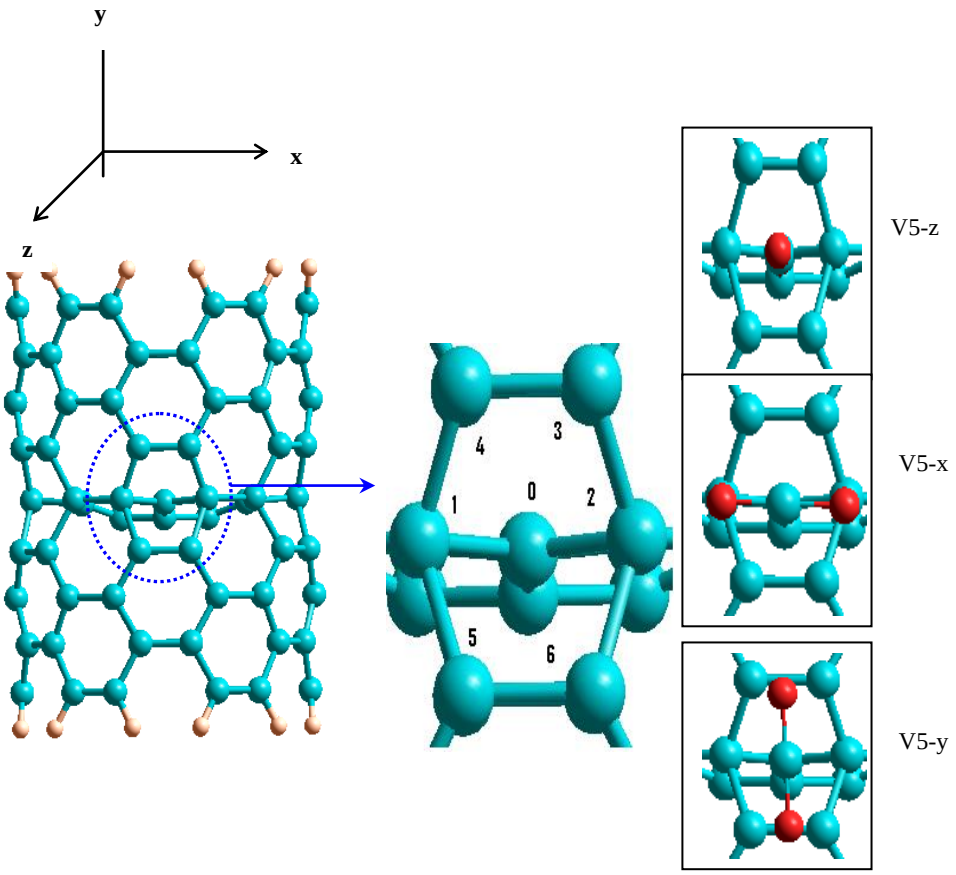


(a)

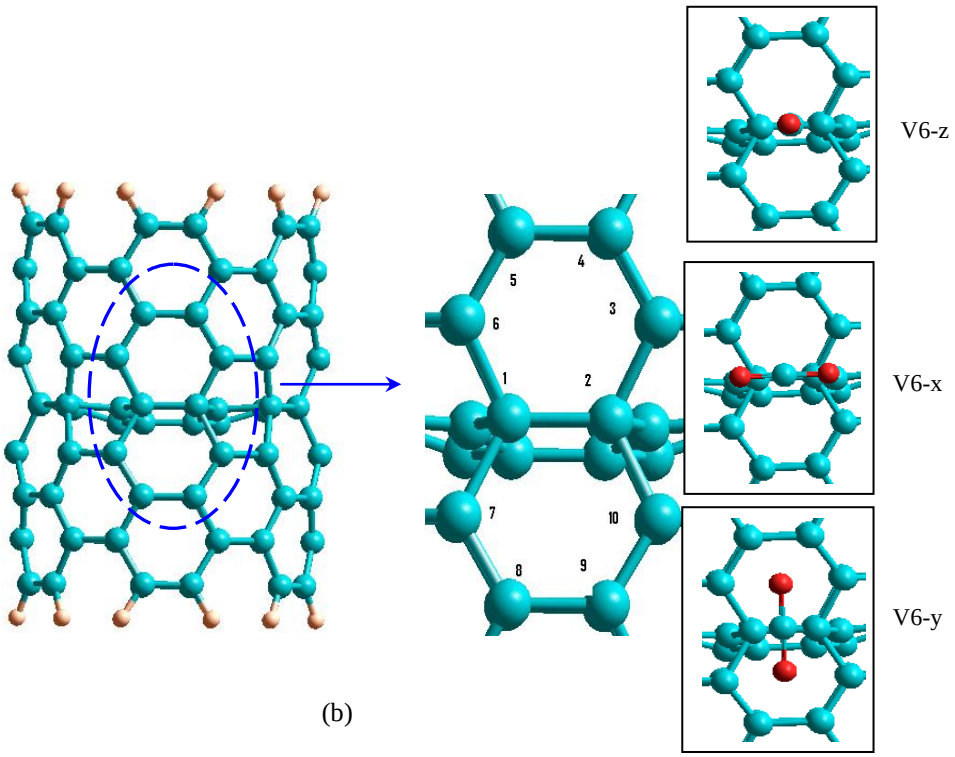


(b)

Fig 2: V5 (a), V6 (b) site between two pentagons and two hexagons on either side of partition wall of (12,0) BCNT. The orientation of CO_2 on these sites is shown on the right.



(a)



(b)

Fig 3: V5 (a), V6 (b) site between two pentagons and two hexagons on either side of partition wall of (5,5) BCNT. The orientation of CO_2 on these sites is shown on the right.

The CO_2 molecule is placed parallel to the z-axis, x-axis and y-axis at these sites labeled as; V5-z, V5-x, V5-y, V6-z, V6-x, and V6-y sites. These sites are shown on the right side of Fig. 2 for (12, 0) and Fig. 3 for (5,5) BCNT. In all, we have selected 12 different positions for calculation of adsorption of CO_2 on BCNTs. We have observed that the adsorption of CO_2 on these tubes takes place in two ways i) physisorption form in which the molecule bonds on the surface with weak van der Waals interaction and ii) chemisorption in which the CO_2 molecule gets dissociated and the oxygen atom of carbon dioxide molecule is chemically bonded with the C-atom of the tube on the surface. The adsorption of the molecules has been discussed with reference to change in bond length, the charge transfer and change in band gap. The adsorption energy E_{ad} of all stable configuration is calculated by the following equation

$$E_{ad} = E_{tot}(CO_2 + BCNT) - E_{tot}(BCNT) - E_{tot}(CO_2);$$

where,

$E_{tot}(CO_2 + BCNT)$ = total energy of combined system CO_2 and BCNT

$E_{tot}(BCNT)$ = total energy of BCNT

$E_{tot}(CO_2)$ = total energy of CO_2.

3.1 The CO_2 Molecule

Fig. 1 (c) shows the PM3 optimized, relaxed structure of carbon dioxide molecule, which is linear. A positive charge 0.522e is developed on carbon atom and a negative charge -0.261 develops on oxygen atom, thereby making the system neutral. The C-O distance is 1.16 Å. First column of Table 1 shows the structural and electronic properties of CO_2 molecule.

Table 1: Optimized structural and electronic parameters of CO_2, (12, 0) BCNT and CO_2 adsorbed on (12, 0) BCNT. All the energy values are given in eV, dimensions are in angstrom (Å) and the dipole moment is in debye (D)

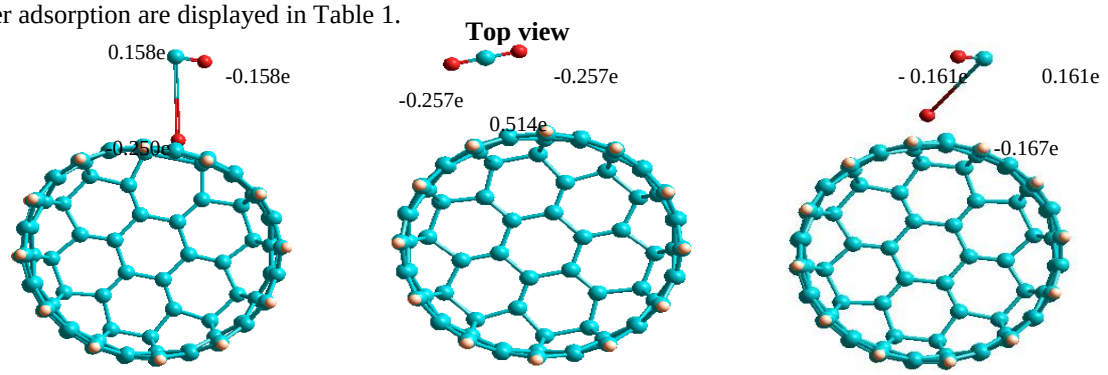
Parameters	**CO_2**	**(12,0) BCNT**	**CO_2 + (12,0) BCNT V-5 site**			**CO_2 + (12,0) BCNT V-6 site**		

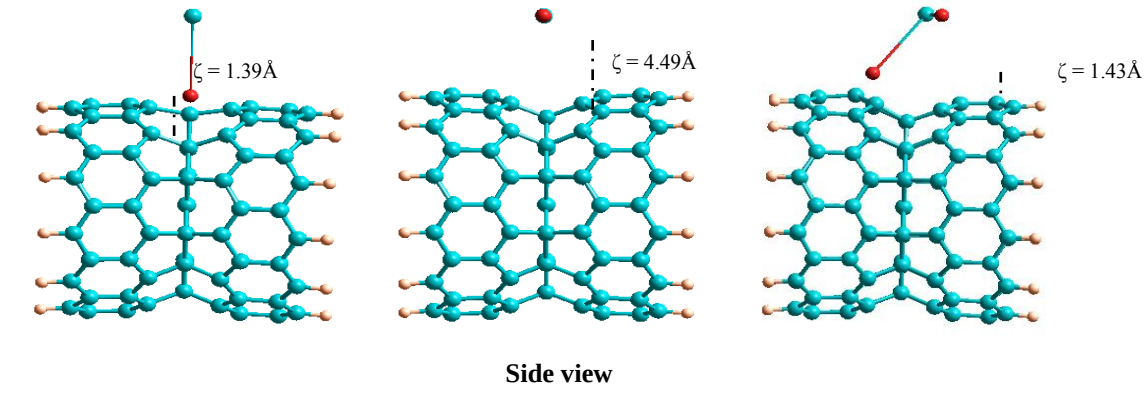
			V5-z	**V5-x**	**V5-y**	**V6-z**	**V6-x**	**V6-y**
d_t		9.56	9.92	9.56	9.55	9.46	9.56	9.56
l_t		8.30	8.60	8.30	8.32	8.35	8.30	8.32
$B.E$	-16.26	-891.76	-899.44	-908.00	-905.79	-901.58	-908.01	-907.27
ΔE_g	13.74	3.80	3.84	3.80	3.90	3.80	3.83	3.90
HOMO	-12.74	-6.84	-6.86	-6.85	-6.92	-6.82	-6.85	-6.96
LUMO	1.03	-3.01	-3.02	-3.02	-2.99	-3.02	-3.20	-3.03
E_{ads}			-8.60	-0.01	-2.20	-6.40	-.01	- 0.75
μ	0.00	0..00	1.20	0.21	1.42	0.78	0.18	3.36
$r(C_0 - C_1)$						2.26	1.50	1.50
$r(C_0 - C_2)$						1.48	1.51	1.51
$r(C_1 \quad C_2)$			2.26	1.57	1.57			
$r(C_2 - C_3)$			1.55	1.51	1.51	1.50	1.51	1.55
$r(C_3 - C_4)$			1.41	1.43	1.37	1.42	1.37	1.58
$r(C_4 - C_5)$			1.48	1.37	1.43	1.37	1.43	1.48
$r(C_1 - C_5)$			1.55	1.51	1.52	1.50	1.51	1.51
$r(C_1 - C_6)$			1.55	1.51	1.51	1.51	1.51	1.52
$r(C_6 - C_7)$			1.47	1.38	1.43	1.41	1.43	1.43
$r(C_7 - C_8)$			1.41	1.43	1.50	1.47	1.37	1.37
$r(C_2 - C_8)$			1.55	1.51	1.54	1.54	1.51	1.51
$r(CNT - CO_2)$			4.34	4.03	4.31		4.19	1.54
$r(C = O)$	1.18		3.62	1.18	3.78	5.65	1.18	1.39
$q\,(C\,in\,CNT)$								
$q\,(O\,in\,CO_2)$								

d_t: diameter of the tube, l_t: length of the tube, r :interatomic distance, $B.E$: binding energy, ΔE_g: energy band gap, HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital, E_{ads}: adsorption energy, μ: dipole moment

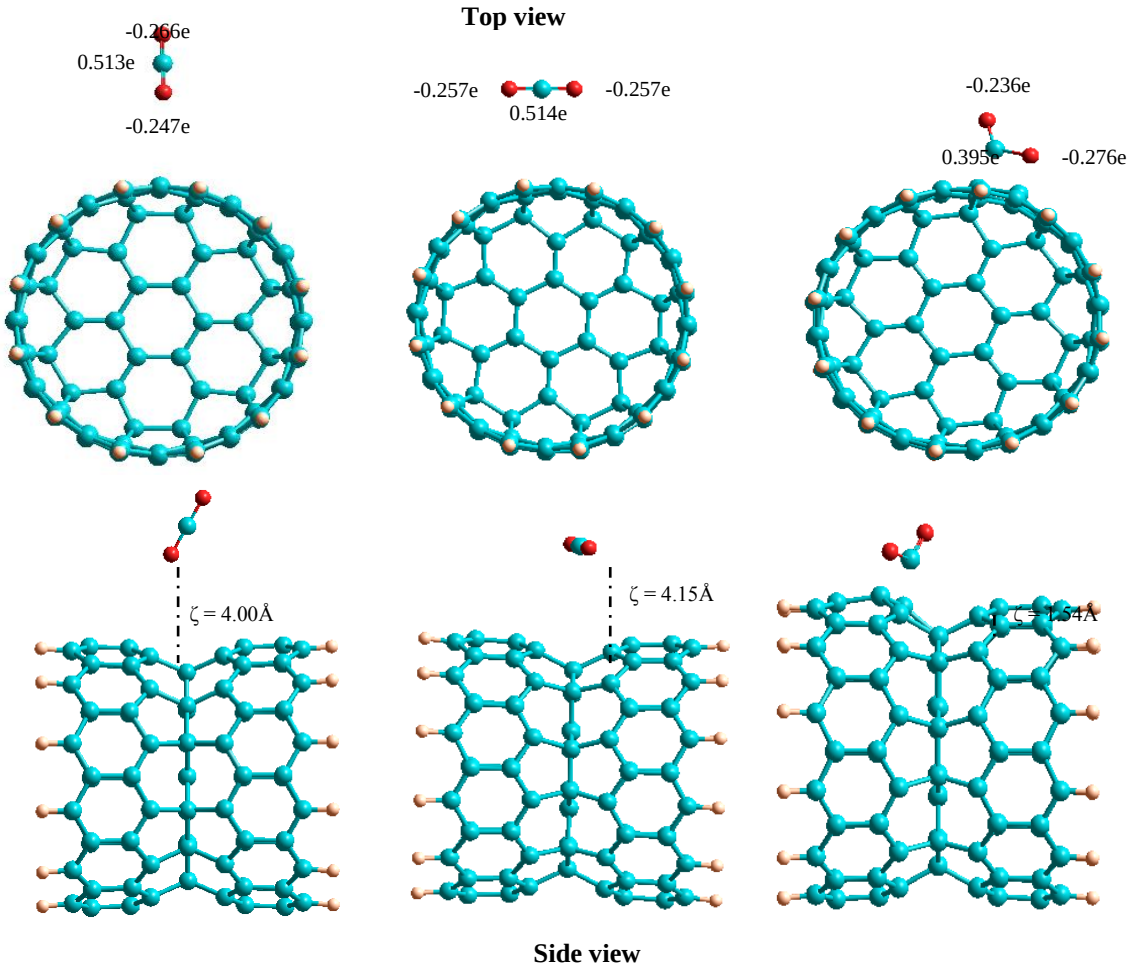
3.2 Adsorption of CO_2 on Zigzag Bamboo-like Carbon Nanotube (12,0 : BCNT)

The optimized geometries of calculated configurations of CO_2 molecule adsorbed on (12,0) BCNT are schematically shown in Fig 4(a) for V5 and 4(b) for V6 sites with CO_2 placed parallel to three different orientations (z, x and y) in each case. The computed structural and electronic parameters of the BCNT before and after adsorption are displayed in Table 1.





(a)

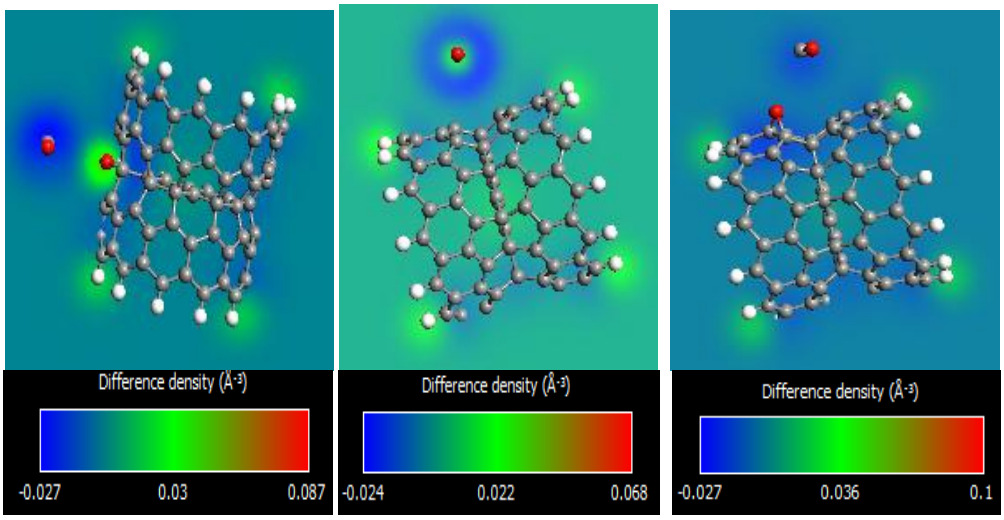


(b)

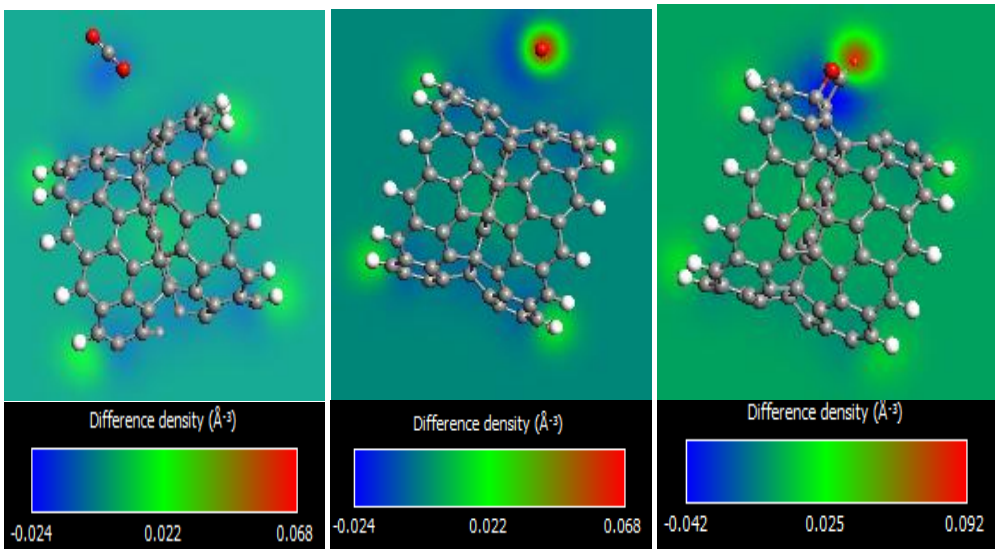
Fig. 4 Optimized molecular structures of CO_2 adsorbed on (12,0) BCNT on V5 (a) and V6 (b) sites with CO_2 oriented parallel to z-, x- and y- axis. ζ- is the bond distance between CO_2 and the BCNT nanotube (CO_2···BCNT).

(12,0) V5-site : Table 1 shows that there is a substantial change in the structural and electronic parameters upon adsorption of BCNT on V5-z and V5-y sites where the adsorption energies are -8.6 and -2.2

eV. In V5-z site the energy band gap increases from 3.80 to 3.84 eV. The bond distance ζ between CO_2 molecule and BCNT are 1.39 and 1.43 Å respectively. The system becomes polarized as the dipole moment of the tube increases from 0.00 D to 1.20 and 1.42 D respectively, It is greater in the later case when the molecule is oriented parallel to the tube axis. There is significant sharing of charges also in these two cases. The high value of adsorption energy can be understood in terms of chemisorption in both these cases. The oxygen atom gets dissociated from CO_2 molecule and binds with the carbon of BCNT. The addition of C-O bond to each of two neighboring sp2 hybridized carbon atoms leads to sp3 hybridization of carbon atoms on the substrate i.e BCNT, so these two are potential sites for chemisorption. Fig. 6 shows the electron difference density mapping of combined CO2 and (12,0) BCNT, which clearly shows that CO_2 molecule dissociates and its oxygen atom binds with the BCNT. The adsorption energy is -0.01 eV when the CO_2 is placed on V5-x and it seems the molecule binds the BCNT with van der Waals interaction and the molecule in this case remains at a distance ζ = 4.49Å from the BCNT.



V5-z V5-x V5-y



V6-z V6-x V6-y

Fig 5: Electron difference density ($Å^{-3}$) mapping of the combined CO_2··(12,0) BCNT systems with CO_2 placed at the mentioned sites.

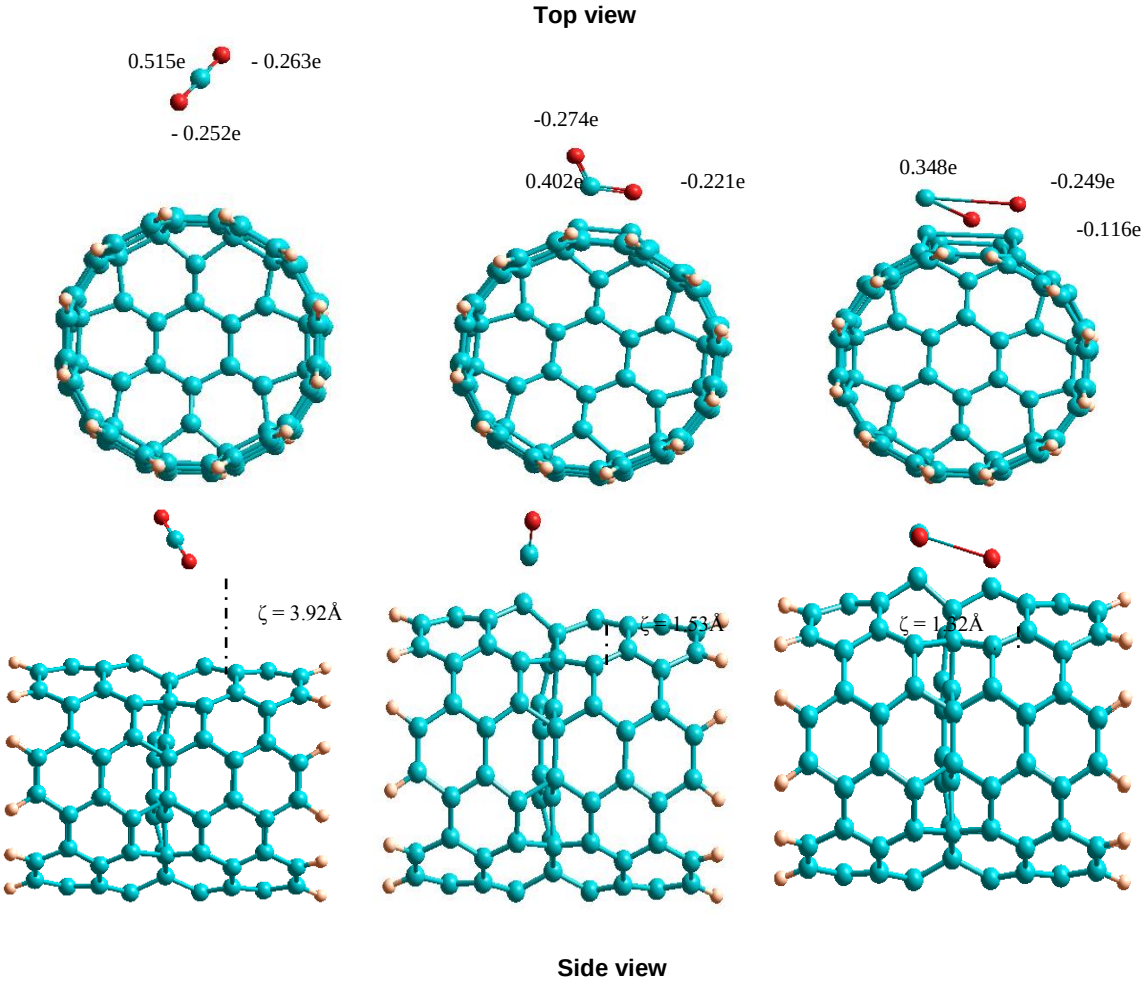
(12,0) V6-site : The adsorption of CO_2 on V6-site (top and side view of BCNT) is shown in Fig. 4 (b). The maximum adsorption energy in this case is -6.40 eV when the molecule is aligned along the z-axis. The adsorption energy along y-axis is -0.75 eV There is maximum change in dipole moment (3.30 D) in this case, among all orientations considered. Here again the hybridization changes from sp2 to sp3. The adsorption energy

is minimum (-0.01 eV), when the molecule is aligned parallel to x-axis i.e V6-x. The magnitude of adsorption energy is same as in V5-x site.

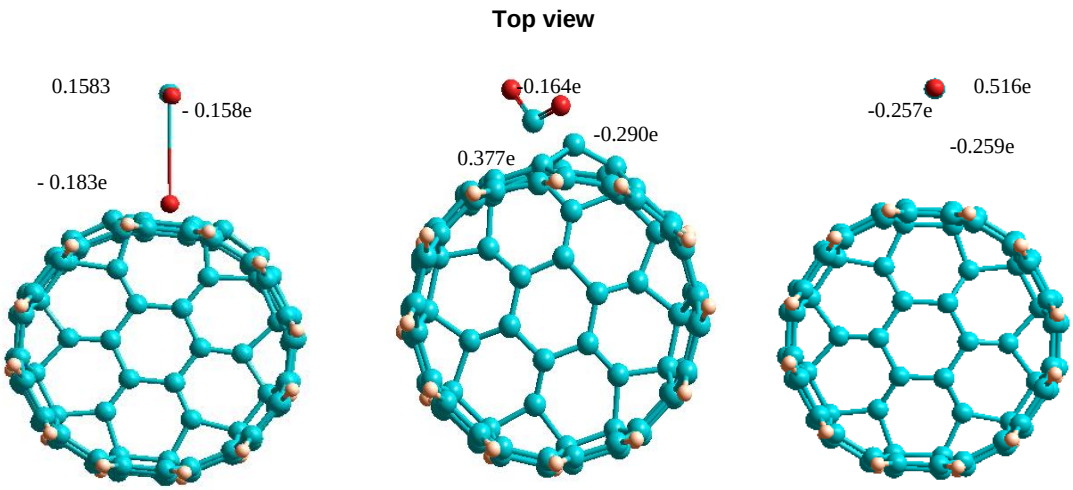
It is obvious that z- orientation in V5 and V6 offers high adsorption energy and shows chemisorption, where as it is small and same (-0.01) in x-orientation in both the cases and are the sites of physisorption.

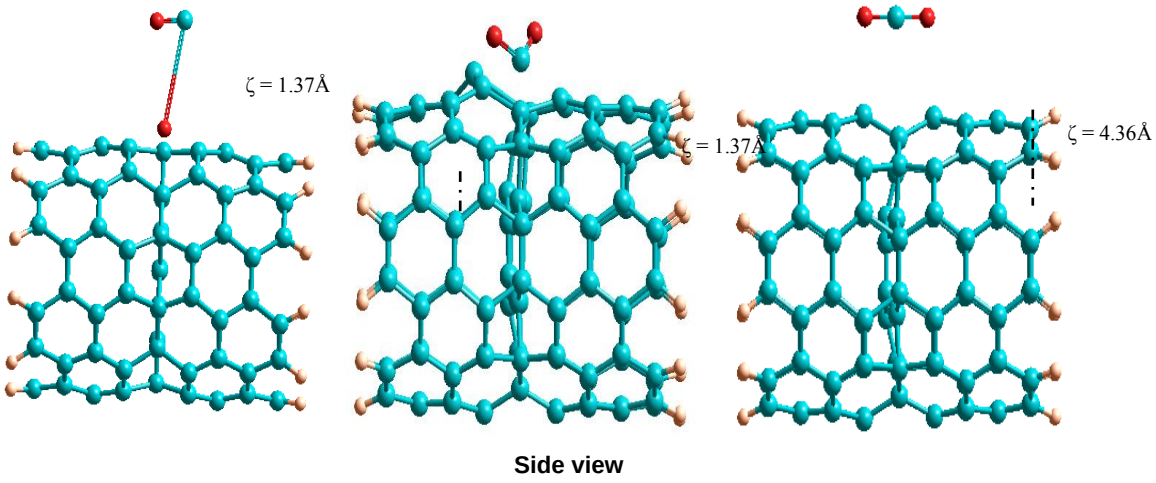
3.3 Adsorption of CO_2 on Armchair Bamboo-like Carbon Nanotube (5,5: BCNT)

The optimized geometries of calculated configurations of CO_2 molecule adsorbed on (5,5) BCNT are shown in Fig 6(a) for V5 and 6(b) for V6 sites with CO_2 placed parallel to three different orientations (z, x and y).



(a)





(b)

Fig. 5 Optimized molecular structures of CO_2 adsorbed on (5,5) BCNT on V5 (a) and V6 (b) sites with CO_2 oriented parallel to z-, x- and y- axis. ζ- is the bond distance between CO_2 and the BCNT nanotube (CO2···BNCT).

The computed structural and electronic parameters of the BCNT before and after CO_2 adsorption are displayed in Table 2. Although the number of atoms in this case is same i.e 144 as that in (12,0) BCNT, the length in this case is greater and diameter is less as compared to (12,0) BCNT.

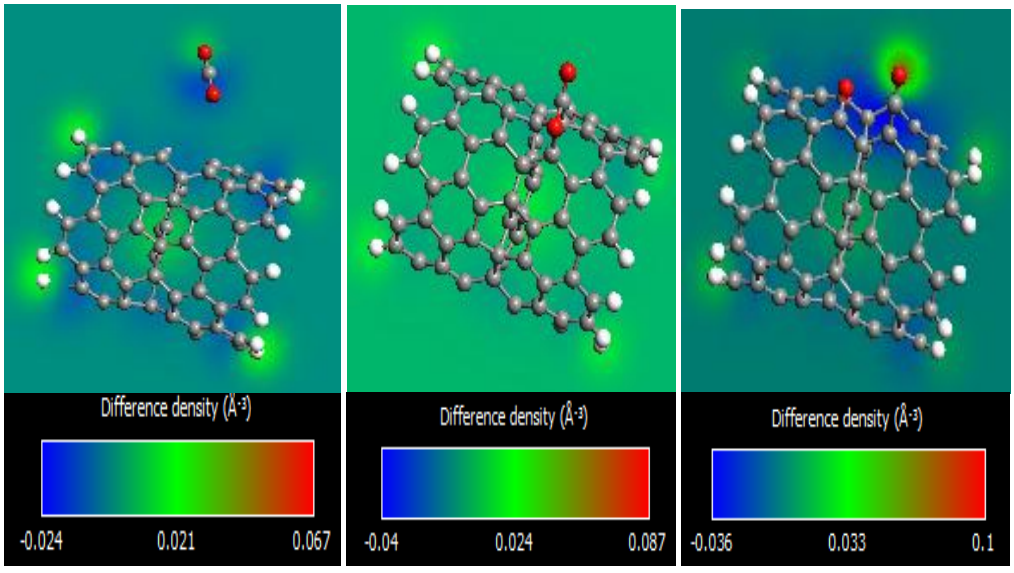
Table: 2 Optimized structural and electronic parameters of CO_2 , (5,5) BCNT and CO_2 adsorbed on (5,5) BCNT. All the energy values are given in eV, dimensions are in angstrom (Å) and the dipole moment is in debye (D)

Parameters	**CO_2**	**(5,5) BCNT**	**CO2 + (5,5) BCNT V-5 site**			**CO2 + (5,5) BCNT V-6 site**		
			z-axis	**x-axis**	**y-axis**	**z-axis**	**x-axis**	**y-axis**
d_t		8.20	8.20	8.23	8.19	8.23	8.30	8.23
l_t		12.30	9.90	9.87	9.88	9.89	10.10	9.90
$B.E$	16.26	-887.01	-903.27	-903.60	-899.86	-900.14	-901.62	-903.27
ΔE_g	13.74	6.42	6.42	6.50	6.40	6.44	6.41	6.43
HOMO	-12.74	-8.20	-8.20	-8.33	-8.25	-8.24	-8.29	-8.21
LUMO	1.03	-1.78	-1.78	-1.87	-1.89	-1.80	-1.88	-1.78
E_{ads}			-0.01	0.30	-3.41	-3.13	-1.70	-.01
μ	0.00	0.57	0.54	3.34	3.59	1.06	3.22	0.60
$r(C_0 - C_1)$		1.53	1.53	1.52	3.59			
$r(C_0 - C_2)$		1.53	1.52	1.52	1.56			
$r(C_2 - C_3)$		1.53	1.54	1.52	1.56	1.52	1.49	1.53
$r(C_3 - C_4)$		1.42	1.43	1.41	2.18	1.44	1.39	1.41
$r(C_1 - C_4)$		1.53	1.54	1.52	1.51			
$r(C_1 - C_5)$		1.54	1.53	1.52	1.50			
$r(C_5 - C_6)$		1.44	1.42	1.55	2.95	1.44	1.41	1.41
$r(C_2 - C_6)$		1.54	1.53	1.54	1.53			
$r(C_1 - C_2)$						2.29	1.50	1.54

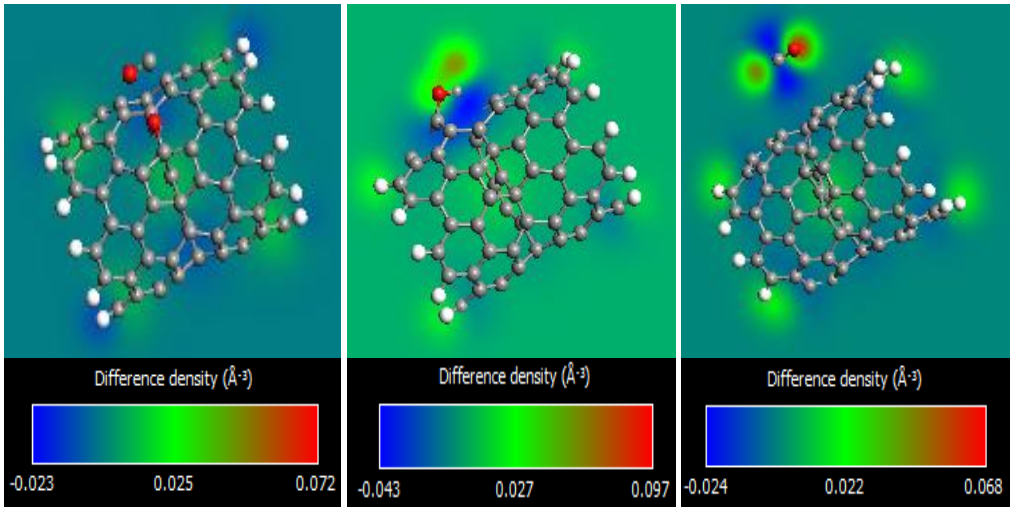
$r(C_4-C_5)$						1.53	1.46	1.47
$r(C_1-C_6)$						1.52	1.53	1.53
$r(C_1-C_7)$						1.52	1.57	1.54
$r(C_7-C_8)$						1.44	1.44	1.41
$r(C_8-C_9)$						1.53	1.50	1.48
$r(C_9-C_{10})$						1.44	1.44	1.41
$r(C_2-C_{10})$						1.52	2.48	1.54
$r(C=O)$			1.19	1.40	3.03	3.70	1.18	1.18
$r(CNT-CO_2)$			4.16	1.53	1.32	1.38	1.54	4.46
$q(C\ in\ CNT)$								
$q(O\ in\ CO_2)$								

d_t: diameter of the tube, l_t: length of the tube, r: interatomic distance, $B.E$: binding energy, ΔE_g: energy band gap, HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital, E_{ads}: adsorption energy, μ: dipole moment

(5,5) V5-site : Adsorption of CO_2 on this site with different CO_2 orientations is shown in Fig. 6(a). Table 2 shows the structural and electronic parameters of lone (5,5) BCNT and CO_2 adsorbed BCNT. The adsorption energy on V5-z site is -0.01 eV. There is no change in energy band gap and no appreciable change is structural or charge transfer in this case. The distance between molecule and tube is ζ=3.92Å . Jio et al. [36] reported this distance in the range 3.18-3.80 for various sites in case of adsorption of CO_2 on AlN nanotubes. The molecule is weakly bound to the tube due to van der Waals interaction. The electron difference density in Fig. 7 shows this weak interaction which may be attributed to physisorption.



V5-z V5-x V5-y



V6-z V6-x V6-y

Fig. 7 Electron difference density ($Å^{-3}$) mapping of the combined CO_2··(5,5)BCNT systems with CO_2 placed at the mentioned sites.

On V-5x site the value of energy is 0.30 eV. Since this value is positive it shows that the reaction is improbable.The maximum adsorption energy (-3.41 eV) has been observed on V5-y site. In this case there is a change in energy band gap of the tube upon adsorption. The electron difference density in Fig. 7 shows that the CO_2 molecule dissociates and the oxygen atom form bond with the carbon atom of thethe nanotube.

(5,5) V6-site: The adsorption on this site is just reverse of that V5 site. The V6-z site is the most probablesite for chemisorption with adsorption energy of -3.13 eV whereas the value is -0.01 eV on V6-y site. The value on V6-x site is 1.70 eV and ζ=1.37Å.

IV. CONCLUSION

In this work we have investigated the adsorption of any gas molecule on bamboo-like carbon nanotubes for the first time. In the context of the challenge to the environment, it is important to explore any promising avenues. CNT's provide a new possibility to reduce the environmental problem, by harnessing CNT's for adsorption. The method used in this study is semi empirical and two bamboo like structures (12,0) and (5,5) are investigated. Relevant structural and electronic parameters have been calculated. The interaction of CO_2 molecules has been studied for two sites (V5 and V6). It is found that the adsorption of CO_2 takes place in to ways (physisorption and chemisorption) Adsorption of CO_2 molecule has been examined, in the context of bond length change, band gap modification and charge transfer. Significant changes are induced by adsorption in the structural and electronic parameters. These changes have been systematically assessed, by comparing them for the sites selected. A comparison with alternative methods of calculation would be interesting; but has not been attempted in the limited scope of the present study. For the sake of comparision we have computed the adsorption energy by placing CO_2 molecule in similar orientations (-z,-x and -y) on the surface of SWCNT (12,0) and (5,5) of same dimensions by using same computational method. The values of adsorption energies obtained on these sites are -0.02, -0.01 and -2.49 eV in (12,0) and -0.02, -0.01 and -0.01 eV in (5,5) SWCNT. These values are small in comparison with the values obtained in BCNTs. So BCNT are more suitable for adsorption of CO_2. Further studies related to adsorption of other gases are in progress.

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