Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 7 (2) 111-126: Summer 2010
(J. Phys. Theor. Chem. IAU Iran)
ISSN: 1735-2126

Investigation of chemical adsorption of CO, CO_2, H_2 and NO molecules on inside and outside of single-wall nanotube using HF and DFT calculations

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Received August 2010; Accepted August 2010

ABSTRACT

In this research, CO gas molecules were approached to single-wall carbon nanotube (SWNT) and (6,0) CNT surface from carbon side and oxygen side in three states (top, bridge, centre) and two shapes (vertical, horizontal), then adsorption energies were calculated by B3LYP/6-31G , B3LYP/3-21G** and HF/3-21G** methods after that they were compared in order to obtain the most stable adsorption state. DFT and HF methods were compared and the better method was selected. Also two basis sets were compared. Besides, the bond length of gas molecule was changed by GAUSSIAN 03 program and was calculated by B3LYP with the basis set of 3-21G** for the nanotube and gas molecules. Next CO, NO, H_2, CO_2 molecules were passed through the nanotube with different intervals and the adsorption energies for SWNT and NO, CO, H_2 and CO_2 molecules were compared and then calculated using B3LYP /6-31G. So the same process was repeated for CD molecules using basis set 3-21G** and adsorption energies on the inside and outside surface of the nanotube were compared.

Keywords: NO adsorption; Cu(111) surface, DFT, Slab method

INTRODUCTION

Carbon nanotube (CNT) is a representative nanomaterial. CNT is a cylindrically shaped carbon structure, which is in the form of a hexagonal mesh, resembles a graphite sheet and it carries a carbon atom located on the vertex of each mesh. The sheet is rolled and its two edges are connected seamlessly. Although it is a commonplace material that is used in pencil leads, its unique structure causes it to present characteristics that are not found with any other materials. CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite. The type attracting most attention is the single-wall CNT, which has a diameter deserving the name of "nanotube" of 0.4 to 2 nanometres. The length is usually in the order of microns, but single-wall CNT with a length in the order of centimetres has recently been released.

The extremities of the CNT are usually closed with lids of the graphite sheet. The lids consist of hexagonal crystalline structures (six-membered ring structures) and a total of six pentagonal structures (five-membered ring structures) placed here and there in the hexagonal structure. The first report by Iijima [1] was on the multiwall form, coaxial carbon cylinders with a few tens of nano meters in outer diameter. Afterwards, single walled nanotubes were reported [2, 3]. They are typically between 1 and 1.5 nm in diameter, but several microns in length. The discovery of carbon nanotubes (CNTs) which are nano-sized materials with excellent mechanical and electrical properties and have been proposed to be used in a variety of application fields [4]. CNTs are a new

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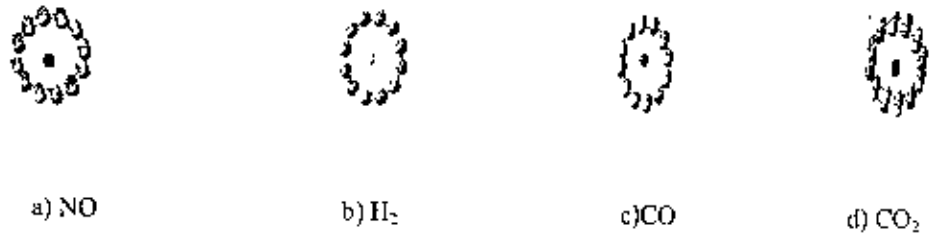
allotrope of carbon originated from fullerene family, which will revolutionaries the future nanutechnologicaI devices [5]. There are two types of CNTs: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) [6]; that they have three cunformations: armchair (n, n), zigzag (n, 0) and chiral (n, m) these conformations have individual properties [7]. SWCNTs have been considered as the leading candidate for nanodevice applicatinns because of their one-dimensinnal electronic bond structure, molecular size, and biocompatibility, controllable property of cunductiog electrical current and reversible respoose to biological reagents hence SWCNTs make possible bonding to polymers and biological systems such as DNA and carbohydrates [8]. In the recent years, carbon nanotubes have been intensively studied due to their importance as building blocks in nanotechnology [9-11]. They not only have outstanding mechanical and electronic characteristics but also hold considemble promise as molecular containers with applications sucb as hydrogen fuel cells, [12,13] nanoelectronic devices, chemical pmbes, and hiosensors [14-17]. The key element that makes nanotubes potentially usefu1 as electrochemical storages is their structures [18]. Recent studies bave shown that the physical properties of single-wall carbon nanotubes (SWNTs) could be modified by adsorption of foreign atoms or molecules [19-21] Gas adsorptiun on carboo nanntubes is an important issuc for botb the fundamental researcb and technical applicatioos of nanotubes Though single-wall carbon nanotubes (SWNTs) have different electronic properties depending un their chirality and diameters, [22] it is difficult to selectively synthesize SWNTs that have appropriate electronic properties for each applicatiun. A practical method to uvercome these difficulties can be, fur example to synthesize SWNTs and then remove undesired types by and etching method,[23] ur to modify synthesized SWNTs by hydrogenatiun and fluorination, [24-26] to provide desired electronic properties.

COMPUTATIONAL AND RESULTS

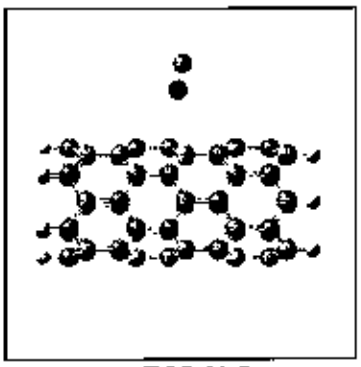
In this study at first SWNT (6, 0) and CO, NO, CO_2, H_2 mulecules were separately optimized using GAUSSIAN 03 program and the molecules were passed through the nanutube with different intervals (Fig.1) and the adsorption eoergies for SWNT, NO, CO, H_2 and CO_2 molecules were compared and then calculated using B3LYP/6-31G (Fig. 3). So the samc process was repeated for CO molecules using hasis set 3-21G** (Fig. 4). In this research CO gas molecules were approached to single-wall carbon nanntubc (SWNT) and (6, 0)CNT surface in three states (top, bridge, centre) and two shapes (vertical, horizontal) (Fig.2), Next, adsorption energies were calculated by B3LYP/6-31G and B3LYP/3-21G** and HF/3-21G** methods and were eompared in order tu obtain the most stable adsorption state (Fig. 5-10). Besides, the bond length of gas molecule was changed by GAUSSIAN 03 program and was calculated by B3LYP with the hasis set of 3-21G** for the nanotub, gas molceules (Fig.11) and its effect on adsorption energy was investigated by the means of the Equatinn (1).

$$E_{ad} = E_{tot}(CO + CNT) - E_{tot}(CO - E_{tot,\ CNT}) \quad (1)$$



a) NO b) H_2 c)CO d) CO_2

Fig.1 Adsorptiun inside nanotube (6, 0).



a) TOP-V-O

b) TOP-H-O

c) TOP-H-C

Fig. 2. Adsorption surface nanotube (6, 0) – CO.

Table1.Adsorption energy (kcal/mol) of gases inside the SWNT (B3LYP/6-31G)

R(Å)	E_{ad}(NO)	E_{ad}(CO2)	E_{ad}(CO)	E_{ad}(H2)
0.5	51.12682	71.62724	111.3235	26.33994
1	72.0621	95.91714	111.8826	29.44607
1.5	82.06382	102.5021	106.0431	24.41414
2	65.60136	70.44692	105.9189	20.56255
2.5	88.15183	134.746	112.8766	21.61863
3	84.73551	170.0293	1991.523	23.48231
3.5	84.85934	160.8352	99.9551	22 9232
4	67.52716	128.6556	93.18375	23.79292
4.5	68.459	123.6859	101 5703	21.61863
5	68.459	151.7031	112 5038	23.23382
5.5	67.03018	158.9715	104.1794	24 10353
6	75.66521	132.5073	91 38219	22.73684
6.5	71.13026	119.8343	95.73077	20.99741
7	75.47884	149.1363	113.1872	22 30198
7.5	83.49264	161.3943	106.1674	24.16565
8	67.89989	141.2666	92 56253	1984.13
8.5	63.05434	120.8904	92.93526	23.79292
9	85 41844	138.8438	111.3856	28 45211

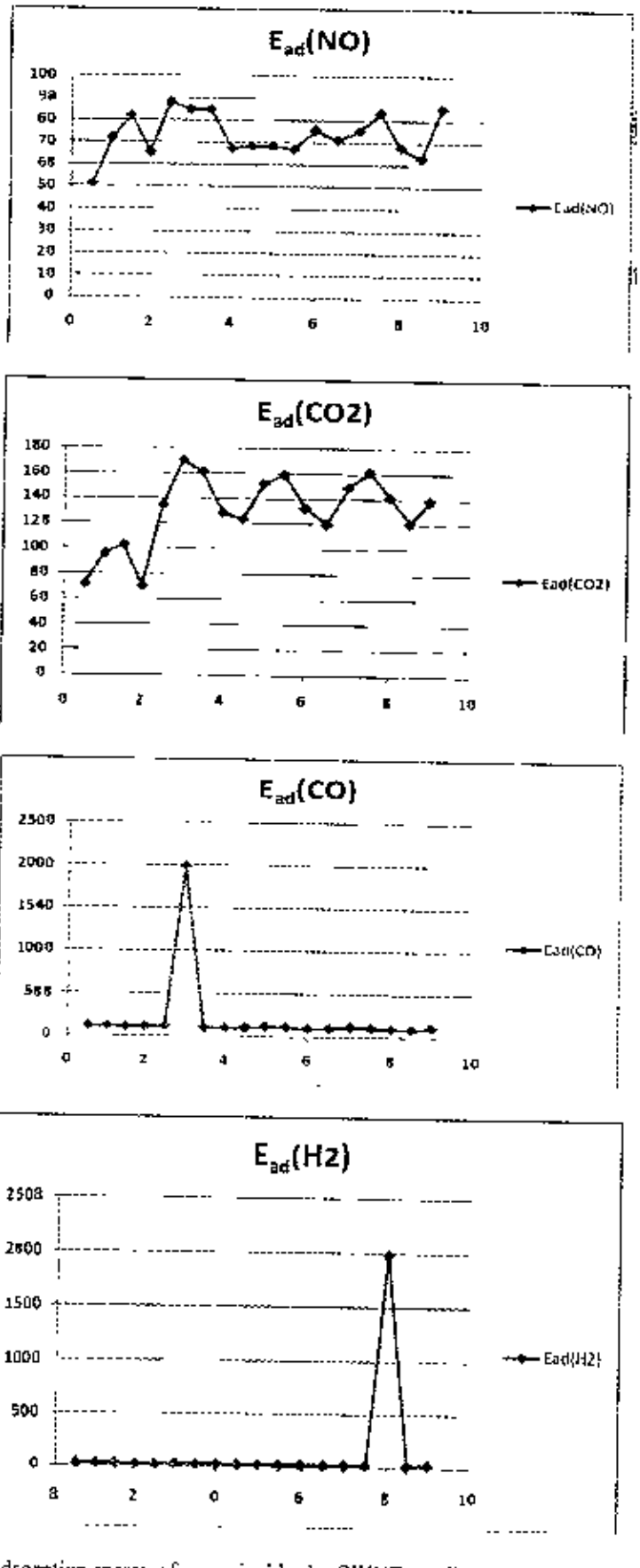


Fig. 3. Adsorption energy of gases inside the SWNT vs. distance (B3LYP/6-31G).

Table 2. Adsorption energy (kcal/mol) of CO gas inside the SWNT (B3LYP/3-21G**)

R(C≡O)(Å)	R(Å)	ECO	ECNT	Ead(CO)
1.15	0.5	-9994.6	-141671	77.591
1.15	1	-9994.6	-141671	93.99134
1.15	1.5	-9994.6	-141671	72.68333
1.15	2	-9994.6	-141671	76.28643
1.15	2.5	-9994.6	-141671	82.93354
1.15	3	-9994.6	-141671	75.23035
1.15	3.5	-9994.6	-141671	63.67556
1.15	4	-9994.6	-141671	66.28471
1.15	4.5	-9994.6	-141671	78.02588
1.15	5	-9994.6	-141671	81.4426
1.15	5.5	-9994.6	-141671	67.15442
1.15	6	-9994.6	-141671	783.8617
1.15	6.5	-9994.6	-141671	76.53422
1.15	7	-9994.6	-141671	82.80929
1.15	7.5	-9994.6	-141671	69.94994
1.15	8	-9994.6	-141671	63.30283
1.15	8.5	-9994.6	-141671	87.65485
1.15	9	-9994.6	-141671	87.64569

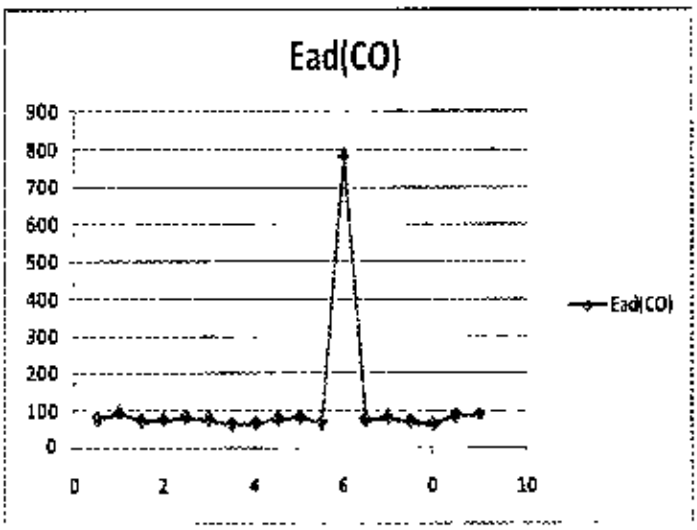
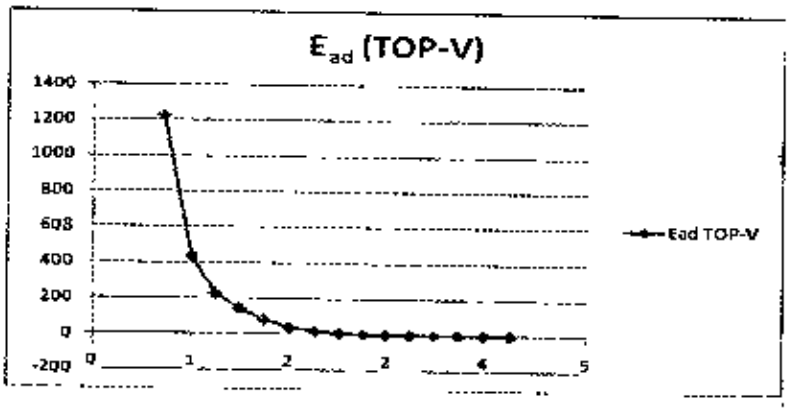
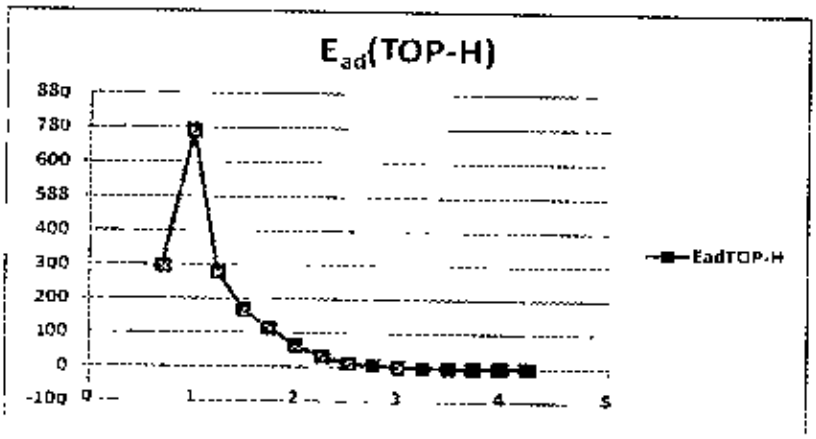


Fig. 4. Adsorption energy of CO gas inside the SWNT vs. distance (B3LYP/3-21G**).

Table 3. Adsorption energy (kcal/mol) of CO on the surface of SWNT (B3LYP/6-31G) fram oxygen side

R (Å)	E_{ad} TOP-V	E_{ad} TOP-H	E_{ad} bridge-V	E_{ad} BRIDGE-H	E_{ad} Centre-V	E_{ad} Centre-H
0.7	1223.813	295.4546	25.03537	1235.554	415.4753	1485.784
1	435.9136	691.7962	321.1733	2267.844	260.7281	605.3838
1.25	226.7471	277.5012	288.6695	320.0551	154.4987	306.823
1.5	143.2545	170.1535	134.5573	193.5116	87.34424	174.3157
1.75	80.38652	116.107	76.16219	114.616	47.95857	101.8809
2	35.47195	64.29679	40.19326	61.87401	26.52631	56.98421
2.25	17.27006	32.3037	20.68679	59.3263	14.3503	31.86125
2.5	6.274373	13.97756	13.04577	54.2586	9.69111	17.3943
2.75	1.180328	6.46074	9.132008	54.12693	11.85781	10.74719
3	-0.24849	2.4849	7.4547	64.2536	6.274373	7.20621
3.25	-0.86972	1.49094	6.70923	67.24563	7.019843	5.96376
3.5	-1.85608	-0.0269	6.150128	59.32415	5.777393	5.288413
3.75	-1.05618	-0.49698	6.21225	78.25463	5.663425	5.21829
4	-1.11821	0.124245	3.72735	61.24563	7.11256	5.404658
4.25	-0.68335	0.125236	4.83251	60.2541	6.26456	5.21829





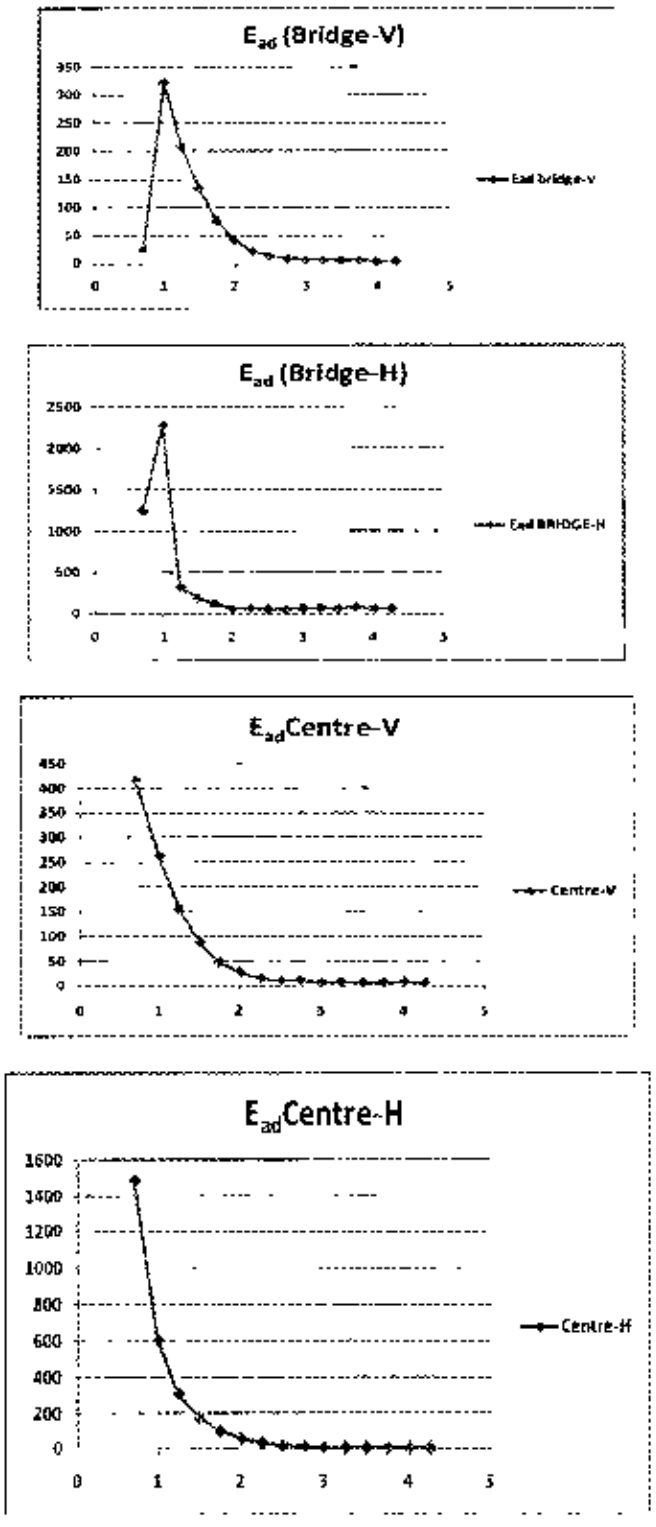


Fig. 5. Adsorption energy vs distance (B3LYP/6-31G) from oxygen side.

Table 4. Adsorption energy (kcal/mol) of CO an the surface of SWNT (B3LYP/6-31G) from carbon side

R(Å)	R(C≡O)(Å)	E_{ad} TDP-V	E_{ad} TOP-II	E_{ad} bridge-V	E_{ad} BRIDGE-II	E_{ad} Centre-V	E_{ad} Centre-H
8.5	1.15	1363.092	1847.461	441.6289	1640.834	355.5892	1422.295
1	1.15	383.9171	578.7953	154.9956	636.6314	201.8981	629.9222
1.5	1.15	130.9542	231.7169	96.22775	352.2346	142.9439	343.9723
2	1.15	86.9715	144	88.08971	209.4771	90.20187	212.2105
2.5	1.15	76.22431	99.14751	68.33475	125.1147	60.88005	123.4374
3	1.15	56.22086	54.35719	47.83433	67.83777	35.90681	69.08822
3.5	1.15	30.44003	28.14149	24.04141	31.55823	23.60655	37.2735
4	1.15	14.3503	13.85332	18.07765	23.1717	14.84728	21.37014
4.5	1.15	4.659188	6.46074	12.54875	11.36842	11.43854	13.60483
5	1.15	1.428818	4.037963	11.55479	7.889558	8.635020	9.380498
5.5	1.15	0.559103	2.547023	9.007763	2.23641	8.28817	7.4547
6	1.15	-0.99396	6.95772	8.510783	5.96376	7.765313	8.013803
6.5	1.15	-0.43486	2.23641	8.138048	6.274373	6.584985	7.516823
7	1.15	-1.05688	2.5638	8.20017	5.95642	7.641868	7.54326
7.5	1.15	-0.42569	2.33658	8.21546	5.89654	7.765313	7.65846

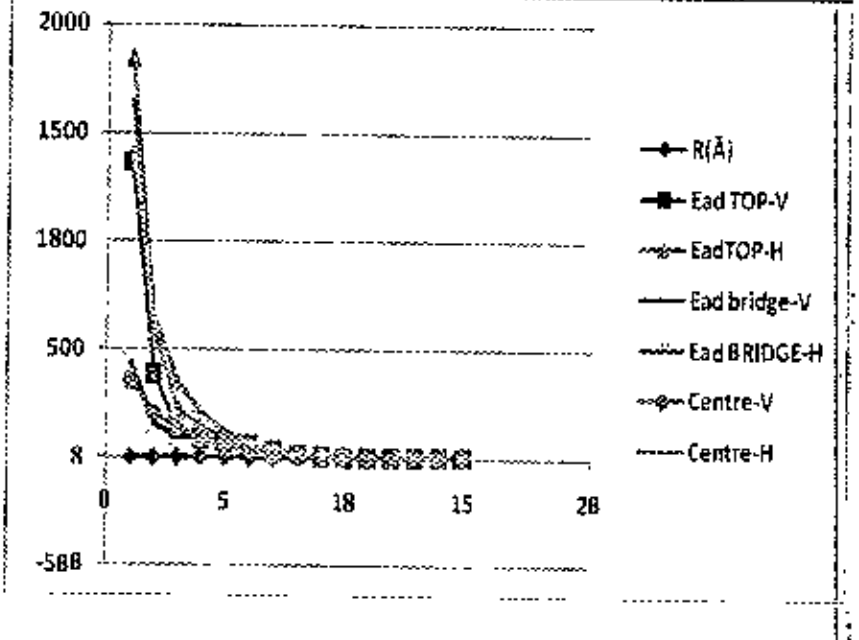
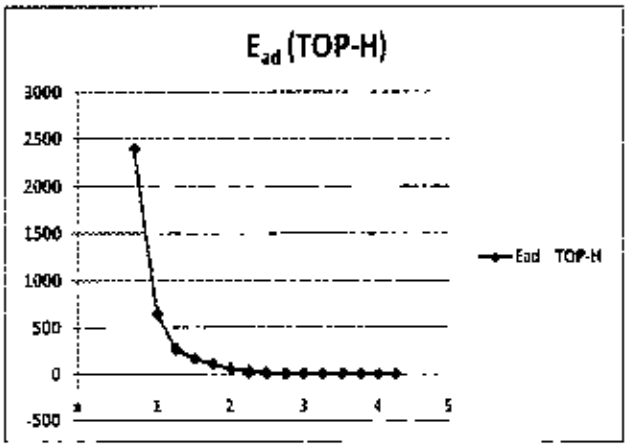
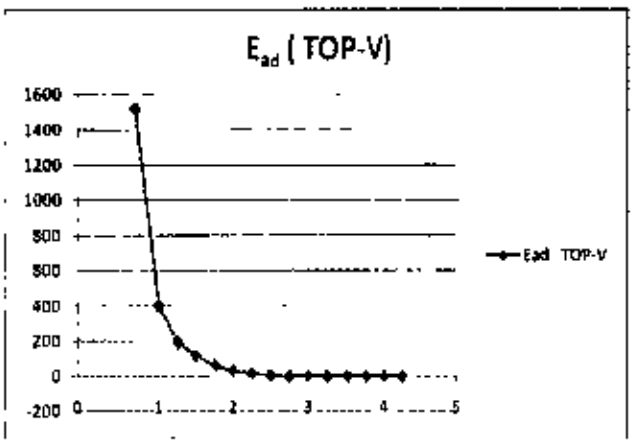


Fig. 6. Adsorption energy vs. distance (B3LYP/6-31G) from carbon side.

Table 5. Adsorption energy (kcal/mol) of CO on the surface of SWNT (B3LYP/3-21G**) from oxygen side

R (Å)	E_{ad} TOP-H	E_{ad} TOP-V	E_{ad} Bridge-H	E_{ad} Bridge-V	E_{ad} Centre-H	E_{ad} Centre-V
0.7	2401.035	1516.224	1454.039	690.6158	1812.61	481.9464
1	648.9316	401.3735	583.8273	316.6384	589.7289	247.1233
1.25	264.4555	191.71	312.3519	121.8843	295.144	140.7696
1.5	160.2761	114.119	180.9007	65.41499	162.8852	75.1061
1.75	104.7385	60.94217	102.5021	32.05521	90.69885	37.90991
2	55.28903	29.01121	52.67988	15.71699	47.02673	18.63675
2.25	25.34598	13.85332	25.4081	8.262293	23.66867	9.225625
2.5	10.43658	5.71527	12.48662	5.156168	11.05781	4.9698
2.75	3.603105	1.118205	91.13201	4.037963	6.336495	3.292493
3	0.74547	0.621225	3.72735	3.789473	3.913718	2.795513
3.25	-0.37274	-0.37274	3.789473	3.851595	2.919758	2.857635
3.5	-0.7453	-0.37275	3.168248	3.97584	2.609145	2.795513
3.75	-0.74547	-0.37274	3.416738	4.037963	2.4849	2.796513
4	-0.68335	-0.37273	3.47886	4.037963	2.671268	2.798043
4.25	-0.62123	-0.37274	3.48775	4.047855	2.174288	2.846532





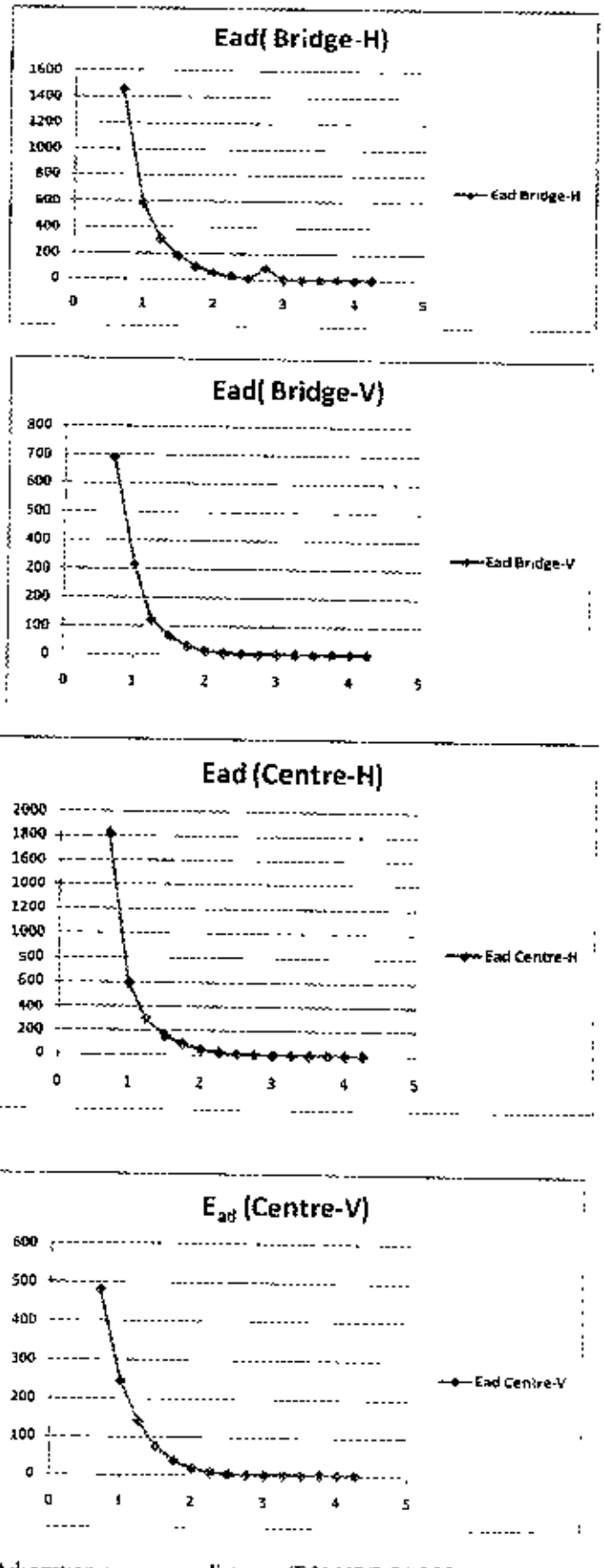


Fig. 7. Adsorption energy vs distance (B3LYP/3-21G**) from oxygen side.

Table 6. Adsorption energy (kcal/mol) of CO on the surface of SWNT (B3LYP/3-21G**) from carbon side

R (Å)	E_{ad} TOP-V	E_{ad} TOP-H	E_{ad} Bridge-H	E_{ad} Bridge-V	E_{ad} Centre-H	E_{ad} Centre-V
0.7	1052.355	1509.515	1623.758	427.7755	1425.587	358.0741
1	288.4348	604.6383	626.9403	144.1242	627.8721	195.9344
1.25	102.0673	306.9473	344.5935	51.68592	334.4675	132.383
1.5	69.82569	166.9853	207.2407	77.09402	197.3632	77.83949
1.75	61.12854	88.21395	118.9825	58.5194	111.6963	49.94649
2	39.88265	43.42363	61.31491	35.40983	55.66176	26.58843
2.25	21.37014	19.44434	30.75064	17.89128	30.12941	16.88973
2.5	18.68507	7.765313	15.65487	12.36238	15.34426	9.44262
2.75	5.653148	5.653148	9.19413	8.572985	8.44866	7.881965
3	3.23837	3.789473	6.21225	5.777393	5.71527	5.528903
3.25	2.360655	3.292493	5.96376	5.71527	4.70625	5.21829
3.5	1.801553	3.168248	4.47282	5.591825	4.286453	4.907678
3.75	1.677308	2.547823	5.404658	5.71527	4.22433	4.907678
4	1.615185	4.037963	5.21829	5.71517	4.659188	4.845555
4.25	1.553063	4.162208	5.484658	5.342535	4.534943	4.835555
4.5	1.615185	4.534943	5.21829	5.46678	4.907678	4.844435

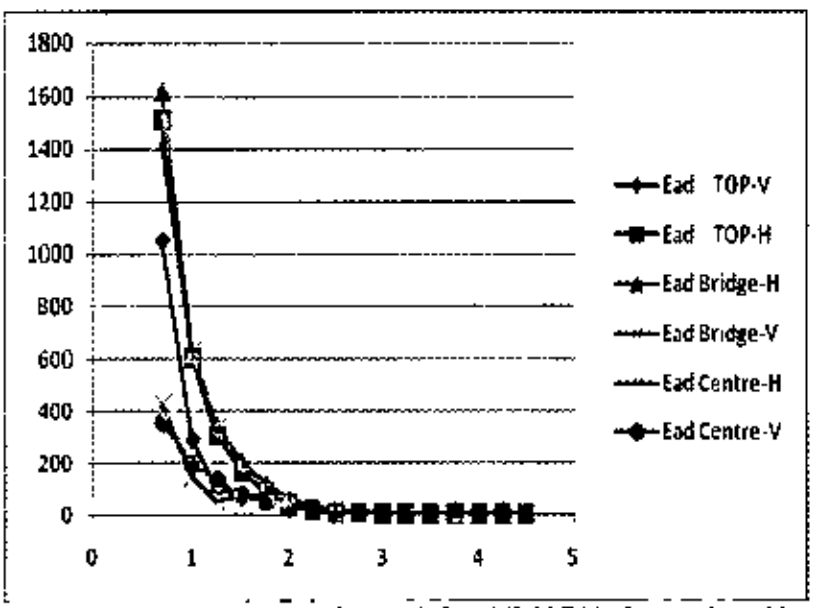


Fig. 8. Adsorption energy vs. distance (B3LYP/3-21G**) from carbon side.

Table 7. Adsorption energy (kcal/mol) of CO on the surface of SWNT (HF/3-21G**) from oxygen side

R (Å)	E_{ad} TOP-H	E_{ad} TOP-V	E_{ad} Bridge-H	E_{ad} Bridge-V	E_{ad} Centre-H	E_{ad} Centre-V
0.7	1639.068	1118.849	859.8281	218.2786	1244.338	485.9555
1	561.6583	391.1559	475.4856	315.4267	543.843	281.148
1.25	256.0849	193.1107	195.9918	197.7082	286.0589	144.8387
1.5	189.714	115.2134	183.2356	118.5642	164.5826	82.48676
1.75	121.58	64.00124	106.7246	39.59588	105.185	47.91716
2	69.53814	33.17342	56.86852	26.63926	56.18259	32.83833
2.25	48.71283	14.35281	35.79825	20.49603	34.57907	20.32849
2.5	26.52756	11.44874	24.85137	16.47581	23.5118	17.14518
2.75	19.32324	3.295083	19.044	15.19852	18.03874	14.74374
3	15.46976	0.837713	15.80484	14.74374	15.97239	14.68789
3.25	14.52835	0.67817	13.85018	14.68789	15.749	14.74374
3.5	13.4834	0.390933	14.52035	13.85018	14.52035	14.52035
3.75	14.01772	0.111695	14.5762	15.3822	14.63205	14.68789
4	14.01772	0.167543	14.63205	14.74374	14.68789	14.69258
4.25	14.01773	0.165435	14.64325	14.73562	14.6325	14.69365

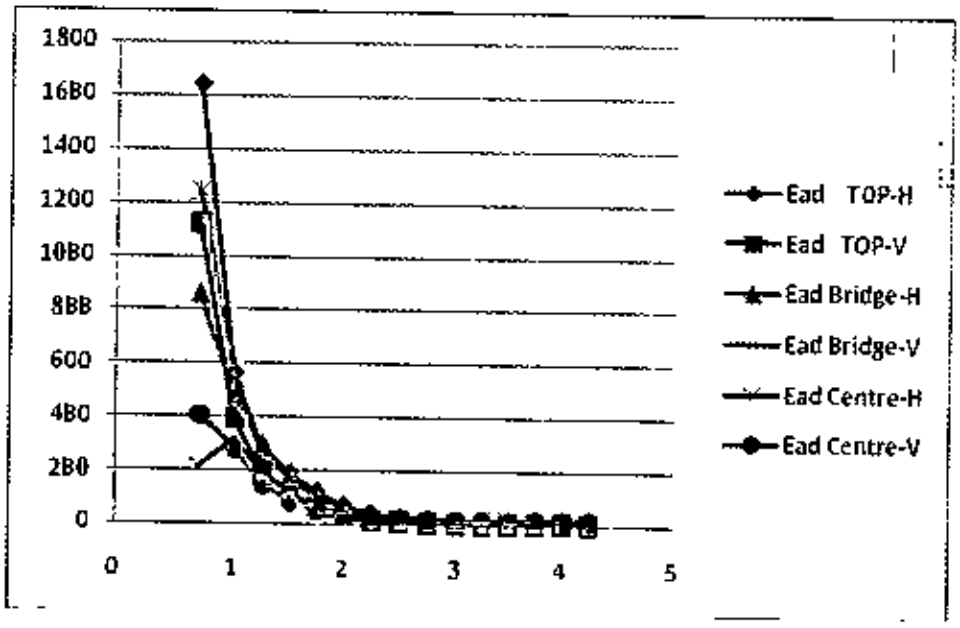


Fig. 9 Adsorption energy vs. distance (HF/3-21G**) from oxigen side.

Table 8. Adsorption energy (kcal/mol) of CO on the surface of SWNT (HF/3-21G**) from carbon side

R (Å)	E_{ad} TOP-V	E_{ad} TOP-H	E_{ad} Bridge-H	E_{ad} Bridge-V	E_{ad} Centre-H	E_{ad} Centre-V
8.7	991.4848	1604.554	968.284	330.4497	1148.727	310.3446
1	293.1435	573.8889	488.1872	158.3835	534.4686	21037753
1.25	123.5347	265.8341	291.4123	117.7265	299.7335	139.6188
1.5	93.8238	166.3139	182.1745	189.9079	184.6877	89.74693
1.75	77.73972	185.4401	107.3947	81.36981	110.6339	56.29428
2	47.69377	61.65564	61.87903	53.33436	62.43751	35.96579
2.25	24.85214	36.97105	37.52952	34.73715	37.58537	24.90799
2.5	11.89552	24.46121	24.62875	25.68985	25.91324	19.37988
2.75	5.826275	18.09459	18.48552	19.15569	19.71417	16.30747
3	-8.05585	15.58145	16.41917	16.6984	15.91654	15.52563
3.25	1.34834	14.01772	14.52035	15.52561	14.24111	14.79959
3.5	2.339	13.79433	14.18527	14.96713	14.29696	15.58145
3.75	-0.72602	12.67738	14.68789	13.79433	14.18327	14.68789
4	-8.7152	13.68264	10.33179	14.5762	14.74374	14.52035

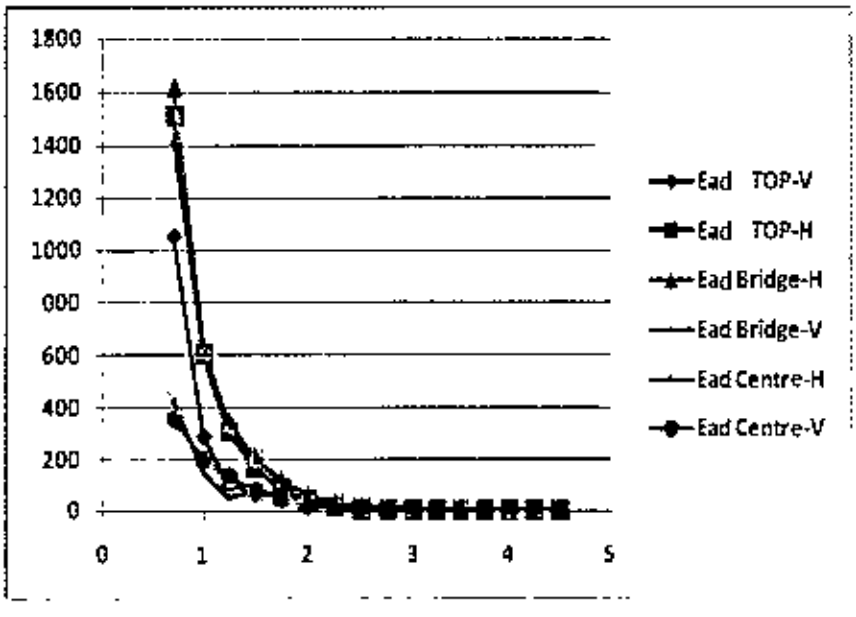


Fig. 10. Adsorption energy vs distance (HF/3-21G**) from earbon side.

Table 9. Adsorption energy (kcal/mol) of CO on the surface of SWNT (B3LYP/3-21G**) from change bond length

R (Å)	R(C≡O)(Å)	Ead TOP-H
3.75	1.15	-0.74547
3.75	1.25	7.019843
3.75	1.35	30.81276
3.75	1.45	57.89817
3.75	1.55	86.10179
3.75	1.65	113.6221
3.75	1.75	139.465
3.75	1.85	163.7549
3.75	1.95	185.8084
3.75	2	286.7437
3.75	2.25	224.8759
3.75	2.5	240.1656
3.75	2.75	255.3856
3.75	3	267.0025
3.75	3.25	778.3088
3.75	3.5	208.9317
3.75	3.75	297.0077
3.75	4	304.8351
3.75	4.25	311.2958
3.75	4.5	317.5081
3.75	4.75	320.6763
3.75	5	323.1612
3.75	5.25	330.1811
3.75	5.5	333.3493
3.75	5.75	326.0189
3.75	6	327.875

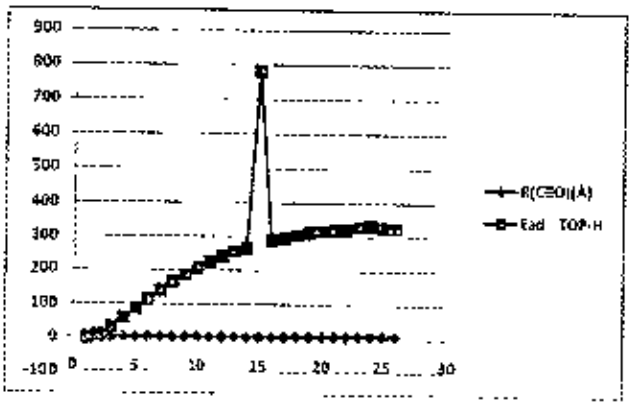


Fig. 11. Adsorption energy vs. distance (B3LYP/6-31G) from change bond length

CONCLUSION

After passing CO, NO, CO_2, H_2 through nanotube with different intervals the conclusion was that all the calculated adsorption energies of these molecules were positive (Table1), this means that the adsorption of the CO, NO, H_2, CO_2 molecules is endothermic for the tube. The adsorption energy of H_2 molecule is lower than CO, CO_2, NO molecules and desorption energy of CO molecule is the highest one. Also by comparing two basis sets (3-21G**, 6-31G) for CO gas, it turned out that with 6-31G desorption energy is higher (Table 1, 2). CO gas molecules were approached single-wall carbon nanotube (SWNT) and (6,0) CNT surface in three states (top, bridge, center) and two shapes (vertical, horizontal), next adsorption energies were calculated by B3LYP/6-31G , B3LYP/3-21G** and HF/3-21G** methods (Table3-8). It was determined that the most stable state for 3-21G** basis set was TOP-H at a distance of 3.75Å from oxygen side, TDP-V at a distance of 4 Å from oxygen side after that bond length of gas molecule was changed by GAUSSIAN program and was calculated by B3LYP with the basis set of 3-21G** for the nanotube and the gas molecules. The conclusion was that all the calculated adsorption energies were positive (Table9), this means that the change of bond length had no effect, so DFT and HF methods were compared and the better method (DFT) was selected.

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