Interaction of HF, HBr, HCl and HI Molecules with Carbon Nanotubes

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Abstract

The present work applies the density functional theory (DFT) to study the interactions between armchair (n,n) single walled carbon nanotubes (SWCNTs) and hydrogen halides confined along the nanotube axis and perpendicular to it. Calculations are performed using the CAM-B3LYP functional. According to the hydrogen halides orientation and the internal diameter of CNTs hollow space, HF, HCl, HBr and HI behave differently. The nanoconfinement alters the charge distribution and the dipolar moment. The encapsulated hydrogen fluoride (HF) molecule is stable along and perpendicular to the nanotubes (5,5) and (6,6) axis. The hydrogen chloride (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI) form stable systems inside the nanotube (6,6) only at the perpendicular orientation. In addition, other phenomena are observed such as leaving the nanotube or decreasing the bond length of the molecule and even the creation of covalent bind between the guest molecule and the host nanotube.

Keywords: Carbon nanotubes; hydrogen halides storage; confinement energy; van der Waals interactions; Mulliken analysis population; DFT/CAM-B3LYP.

1. Introduction

Single walled carbon nanotubes (SWCNTs) attract researchers' interest since their discovery[1] in industry and academy, thanks to their unique electrical and mechanical properties and their potential applications in several fields. The greatest advantage of this SWCNTs is their hollow space which could confine numerous molecules in order to storage them[2–6] or to contain chemical reactions.[7] They are used to remove heavy metals in wastewater treatment[8] and in drug delivery.[9–15] Carbon nanotubes are known to have a great surface of reactivity outside and inside them.

Doping of the exterior surface of a nanotube or the adsorption of atoms or molecules inside it offers the possibility to create exceptional materials with new properties. In particular, the confinement processes modifies the properties of the confined molecules in different ways.[16–20] In previous studies, we investigated the local influence of CNT's walls on small molecules H_2[21,22] and F_2.[23] The former molecule H_2 allowed us to study the effect of the confinement on the electron of the single bond H–H. Some differences have been detected on H_2 behavior between its confinement in CNTs and their boron-nitrogen homo-

logues.[22] The latter molecule F_2, even apolar in nature, introduced the lone pair effect. This studies focus on the comprehension of the intermolecular interactions nature in endohedral complexes. Differences in behavior of each one of those molecules are CNT's diameter dependent and were rationalized invoking the relatives areas under atomic or van der Walls radii control. The purpose of this paper is to study the interaction between polar molecules that are hydrogen halides (hydrogen fluoride HF, hydrogen chloride HCl, hydrogen bromide HBr and hydrogen iodide HI) and the interior of carbon nanotubes of different diameters.

Hydrogen fluoride HF is toxic and strongly corrosive; it dissolves most minerals (oxides, silicates), metals and plastics. Fluoride ions F^- penetrate into deep tissue and react highly with magnesium and calcium. However, HF is a potential fuel generator. It reacts in solution with alkali and light metals by releasing hydrogen (H_2). Its storage inside carbon nanotubes would constitute, on the one hand, an adequate way to avoid its corrosion and its toxicity. On the other hand, it would represent an interesting way of controlling production of dihydrogen.

Another application concerns environmental area. Different techniques exist to uptake the excess fluoride

from wastewater. Among them, nanotube supported alumina could highlights a great potential to adsorb and remove fluoride from water. [24]

Produced carbon nanotubes still contain impurities like amorphous carbon, and catalytic metal particles. Further physical and chemical applications of CNTs require their removal. Hydrochloric acid (HCl) solution is very often used to purify carbon nanotubes. This in-situ presence of HCl may allow insertion of this gas inside the nanotube generating a doping phenomenon. Such property generated considerable interest because of the possible use of CNTs as gas sensors. [25–27]

The aim of this work is twofold. First, to extend and to deepen the knowledge of the encapsulation phenomena inside carbon nanotubes, by including an additional layer of difficulty which is the intervention of the permanent dipole moment. Second, to make a contribution to potential applications of HX acids confinement (X = F, Cl, Br and I).

Unfortunately, there is a lack of study focusing on the encapsulation of these molecules inside or outside carbon nanotubes. The encapsulation of HF dimer inside (n,n) CNTs is recently investigated by Roztoczyńska and al. using the M06-2X exchange–correlation functional.[28] This work was limited to using a series of energy scans to highlight the orientation influence of HF dimers with respect to carbon nanotubes. Liang and al. revealed the stability of HCl molecule inside the CNT (14,0)[29] by studying the electronic and band structure for this complex. There is also few works related to the encapsulation of hydrogen halides inside fullerenes.[30–32]

2. Methodology

In the present paper, we carried out geometry optimizations for armchair (n,n) carbon nanotubes with n = 3,4, 5 and 6 with HF, HCl, HBr and HI molecules inside using the density functional theory. To gain insight into the interaction between these molecules and carbon nanotubes, we perform quantum calculation using the new hybrid exchange-correlation function CAM-B3LYP presented by Yanai and al.[33] and STO-3G basis set. STO-3G basis

set[34] is a minimal basis set, but in term of calculating energy, it gives trusted results [21,23] without consuming a long calculation time. Carbon nanotubes were produced involving three unit cells with TubeGen 3.4 program.[35]

Terminal carbon atoms are hydrogenated to saturate their valence. The formulas of the considered (3,3), (4,4), (5,5) and (6,6) carbon nanotubes are : $C_{36}H_{12}$, $C_{48}H_{16}$, $C_{60}H_{20}$ and $C_{72}H_{24}$ respectively. The optimized diameters of the chosen nanotubes are varying from 5.49 Å to 8.23 Å. All electronic structure calculations were realized using Gaussian 09 suite of programs.[36] Kohn –Sham density functional (DFT) is extensively used since its cheap cost and the possibility to employ it to explore several chemical, physical and biological systems. The coulomb attenuated method CAM-B3LYP is an improved version of the B3LYP functional by the inclusion of long range dispersion energy and it is appropriate to describe the noncovalent interactions.[33] This function gives a better description of the energy when the charge transfer is involved.

3. Results and Discussion

Former studies demonstrated that the orientation of a confined molecule affects notably the interaction between the guest molecule and the nanotube.[22–23,37–40] For that reason, two orientations of hydrogen halides molecules were considered: parallel (//) and perpendicular (⊥) to the CNT's axis as shown in figure 1 and will be noted respectively HX(//)@CNT(n,n) and HX(⊥)@CNT(n,n).

The binding energy (E$_{bind}$) of the hydrogen halides and the nanotube is calculated as following: **E$_{bind}$ = E(HX@ CNT(n,n)) – E(H-CNT(n,n)) – E(HX)**

Where E(HX@CNT(n,n)), E(H-CNT(n,n)), E(HX) indicate the energy of the inclusion complex, the hydrogenated CNTs and the isolated HX molecules respectively. The calculated confinement energies were corrected to the basis set superposition error (BSSE).[41,42] Figure 2 depicts the final situation of each introduced molecule versus CNT's diameter. Depending on the CNT'S diameter and the halogens radius, halogen halides exhibit different behavior as summered in table 1. To better explain each phenomenon, we will focus on each nanotube separately. First
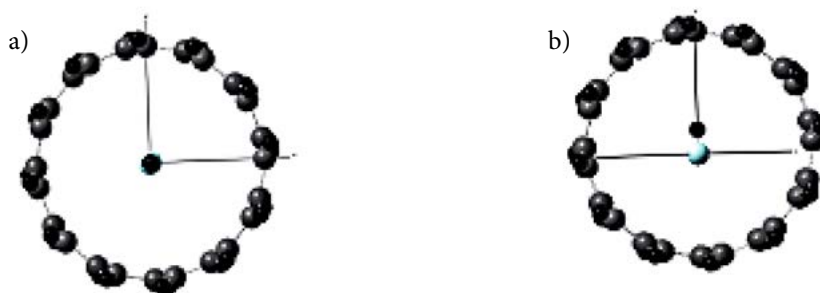

Figure 1. HX studied orientations inside SWNT a) parallel to the nanotube axis noted HX(//)@CNT(n,n) b) perpendicular to the nantotube axis noted HX(⊥)@CNT(n,n)

we discuss the wider nanotube (3,3) which diameter is 4.12 Å. HF and HCl, placed in parallel position along the (3,3) nanotube axis, keep their orientation (Figure 2: a1 and b1). All values of the studied parameters are far from the parameters of the unconfined molecules. When they are placed perpendicular to the (3,3) nanotube axis, we notice a reorientation of these two molecules to the parallel position (Figure 2: a2 and b2). The obtained values of energies, bond lengths and dipolar moment are in the same range of the obtained values at parallel position (Table 2). Roztoczyñska and al. obtained an energy up to +200 kcal mol^{-1} for HF dimer enclosed inside the nanotube (3,3).[28] This result proves the importance of the repulsion forces inside the wider nanotubes in general, in presence of molecules with large radius. HBr and HI sited parallel and perpendicular to the CNT (3,3) axis react with its cage and establish covalent bonds with it (Figure 2: c1, d1, c2, d2). Those figures display the presence of covalent bonds made by the hydrogen atoms. We expected that this result does not have any chemical significance and shows the limits of the computational chemistry of such systems under constraint. In fact, the electronegativity induces a negative charge accumulation from the halogen atoms side, so we can estimate that they present a radius greater than the radius of the isolated atoms. Br and I atoms almost get into the area under the atomic radius of the carbon atoms and set up real chemical bonds with them (Figure3: 3a and 3e). However, the charge distribution is more destabilized inside the nanotube (3,3). Despite the fact that the mulliken electric charge is dependent of the method and basis set because it is a local observable, it gives an idea about the charges of each atom.

As seen in table 2, the charges observed on F, Cl and Br atoms are negative, the charges of H atoms are positive. However, in the case of HI molecule, mulliken gives a negative charge on H atom and positive charge on I atom. This result is due to the choice of the basis of calculation which should be more suitable for iodine atom. In the case of the encapsulation of

HBr and HI inside the CNT (3,3), H, Br and I atoms are linked to the carbons of the nanotube's cavity, that's why their atomic charges are different from the atomic

charges of unconfined HBr and HI molecules. Starting from the CNT (4,4), all the studied molecules introduced at the parallel position are kept inside the nanotubes (Figure2: a3, b3 c3 and d3). As shown in table 2, HF molecule forms a stable system with the nanotubes (5,5) and (6,6) since the confinement energies values are negative or very week equal to –0.9276 kcal mol^{-1} and 0.0290 kcal mol^{-1} repectively. Theoretical studies which investigated the encapsulation of HF molecule inside the fullerene showed that this molecule forms a stable system. Shameema and al, for example reveal a stabilization energy equal to – 2.5 kcal mol^{-1} using the HF/6-31G method.[31] The authors of this study explain that the encapsulation of polar guest molecules polarizes the cage in a way that the carbon atoms placed near the positively charged atoms of the guest species turn into negatively charged and those close to the negatively charged atoms become positively charged. Inside the wider nanotubes, the charge distribution has not a significant change in comparison with the unconfined molecules.

That is why there is a decrease in the net dipole moment of these systems. According to this study, the dipole moment of the free HF molecule is 2.3 Debye, and its dipole moment inside C60 is 0.54 Debye.[31] As a general rule, when the diameter of the CNT increases, the confinement energy value is lower. Values of confinement energies inside the nanotube (6,6), are under 0.001 kcal mol^{-1} in all the studied cases showing the attenuation of the interaction between the guest species and the host cage. In fact, figures 3 a, b, c and d illustrate the interaction between the van der Waals radii of the carbon atoms and the guest molecules. When the nanotube diameter is bigger, the overlap between vdW radiis becomes lower, especially with the fluorure, chlorure and bromure atoms.

At the perpendicular position, only HF molecule (Figure 2a) remains inside the nanotube (4,4), HCl, HBr and HI guest molecules leave it (Figure 2b, 2c, 2d). Outside the nanotube, HCl molecule is re-oriented at the parallel position. Despite the negative energy equal to –3.5 kcal mol^{-1}, the bond length is stretched to 1.3495 Å, signifying that even outside the nanotube, HCl molecule is under the influence of van der Waals radii of terminal hydrogen at-

Table 1. Observed phenomena inside the studied nanotubes at parallel and perpendicular orientations

Orientation	Molecule	CNT (3,3)	CNT (4,4)	CNT (5,5)	CNT (6,6)
Parallel	HF	Destabilized binding	Inside shortness of the bond lengh	Stabilization	Stabilization
	HCl	Destabilized binding	Destabilized binding	Confinement	Confinement
	HBr	Covalent interaction	Destabilized binding	Confinement	Confinement
	HI	Covalent interaction	Destabilized binding	Confinement	Confinement
Perpendicular	HF	Re-orientaion	Inside shortness of the bond length	Stabilization	Stabilization
	HCl	Re-orientaion	Leaving CNT	Confinement	Stabilization
	HBr	Covalent interaction	Leaving CNT	Confinement	Stabilization
	HI	Covalent interaction	Leaving CNT	Leaving CNT	Confinement
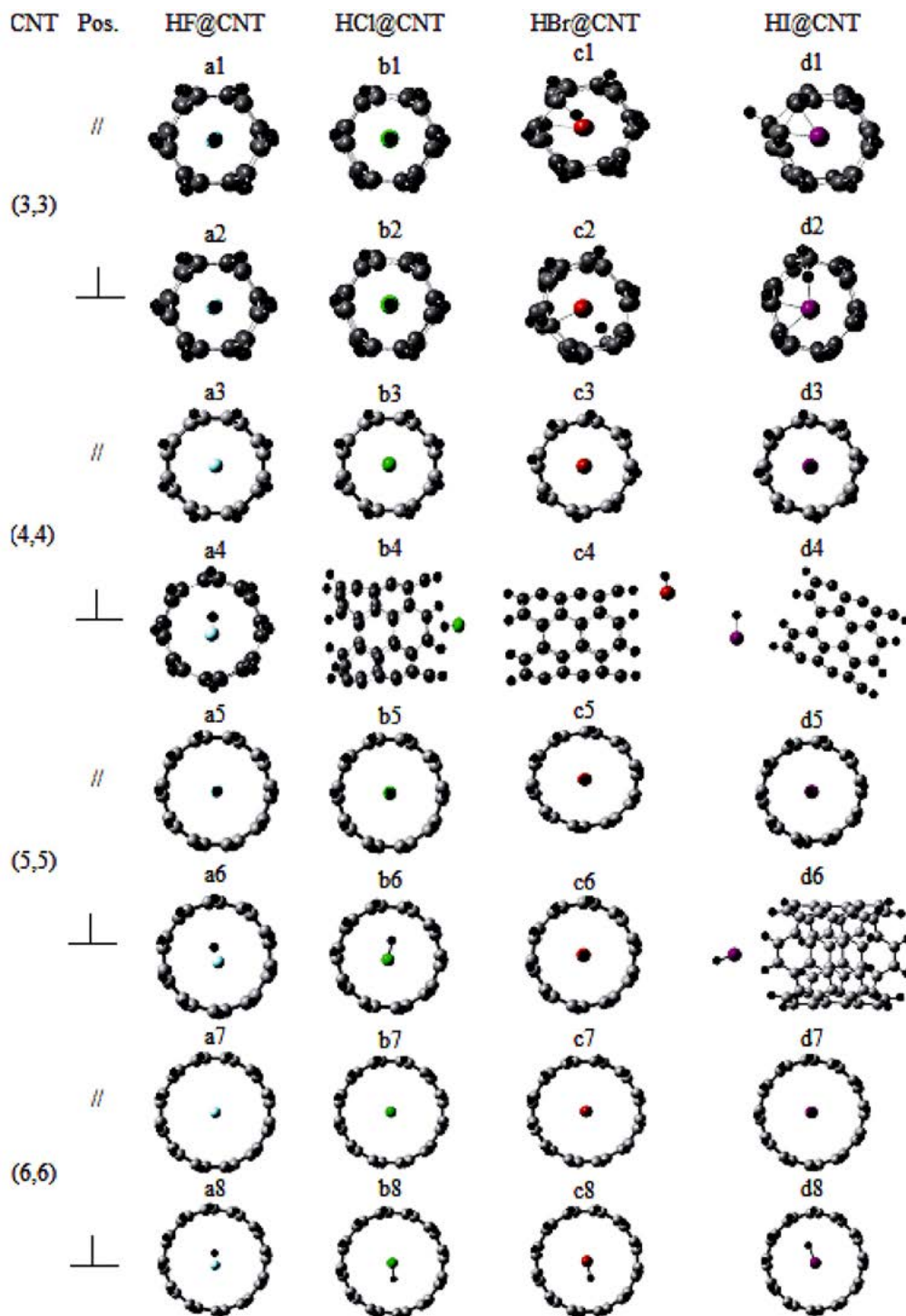
Figure 2. Interaction of HX molecules with the (3,3), (4,4), (5,5) and (6 ,6) CNT's at both parallel and perpendicular orientations

oms. Figure 3.e shows a significant overlap between the vdW radii of halogens and the carbon atoms of the wall of the CNT. As a result, those molecules are "chased" outside the CNT in order to decrease the electrostatic forces involved. HBr and HI molecules are also expelled outside the nanotube (4,4). Their bond lengths and dipolar moments values are higher than those of unconfined molecules (Table 2). The charge distribution is highly affected. We notice that when the van der Walls radius of the halogen atom is greater than the radii of the nanotube, the molecule is expelled out of it. In fact, the halogen halide in this condition is trapped inside a repelled area. The same phenomena was observed for water which flow rate varies when the CNT diameter changes.[43]

Table 2. Parameters of the optimized geometries when HX molecules are placed along and perpendicular to the nanotube axis. d, μ and q design internuclear distance, dipole moment and Mulliken atomic charges, respectively.

System		HF					HCl					HBr					HI				
		d_{XH}	E	μ	qX	qH	d_{XH}	E	μ	qX	qH	d_{XH}	E	μ	qX	qH	d_{XH}	E	μ	qX	qH
XH		0.99	–	1.15	–0.22	0.22	1.34	–	1.74	–0.18	0.18	1.43	–	1.25	–0.04	0.04	1.61	–	1.35	0.01	–0.01
(3,3)	//	0.97	64.30	0.25	–0.19	0.28	1.33	231.48	0.43	–0.18	0.15	2.17	129.14	–	0.23	0.11	4.15	–129.46	–	0.82	0.08
(4,4)	//	0.99	5.21	0.26	–0.23	0.23	1.33	35.95	0.48	–0.18	0.17	1.43	58.27	0.37	–0.03	0.04	1.61	112.84	0.10	0.05	–0.02
(5,5)	//	0.99	–0.93	0.46	–0.22	0.22	1.33	1.72	0.71	–0.18	0.18	1.43	3.87	0.49	–0.04	0.05	1.61	13.13	0.55	0.01	0.00
(6,6)	//	0.99	0.03	0.5	–0.22	0.22	1.33	0.03	0.79	–0.18	0.18	1.43	0.12	0.48	–0.05	0.05	1.61	0.54	0.60	0.00	0.00
(3,3)	⊥	0.97	64.38	0.247	–0.16	0.28	1.33	231.41	0.42	–0.18	0.18	–	263.48	–	0.23	0.17	–	358.70	–	0.81	0.08
(4,4)	⊥	0.98	2.71	0.31	–0.23	0.22	1.35	–3.51	2.11	–0.28	0.22	1.43	–2.39	1.75	–0.03	0.05	1.61	–1.35	1.32	–0.05	–0.05
(5,5)	⊥	0.99	–0.40	0.42	–0.23	0.22	1.34	0.16	0.79	–0.18	0.22	1.43	3.87	0.49	–0.04	0.05	1.61	–0.38	1.60	0.0	–0.02
(6,6)	⊥	0.99	–0.19	0.48	–0.22	0.22	1.34	–1.01	0.79	–0.18	0.22	1.43	–0.61	0.59	–0.04	0.04	1.61	–0.17	0.67	0.00	0.00

Figure 3. Schematic overlap between atomic/ van der Waals radius of the CNT and the confined hydrogen halides at both parallel and perpendicular positions

By increasing the carbon nanotube's diameter, only HI molecule leaves the CNT (5,5) at the perpendicular orientation. HF placed perpendicular forms a stable complex with the nanotubes (5,5) and (6,6) with a stabilization energy equal to –0.4017 kcal mol^{-1} and –0.1864 kcal mol^{-1}, respectively. HCl, HBr and HI molecules form a stable system with the CNT (6,6) as their obtained corrected energies are equal to –1.0119 kcal mol^{-1}, –0.6142 kcal mol^{-1}, –0.1715 kcal mol^{-1}, respectively. In all those cases, the bond lengths of confined molecules reach the value of the molecules at the free state. The atomic charges attain also the same values of the unconfined molecules, with the exception of HI molecule for which the charge distribution is still highly dislocated. The dipolar moments, as men-

tioned above are under the values of the dipolar moments of the free molecules. There is an important overlap (figure 3g and 3h) betweeb van der Waals radiis of the hydrogen halides molecules and the carbon atoms: this overlap has a destabilisant and repulsive nature for the HI molecule and it has a stabilisant and attractive nature for HF, HCl and HBr molecules.

5. Conclusion

Theoretical calculations have been made to investigate the encapsulation of HF, HCl, HBr and HI molecules inside carbon nanotubes (3,3), (4,4), (5,5) and (6,6). Calculations are made using DFT/CAM-B3LYP functional with STO-3G basis sets. Dipolar moments of all confined molecules are affected. At the parallel and perpendicular directions, HF molecule forms a stable system with the nanotubes (5,5) and (6,6). HCl, HBr and HI molecules placed perpendicular, form a stable complex with the CNT (6,6). In all those cases, the bond lengths and the atomic charge of confined molecules reach the values obtained for the unconfined molecules.

6. References

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Povzetek

V tem delu smo s teorijo gostotnega funcionala (DFT) preučevali interakcije med armchair (n,n) enojnimi panelnimi ogljikovimi nanocevkami (SWCNT)s in vodikovimi halogenidi, ujetimi vzdolž osi nanocevk in pravokotno nanjo. Izračune smo izvedli z uporabo CAM-B3LYP funkcionala. V skladu z orientacijo vodikovih halogenidov in notranjim premerom praznin CNTs, se HF, HCl, HBr in HI različno obnašajo, ker ujetost v nano praznino spremeni porazdelitev naboja in dipolni moment. Inkapsulirana molekula vodikovega fluorida (HF) je stabilna vzdolž in pravokotno na osi (5,5) in (6,6) nanocevk. Vodikov klorid (HCl), vodikov bromid (HBr) in vodikov jodid (HI) tvorijo stabilne sisteme znotraj (6,6) nanocevk le v navpični smeri. Poleg tega opazimo druge pojave, kot so zapuščanje nanocevke ali zmanjšanje dolžine vezi molekule in celo tvorbo kovalentne vezi med molekulo in nanocevko.