The bonding of NO_2, NH_3, and CH_2NH to models of a (10,0) carbon nanotube

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Abstract

We have studied the bonding of NO_2, NH_3, and CH_2NH to a (10,0) carbon nanotube using the MP2 and ONIOM methods with extended basis sets. We find bond strengths of 3.5, 3.6, and 6.3 kcal/mol for NO_2, NH_3, and CH_2NH, respectively, using the ONIOM method with the high accuracy part treated at the MP2/aug-CC-pVTZ level and the remainder of the CNT approximated at the UFF level and including an estimate of basis set superposition error using the counterpoise method.

1. Introduction

Recently carbon nanotubes (CNTs) have been functionalized using atomic H from a glow discharge and the functionalization is confirmed by an IR band at 2924 cm^{-1} corresponding to the CH stretching mode [1]. The addition of H atoms to CNTs has also been studied computationally [2]. The addition of H atoms leads to formation of a strong chemical bond, however most molecules have been found to form only weak bonds. The addition of a number of gas molecules to CNTs using density functional theory within the local density approximation (LDA) has also been reported by Zhao, Buldum, Han, and Lu [3]. Kong, Franklin, Zhou, Chapline, Peng, Chao, and Dai [4] observed that NH_3 and NO_2 change the conductivity of a CNT in opposite directions and suggested that CNTs might be used as chemical sensors. They believed that charge transfer may play a role in the conductivity change. More recently Li, Lu, Ye, Cinke, Han, and Meyyapan [5] have studied the practical application of CNTs as chemical sensors in the case of NO_2 and nitrotoluene. In the case of NO_2 and NH_3 the conductivity is changed in opposite directions; thus, these two gases may be distinguished On the other hand, NH_3 and CH_2NH are both amines and might be expected to change the conductivity in the same direction and it may be difficult to distinguish these two molecules. Therefore we have studied the bonding of these three molecules to a (10,0) CNT in order to see if there is a qualitative correlation between features of the bonding such as charge transfer and the binding energies. In the future the conductivity change should also be studied.

2. Computational Methods

Our calculations are based on a (10,0) nanotube which is approximately 10 Å long and the ends are capped with a cap reported by Brinkman et al. [6] and are optimized using AM1 [7]. Our calculations use the MP2 method [8] and were carried out with Gaussian98 [9].

We first carried out preliminary calculations for the series of molecules NH_3, CH_2NH, SO_2, H_2S, H_2O, CH_4, and NO_2. These calculations were mostly carried out using cluster B, shown in Fig. 1, at the MP2/6-31G* level. This calculation is modeling sites directly above a surface CC bond. In the NH_3 and CH_2NH cases the preferred bonding site is six-fold and a more extensive model had to be used as described below. As discussed by Walch [10], cluster B does not have a simple VB structure. This led to difficulties for cluster B plus NO_2 and the larger cluster A, shown in Fig. 2, had to be used. The calculations were carried out at the MP2/6-31G level and the projected MP2 method was used (for the doublet state).

We also carried out calculations using the ONIOM method of Morokuma and coworkers [11] with the high accuracy part treated at the MP2/aug-CC-pVTZ level and the remainder of the CNT approximated at the UFF [12] level. The basis set superposition error was estimated using the counterpoise method [13]. In all cases we used the ONIOM extrapolated energies. The high accuracy piece in these calculations was a distorted benzene with the six carbon atoms fixed at the positions obtained for the (10,0) nanotube and tied off with H atoms. The positions of the H atoms were optimized. See Figures 3 through 5.

3. Results and Discussion

Fig. 1 and Table I show results for the bonding of NH_3, CH_2NH, SO_2, H_2S, H_2O, and CH_4 to cluster B. In the course of these calculations it was found that the preferred orientation was with the dipole moment of the added molecule pointing toward the surface. Clearly a CNT is symmetric and has no dipole moment, however a cluster cut from a CNT, such as cluster A, can have a dipole moment. In this case, the dipole moment is found to be pointed toward the center of the tube. Indeed this suggests that a given region of the CNT surface has a local dipole moment, but the orientation of these local dipole moments is such that they cancel out giving zero dipole moment for the CNT as a whole. Similarly the CH_4 molecule can be thought of as a symmetric arrangement of four local dipole moments each associated with a polar CH bond. We find that the dipole moment (or local dipole moment) of the adsorbed molecule aligns parallel to the local dipole of the surface. While this is probably only a qualitatively valid observation, in the sense that the local dipole moment of the CNT model is expected to be cluster size dependent, it did provide guidance in finding the correct orientations for NO_2 and CH_2NH, for which the orientations tried initially had the dipole moment pointing away from the surface.

For NO_2, calculations using cluster B did not converge and tended toward a high-spin (quartet) state. Calculations with cluster A did converge to a doublet state. Fig. 2 shows the three orientations with respect to the surface which were considered. Orientations a and b are directly above a two-fold site (surface CC bond) and have the NO_2 dipole moment oriented away from and toward the CNT surface, respectively. Orientation c is for a six-fold site with the NO_2 dipole moment oriented toward the CNT surface. From Table II it is seen that the two-fold site b is the most strongly bound orientation, but that the six-fold site c is only 0.8 kcal/mol less strongly bound. This result suggests a relatively small barrier to diffusion along the direction of surface CC bonds.

As discussed by Walch [14] and by Cinke, Li, Bauschlicher, Ricca, and Meyyapan [15] rather extensive calculations are required to obtain accurate binding energies for adsorbates on CNTs. All of these authors noted the extreme importance of the BSSE correction and that MP2 tends to overestimate the binding energy. Cinke, Li, Bauschlicher, Ricca, and Meyyapan [15] also noted the importance of a correction for overestimation of the quadrapole-quadrapole interaction in the case of the very weak interaction of CO_2 with a (10,0) nanotube.

Table III shows the binding energies obtained from the ONIOM calculations. Figures 3-5 show the structures for the high accuracy piece plus NO_2, NH_3, and CH_2NH. As discussed above NO_2 bonds at a two-fold site, while NH_3 and CH_2NH bond at a six-fold site. We find bond strengths of 3.5, 3.6, and 6.3 kcal/mol for NO_2, NH_3, and CH_2NH, respectively, after correction for BSSE. Thus, all three of these molecules are fairly strongly bound to the (10,0) CNT.

Comparing the results without BSSE correction with cluster B to the ONIOM results shows significantly smaller binding energies with the cluster B model. This underscores the sensitivity of the computed binding energies to the method of calculation.

Table IV shows the charge transfer based on Mulliken populations. Here it is seen that there is very little charge transfer and in all cases the charge transfer is in the same direction resulting in a slight negative charge on the adsorbed molecule. It is probable that the bonding in each case is mainly electrostatic with the dipole-dipole contribution being the leading term.

4. Conclusions

We have studied the bonding of NO_2, NH_3, and CH_2NH to a (10,0) carbon nanotube using the MP2 and ONIOM methods with extended basis sets.

For the molecules NH_3, CH_2NH, SO_2, H_2S, H_2O, and CH_4 we find that the orientation is consistent with a dipole-dipole dominant term. In all cases the dipole moment of the added molecule is pointed toward the surface. There is very little net charge transfer between the CNT and the adsorbed molecule.

We find bond strengths of 3.5, 3.6, and 6.3 kcal/mol for NO_2, NH_3, and CH_2NH, respectively, using the ONIOM method with the high accuracy part treated at the MP2/aug-CC-pVTZ level and the remainder of the CNT approximated at the UFF level and including an estimate of basis set superposition error using the counterpoise method.

Acknowledgements

SPW was supported by NASA contract NAS2-99092 to ELORET. We thank A. Ricca for providing coordinates for the (10,0) carbon nanotube and for helpful discussions.

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Table I. Energetics for cluster B plus NH_3, CH_2NH, SO_2, H_2S, H_2O, and CH_4. MP2/6-31G* basis.

molecule	MP2	ΔE(kcal/mol)
Cluster B	-232.45439	
NH_3	-56.35421	
	-288.80860	0.0
Cluster B + NH_3	-288.81298	-2.7
Cluster B	-232.45439	
CH_2NH	-94.31521	
	-326.76960	0.0
Cluster B + CH_2NH	-326.77680	-4.5
Cluster B	-232.45439	
SO_2	-547.68248	
	-780.13687	0.0

Cluster B + SO_2	-780.14221	-3.4
Cluster B	-232.45439	
H_2S	-398.78841	
	-631.24280	0.0
Cluster B + H_2S	-631.24794	-3.2
Cluster B	-232.45439	
H_2O	-76.19685	
	-308.65124	0.0
Cluster B + H_2O	-308.65811	-4.3
Cluster B	-232.45439	

CH_4	-40.33255	
	-272.78694	0.0
Cluster B + CH_4	-272.78942	-1.6

Table II. Energetics for cluster A plus NO_2. MP2/6-31G basis set.

molecule	MP2	ΔE(kcal/mol)
Cluster A	-612.83751	
NO_2	-204.31171	
	-817.14922	0.0
a	-817.15206	-1.8
b	-817.15453	-3.3
c	-817.15315	-2.5

Table III. Binding energies for (10,0) CNT + NO_2, NH_3, and CH_2NH[a].

molecule	ΔE, kcal/mol	+CP[b]
NO_2	-4.2	-3.5
NH_3	-4.3	-3.6
CH_2NH	-7.3	-6.3

[a] ONIOM calculations using a (10,0) CNT model and with the high accuracy part treated at the MP2/aug-CC-pVTZ level and the remainder of the CNT approximated at the UFF level.

[b] Including a counterpoise correction.

Table IV. Charge transfer for NO_2, NH_3, and CH_2NH on a (10,0) CNT.

molecule	CNT10.H	X
NO_2	0.0018	-0.0018
NH_3-1d	0.0094	-0.0094
CH_2NH	0.0133	-0.0133

Figure Caption

Fig.1 Structures for cluster B plus a) NH_3 b) CH_2NH c) SO_2 d) H_2S e) H_2O and f) CH_4.

Fig. 2 Structures for cluster A plus NO_2 in 3 orientations.

Fig. 3 Structure of CNT10 plus NO_2.

Fig. 4 Structure of CNT10 plus NH_3.

Fig. 5 Structure of CNT10 plus CH_2NH.

Fig. 1

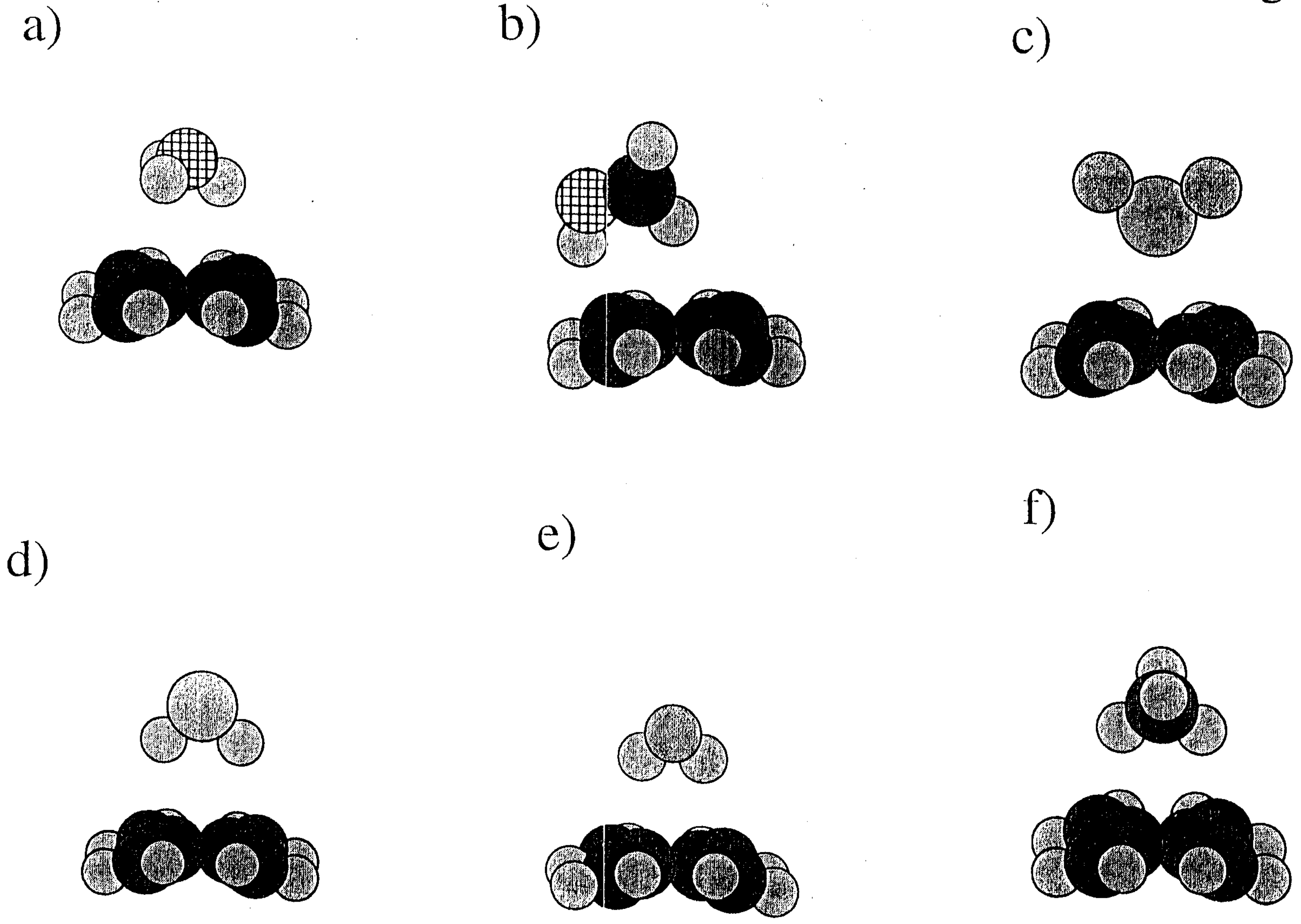

Fig. 2

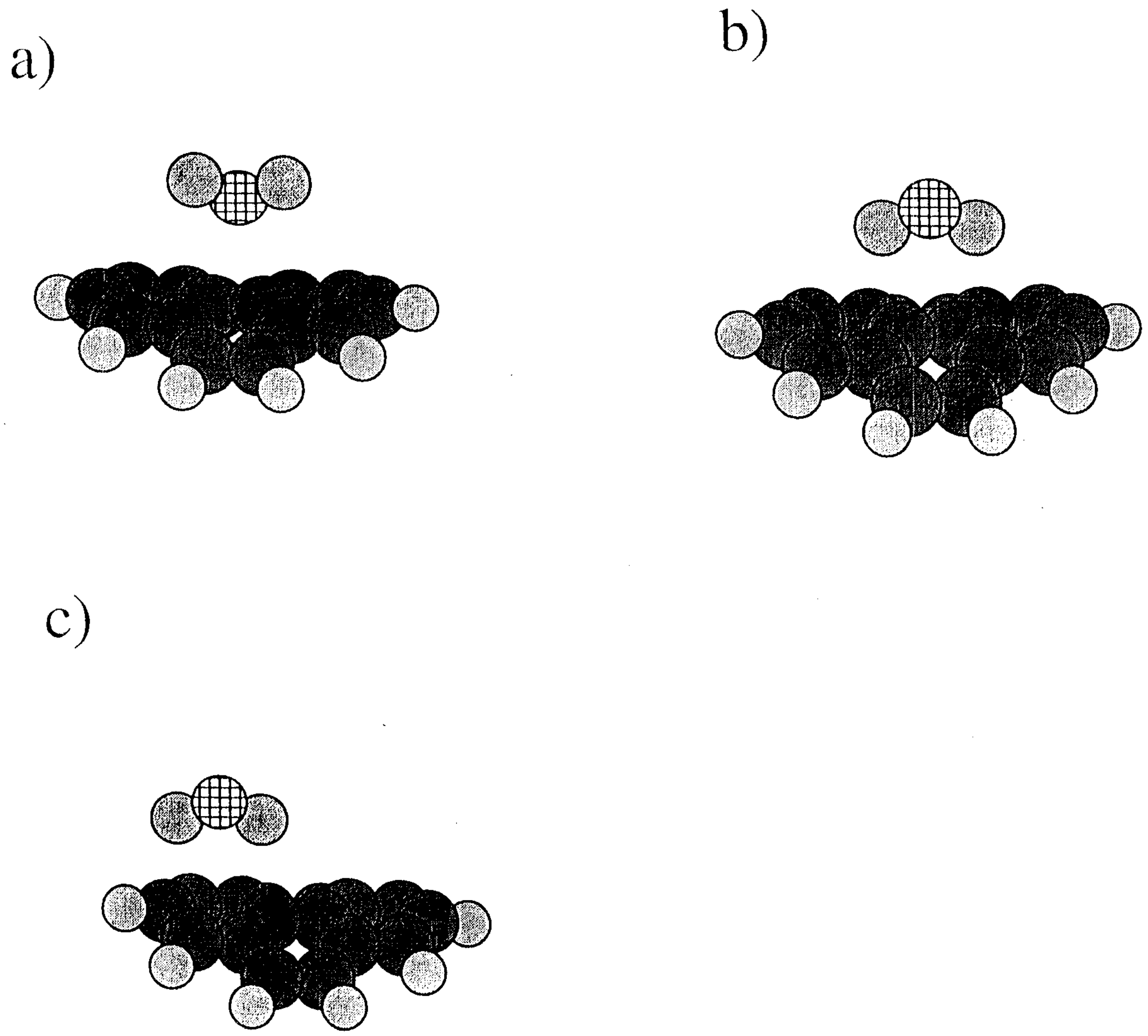

Fig. 3

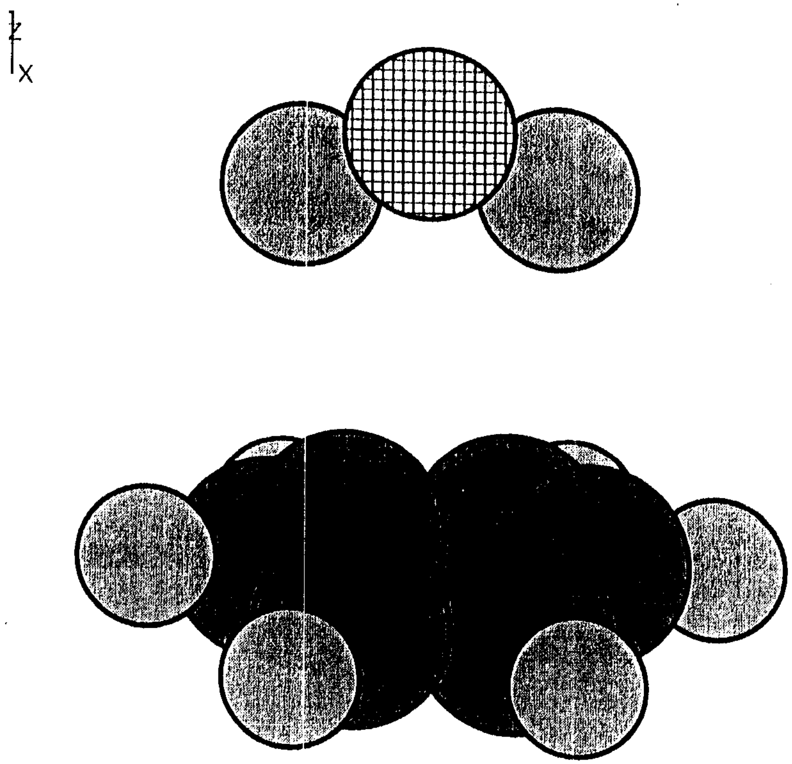

Fig. 4

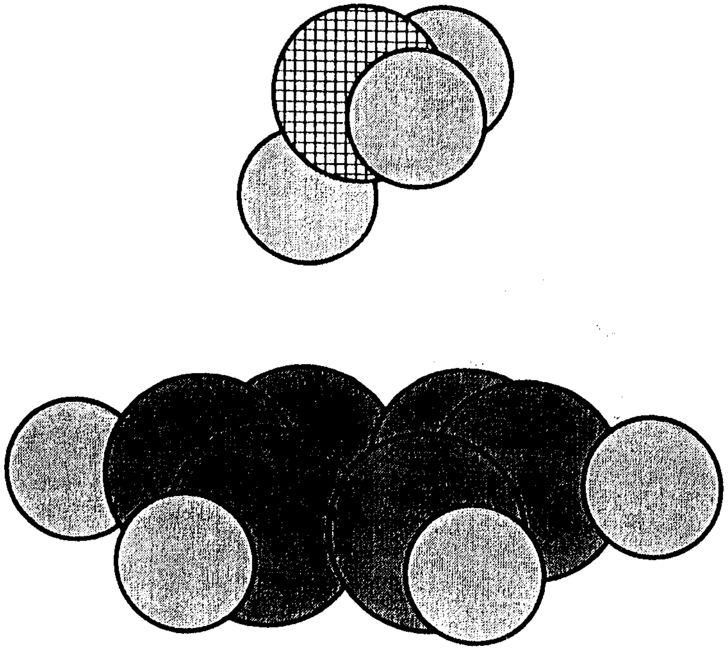

Fig. 5