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Why boron nitride nanotubes are preferable to carbon nanotubes for hydrogen storage? An *ab initio* theoretical study

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Abstract

Using *ab initio* calculations we investigated the hydrogen storage in single-walled boron nitride nanotubes. We present the *nature* of hydrogen interaction in selected sites of a (5,5) and (9,9) BN nanotube. Our results show that BN nanotubes are preferable to carbon nanotubes for hydrogen storage applications due to their heteropolar binding nature of their atoms. In addition, by increasing the nanotube's diameter – decreasing its curvature, more efficient binding energies of hydrogen can be achieved.

Keywords: Hydrogen storage; Carbon nanotubes; BN nanotubes; Physisorption; *Ab initio*

1. Introduction

Since Iijima [1] reported the synthesis of carbon nanotubes (CNTs) in 1991, CNTs were proposed as good candidate—materials for hydrogen storage allegedly possessing extraordinary high and reversible hydrogen adsorption [2–5]. Despite of the existence of extensive experimental and theoretical studies [6–9] in the literature, the reported data about the storage capacity of CNTs vary greatly. In the theoretical studies of hydrogen adsorption on CNTs, both chemisorption [10–12] and physisorption [13–21] were investigated. Similarly to the experimental cases, the reported theoretical results also vary. Only very recently, the understanding on the basic mechanisms of hydrogen storage in carbon based materials revealed. As a result, the DOE target for hydrogen storage capacity cannot be attained using pure carbon based materials [21]. Intercalation [22,23], pillaring [23] or even importing composite heteroatoms in carbon-based materials attracted the current scientific interest.

The latter direction, imported to the hydrogen storage field new materials such as the boron nitride nanotubes (BNNTs). Since their discovery [24–27], BNNTs were tested as new materials for hydrogen storage [28]. Experimentally, Ma et al. [29], reported that multi-walled bamboo like BNNT samples, could store hydrogen up to 2.6 wt% at room temperature. Also, Tang et al. [30], discovered that BNNTs with a collapsed structure could store up to 4.2 wt% hydrogen at room temperature. These experimental results revealed that BNNTs are considered to be a better hydrogen storage medium than CNTs. Theoretically, hydrogen adsorption has been investigated by semi-empirical [31,32] and by first principles [33] methods in BN cages. Han et al. [34], presented a reactive force field to model large molecular and condensed phase systems of H, B and N atoms and tested it for hydrogen interaction with BNNTs [34]. Chemisorption of H atoms in BNNTs walls are also investigated by first principle methods [35]. A question that arises from all the previous studies is why BNNTs posses higher hydrogen storage than the CNTs? Some general points were extrapolated by Jhi and Kwon [36] where they studied the adsorption of molecular hydrogen on BNNT with the use of pseudopotential density functional theory. Yet a systematic study of the physisorption procedure of molecular hydrogen in BNNTs is absent in the literature.

In this letter we study the interaction of H_2 with all possible sites of BNNTs wall and in all different approach orientations, applying *ab initio* methods. Only with the use of high accuracy quantum chemistry techniques we can understand the nature of the hydrogen interaction with these nanotubes. Additionally to the nature of hydrogen's binding in these nanotubes, the

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curvature effect is also studied. For purposes of comparison, calculations on the same theoretical level were also performed for CNTs.

2. Computational details

In order to treat our system with high accuracy *ab initio* methods without ending up in prohibitively large computations, we applied the *cluster* approximation. In this method, we separate a part of the large system and treat it individually as a cluster. To model carbon nanotubes, we formed an oriented and curved coronene-like graphene sheet model using a two-phase process. Firstly, a polycyclic C_{24} cluster was obtained by cutting a symmetric part from the corresponding (5,5) and (9,9) CNTs. Secondly, the dangling bonds of the sp^2 hybridized C_{24} clusters were saturated by hydrogen atoms resulting in the $C_{24}H_{12}$ model-cluster (Fig. 1). For the BNNTs we replaced the carbon atoms with boron and nitrogen atoms, respectively. All the cluster models $C_{24}H_{12}$ and $B_{12}N_{12}H_{12}$ of (5,5) and (9,9) nanotubes were partly optimized keeping the dihedral angles of the atoms frozen. In this way we kept the curvature of each cluster frozen and relaxed the interatomic distances and angles, in order to model the real nanotube system. For the (5,5) and (9,9) armchair-type BNNTs no outward displacements of N atoms are expected in contrast to the zig-zag type [27], so the formula of the partially optimization applied here can model with great accuracy the real nanotube.

The method we used was density functional theory with the B3LYP hybrid functional and the calculations were performed using the Gaussian 98 program package [37]. Aiming to high accuracy, we used two different basis sets in order to describe our system. The interacting hydrogen molecule together with six closest to it carbon atoms (or the equivalent 3B and 3N) were treated with a larger basis set than the other atoms of the cluster. The large basis set was chosen to be of triple zeta quality plus polarization and diffusion functions for both heavy and light atoms (6-311++G**) while the smaller one was the 3-21G. Unfortunately, higher accuracy method such as MP2 and coupled cluster that describe better the weak interactions cannot be applied in such large system. Despite of the existence of several approaches to describe van der Waals interactions within density functional theory, a widely accepted and reliable methodology has not been established yet (for example see Ref. [36] and references therein). Since we used a functional theory that underestimates the dispersion forces in molecules and predicts relatively small binding energy values, we did not make any further correction using basis set superposition error (BSSE). The small binding energy numbers presented in this work, have to be taken into account comparatively and qualitatively. The binding energy of a H_2 molecule on the BNNTs wall was calculated as follows: $\mathrm{BE} = E_{B_{12}N_{12}H_{12}-H_2} - E_{B_{12}N_{12}H_{12}} - E_{H_2}$, where $E_{B_{12}N_{12}H_{12}-H_2}$ was obtained from the scan of the potential energy of the BNNT-molecular hydrogen structure, $E_{B_{12}N_{12}H_{12}}$ is the energy of the $B_{12}N_{12}H_{12}$ cluster and E_{H_2} is the energy of the H_2 molecule. The equivalent expression for the binding energy of hydrogen's interaction with CNTs is $\mathrm{BE} = E_{C_{24}H_{12}-H_2} - E_{C_{24}H_{12}} - E_{H_2}$.

3. Results and discussion

A hydrogen molecule can approach the nanotube walls from outside (out) that is the most common case, as well as from the inside (in). In addition there are three different binding sites: on top of an atom C, N or B (top), in the middle of a C–C or B–N bond (bridge) and in the center of a C hexagon (C_6) or BN hexagon (B_3N_3) (hollow). All these are combined with the several approach orientations of the hydrogen molecule. We examined the most important, which were: three for the bridge case (perpendicular (P), longitudinal (L) and transversal (T) configurations according to the bond), two for the hollow case (perpendicular and longitudinal configurations according to the C–C axis of two antidiametric carbon atoms of the C-hexagon,

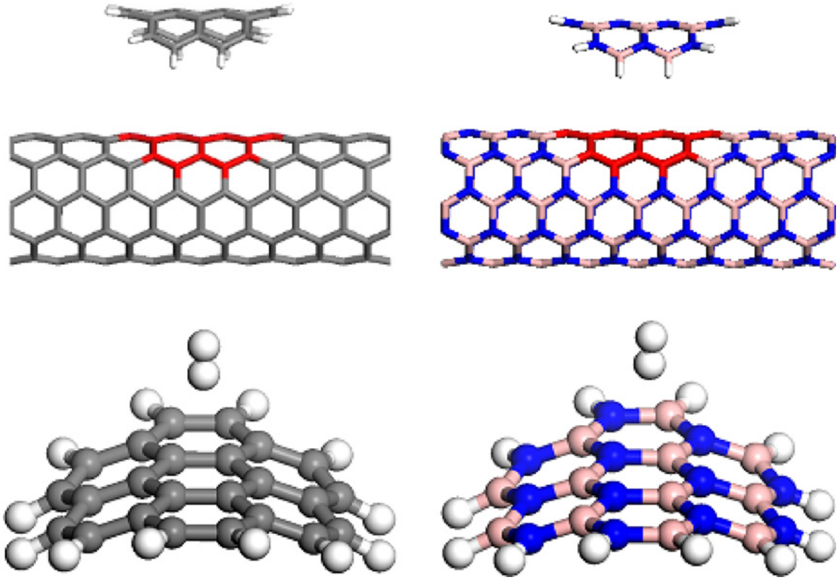

Fig. 1. $C_{24}H_{12}$ and $B_{12}N_{12}H_{12}$ resulting cluster models representing the (5,5) and (9,9), CNT and BNNT.

or according to the B–N axis of two antidiametric atoms of the BN-hexagon) and one for the top case (the perpendicular configuration according to the nanotube axis). Considering for each site and configuration, the inside and the outside cases, we end up in 12 different approaches of H_2 to the CNT and in 14 different approaches of H_2 to the BN walls. For each of all these cases we investigate the CNT-H_2 and BNNT-H_2 potential energy surface (PES).

Some general points from the BNNT-H_2 PES results can be summarized as follows: (a) in all pathways the potential is attractive, presenting a well of maximum −1.0 kcal/mol approximately, that characterizes a physisorption procedure. (b) The stronger interaction takes place inside the nanotube. The inner positions of molecular hydrogen possess larger binding energies than the equivalent outer ones. (c) In the case of the perpendicular to the tube walls approach, the H_2 molecule is slightly polarized giving further rise to the hydrogen's binding energy compared to the longitudinal and transversal configuration. Similar attitude was also observed in our previous study [21], we investigated the hydrogen storage in (5,5) CNTs and bundles of those, using both *ab initio* and molecular dynamics simulations.

Continuing our investigation, we limit our results analysis on the hydrogen's interaction with the outer nanotubes' walls for two reasons: the first is that the cluster-model cannot give the whole interaction of hydrogen with the inner sites of the nanotubes but only a part of it. The second is that the entrance of hydrogen molecule inside the small-diameter nanotubes is not gravimetrically efficient and depends on the nanotubes' diameters.

In Fig. 2 we present the potential energy curves of H_2 approaching an atom of a (5,5) and (9,9) both carbon and boron nitride nanotubes (Top case, Perpendicular configuration). It is clear that hydrogen molecule prefers to interact with the nitrogen atoms of the BNNTs. Comparing the potential curves of nanotubes with the same diameter we found that boron and nitrogen atoms attract the hydrogen molecule better than carbon. For the (5,5) tubes the binding energy (BE) of H_2 interacting with the C atom (in CNT) increases 97%, from −0.39 kcal/mole to −0.77 kcal/mole when it interacts with a N atom and 13%, to −0.44 kcal/mole when it interacts with a B atom (in BNNT). Similarly, for the (9,9) tubes the BE of H_2 interacting with the C atom increases 69%, from −0.51 kcal/mole to −0.86 kcal/mole when it interacts with a N atom and 20%, to −0.61 kcal/mole when it interacts with a B atom. The aforementioned values are also presented in Table 1.

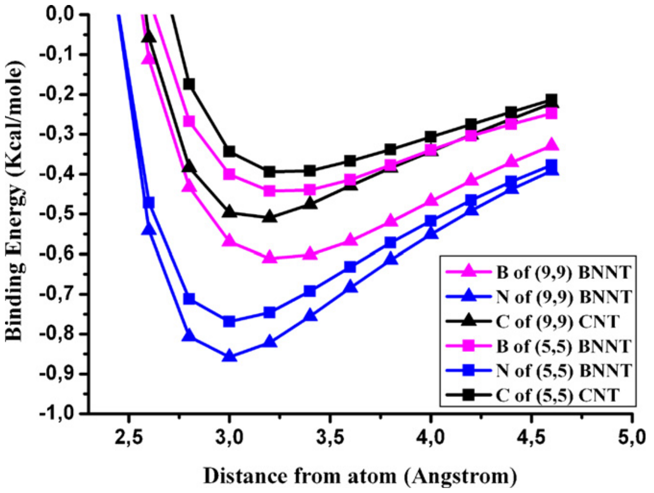

Fig. 2. Top case: binding energy curves of hydrogen on (5,5) (square), (9,9) (triangle), CNT and BNNT with hydrogen on top of C (black), N (blue), B atom (magenta). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Table 1
Binding energy values of all different molecular hydrogen's approaches presented in this work for the (5,5) and (9,9) both CNT and BNNT

Top			
(5,5)		(9,9)	
CNT Perp	BNNT Perp	CNT Perp	BNNT Perp
−0.39	−0.77 (N), −0.44 (B)	−0.51	−0.86 (N), −0.61 (B)

Hollow							
(5,5)				(9,9)			
CNT		BNNT		CNT		BNNT	
Perp	Long	Perp	Long	Perp	Long	Perp	Long
−0.36	−0.19	−0.68	−0.40	−0.66	−0.39	−0.80	−0.52

Bridge											
(5,5)						(9,9)					
CNT			BNNT			CNT			BNNT		
Perp	Long	Trans	Perp	Long	Trans	Perp	Long	Trans	Perp	Long	Trans
−0.44	−0.13	−0.11	−0.84	−0.43	−0.50	−0.49	−0.21	−0.13	−0.81	−0.48	−0.54

The values presented are in kcal/mole.

Studying the curvature effect in hydrogen interacting BNNTs, we observed that when the BNNTs diameter increases, the binding energy of the hydrogen also increases in each particular site of the interaction. For example, hydrogen binds on a N atom of a (5,5) BNNT with −0.77 Kcal/mole while on the same atom of a (9,9) BNNT with −0.86 Kcal/mole. Same behavior was also found for the approach on a boron atom and was also observed in CNTs using both *ab initio* and grant canonical Monte-Carlo simulations [38].

The potential energy curves of hydrogen's approach on the center of a ring of a (5,5) and (9,9) both carbon and boron nitride nanotubes (Hollow case, Perpendicular and Longitudinal configuration) is presented in Fig. 3. For the cases shown in Fig. 3, the most favorable pathway of hydrogen is the one, which interacts with the (9,9) BNNTs ring, with a perpendicular configuration. The general conclusions, revealed from this figure are that (a) BNNTs sites are preferred to equivalent CNTs sites (the BE of hydrogen on a ring of a (5,5) tube with perpendicular configuration, increased 89%, from −0.36 on CNT to −0.68 kcal/mole on BNNT, while in the (9,9) tubes, increased 21%, from −0.66 on CNT to −0.80 kcal/mole on BNNT), (b) the perpendicular configuration of hydrogen is always preferred to the longitudinal of the same tubes and (c) similarly to Fig. 1, when the BNNTs diameter increases, the binding energy of the hydrogen also increases in each particular site of the interaction. All the previous results are clearly demonstrated in Table 1.

The last group of potential energy pathways concerns hydrogen's approach on top of a B–N or C–C bond of the (5,5) and (9,9) tubes (Bridge case, Perpendicular, Longitudinal and transversal configuration) (Fig. 4). An interesting remark that can be pointed out from these pathways is that only the type of the tube (CNT or BNNT) plays important role on the binding energy of hydrogen and not the diameter of the tube as observed in the previous cases (see also Table 1). This happens because H_2 approach the middle of the bond and interact with both atoms. In this way the neighboring to the atoms in the tube wall, which positions define the curvature, are lying in a non interacting distance. In addition, the pathways with perpendicular configuration appear to be preferable to the longitudinal and the latter to the transversal. The same trend of hydrogen's configuration was also observed in CNTs [21].

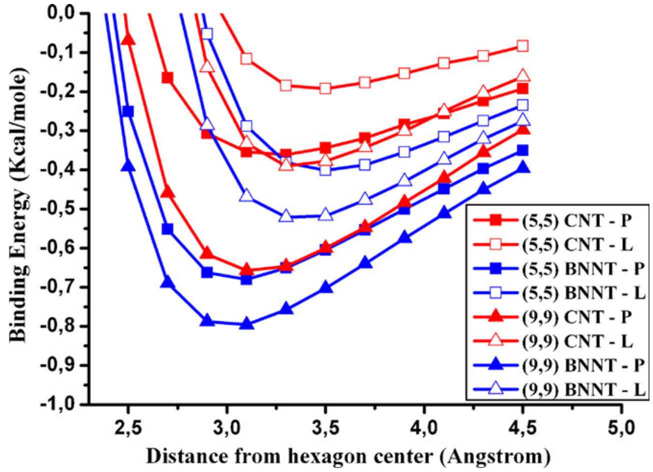

Fig. 3. Hollow case: binding energy curves of hydrogen on (5,5) (square), (9,9) (triangle), CNT (red) and BNNT (blue) with hydrogen on top of a ring, with perpendicular (filled figure) and longitudinal (open figure) configurations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

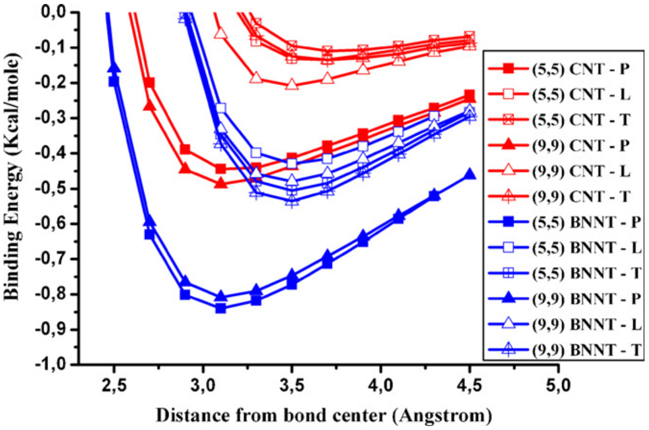

Fig. 4. Bridge case: binding energy curves of hydrogen on (5,5) (square), (9,9) (triangle), CNT (red) and BNNT (blue) with hydrogen on top of a bond, with perpendicular (filled figure), longitudinal (open figure) and transversal (open with line figure) configurations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

In the case of the perpendicular to the tube walls approach, the H_2 molecule is slightly polarized. This small dipole is induced by the nanotube's π electron clouds giving further rise to the hydrogen's binding energy, in the case of the perpendicular configuration, when compared with the longitudinal and the transversal configurations. In addition, in the BNNTs case, the ionic character of its bonds is enhanced compared to the covalent character of CNTs bonds. So, we observed as expected, larger charged induced dipoles to the hydrogen molecule (perpendicular configuration), than in the case of the CNTs. This fact, result in a stronger interaction between the molecular hydrogen and the BNNT. An analogous charged induced dipole was also reported in H_2 interaction with alkali doped CNTs [22]. This charge transfer that can take place between the atoms of a material may be the key point that can influence the binding energy of hydrogen and consequently the hydrogen storage capacity.

The results presented in this work, are in very good agreement with the results of Jhi and Kwon [36]. Despite their larger calculated binding energy values, they found that the most favorable sites that hydrogen interacts with a BNNT is on top of a ring together with on top of a N atom and less favorable site appears on top of a B atom. In addition, the mean value of the binding energy increase found in BNNTs of all the cases studied in this work is about 40% larger compared to that of CNTs, which is in very good agreement with the previously mentioned work [36].

Our results show that BNNTs are a preferable medium for hydrogen storage than CNTs. Comparing all the binding energy curves of molecular hydrogen interacting with all possible sites of physisorption on nanotube's wall and in several structural configurations one can easily conclude that more efficient binding of hydrogen can be attained with BNNTs instead of CNTs. The ionic character of the BNNTs bonds is the key point that increases the binding energy of hydrogen. In parallel, we showed that by increasing the nanotube's diameter – decreasing its curvature, more efficient binding could be achieved. The combination of both using heteropolar chemically bonded materials and taking into account their curvature; can be a pathway to find new materials possessing higher hydrogen storage capacity. The experimental evidences of the first factor arose from Ma's [29] and Tang's [30] recently published work. Yet, in order to achieve the second factor more experimental efforts have to be made in gaining the control of the synthesis of these novel nanomaterials.

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References

[1] S. Iijima, Nature 354 (1991) 56.
[2] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[3] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.
[4] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, Appl. Phys. Lett. 74 (1999) 2307.
[5] P. Chen, X. Wu, J. Lin, K. Tan, Science 285 (1999) 91.
[6] G.E. Froudakis, J. Phys.: Condens. Matter. 14 (2002) 453.
[7] A.C. Dillon, M.J. Heben, Appl. Phys. A 72 (2001) 133.
[8] V. Meregalli, M. Parrinello, Appl. Phys. A 72 (2001) 143.
[9] H.M. Cheng, Q.H. Yang, C. Liu, Carbon 39 (2001) 1447.
[10] G.E. Froudakis, Nanoletters 1 (2001) 179.
[11] C.W. Bauschlicher Jr., Nanoletters 1 (2001) 223.
[12] C.W. Bauschlicher Jr., C.R. So, Nanoletters 2 (2002) 337.
[13] S.S. Han, H.M. Lee, Carbon 42 (2004) 2169.
[14] Q. Wang, J.K. Johnson, J. Chem. Phys. 110 (1998) 577.
[15] K.A. Williams, P.C. Ecklund, Chem. Phys. Lett. 320 (2000) 352.
[16] H. Dodziuk, G. Dolgonos, Chem. Phys. Lett. 356 (2002) 79.
[17] X. Zhang, D. Cao, J. Chen, J. Phys. Chem. B 107 (2003) 4942.
[18] J.S. Arellano, L.M. Molina, A. Rubio, J.A. Alonso, J. Chem. Phys. 112 (2000) 8114.
[19] J.S. Arellano, L.M. Molina, A. Rubio, M.J. López, J.A. Alonso, J. Chem. Phys. 117 (2002) 2281.
[20] Y. Okamoto, Y. Miyamoto, J. Phys. Chem. B 105 (2001) 3470.
[21] G. Mpourmpakis, E. Tylianakis, G. Froudakis, J. Nanosci. Nanotechnol. 6 (2006) 87.
[22] G.E. Froudakis, Nanoletters 1 (2001) 531.
[23] W.Q. Deng, X. Xu, W.A. Goddard, Phys. Rev. Lett. 92 (2004) 166103.
[24] N.G. Chopra, R.J. Luyken, K. Cherry, V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, Science 269 (1995) 966.
[25] A. Loiseau, F. Willaime, N. Demoncy, G. Hug, H. Pascard, Phys. Rev. Lett. 76 (1996) 4737.
[26] A. Rubio, J.L. Corkill, M.L. Cohen, Phys. Rev. B 49 (1994) 5081.
[27] M. Menon, D. Srivastara, Chem. Phys. Lett. 307 (1999) 407.
[28] P. Wang, S. Orimo, T. Matsusima, H. Fujii, G. Majer, Appl. Phys. Lett. 80 (2002) 318.
[29] R. Ma, Y. Bando, H. Zhu, T. Sato, C. Xu, D. Wu, JACS 124 (2002) 7672.
[30] C. Tang, Y. Bando, X. Ding, S. Qi, D. Golberg, JACS 124 (2002) 14550.
[31] T. Oku, I. Narita, Physica B 323 (2002) 216.
[32] I. Narita, T. Oku, Diamond Relat. Mater. 11 (2002) 945.
[33] Q. Sun, Q. Wang, P. Zena, Nanoletters 5 (2005) 1273.
[34] S.S. Han, J.K. Kang, H.M. Lee, A.C.T. van Duin, W.A. Goddard, J. Chem. Phys. 123 (2005) 114703;
S.S. Han, J.K. Kang, H.M. Lee, A.C.T. van Duin, W.A. Goddard, J. Chem. Phys. 123 (2005) 114704.
[35] X. Wu, J. Yang, J.G. Hou, Q. Zhu, J. Chem. Phys. 121 (2004) 8481;
X. Wu, J. Yang, J.G. Hou, Q. Zhu, Phys. Rev. B 69 (2004) 153411.
[36] S.H. Jhi, Y.K. Kwon, Phys. Rev. B 69 (2004) 245407.
[37] M.J. Frisch, et al., GAUSSIAN 98 ~Revision A.11!, (1998).
[38] G. Mpourmpakis, et al., submitted for publication.