

THEORETICAL INVESTIGATION OF MOLECULAR HYDROGEN ADSORPTION BY CARBON NANOTUBE BUNDLES

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We perform detailed calculations for the adsorption of a single hydrogen molecule by the carbon nanotubes (CNTs) bundles by using Density Functional based Tight Binding (DFTB) method. We have considered an armchair (3, 3) CNTs bundle which consists of seven tubes. It has been found that the binding energy of H₂ in the interstitial channels between three tubes site is much higher than the others while, the binding distance of H₂ in this site is much smaller than that in other sites. The results also show that H₂ molecule become chemisorbed on the outer surface of the tubes via the covalent bonds. Furthermore, the mechanism of the C–H bond formation is studied by density functional based tight binding molecular dynamics simulation which has been carried out at room temperature.

(Received August 3, 2009; accepted September 30, 2009)

Keywords: Adsorption; CNTs bundles; Hydrogen storages; *ab initio* MD simulation; DFT

1. Introduction

One of the most widely envisioned sources of fuel cell vehicle (FCV) is hydrogen (H₂), the most abundant element in the universe. Therefore, it is necessary to have a convenient storage system of H₂ to start FCV on demand. The presently used systems such as high pressure H₂ tank or liquefied H₂ in a cryogenic vessel possess severe disadvantage [1-4]. Therefore, particular attention has been paid to the carbon nanotube as a potential hydrogen storage medium due to its light mass density and high surface to volume ratio, high strength, as well as their excellent kinetics, which is based on weak van der Waals force between H₂ and the surface of the materials [5-7]. Among these, the study of adsorption within bundles of carbon nanotubes has stimulated considerable interest [8-20]. The main advantage of the SWNT bundles is that they provide a large number of adsorption sites: the interstitial channels between three adjacent tubes (ICs), the grooves (G), rounded outer surface of the bundle (S) and inside the empty nanotubes (INT).

The results of the recent experimental studies reveal that the adsorption occurs either in the ICs [9-11], or in the G sites on the outer surface of the bundles [12, 13, 16, 17] or in both types of sites [13-15]. These different adsorption scenarios are still a subject of debate since the interpretation of experimental data is complicated by the quality of the SWNT samples.

Despite of the numerous experimental investigations, however, the theoretical study of the H₂ adsorption on the bundles of carbon nanotubes has been less considered. This is perhaps due to the quite large unit cell and thus large computation resources needed, especially for finding the optimized structures. Indeed, few theoretical works have been reported on the interactions of H₂ with bundles of carbon nanotubes. In this work we intend to extend our understanding of the interaction of molecular hydrogen with CNTs bundles by means of Density Functional Theory based Tight Binding (DFTB) calculations. Since the main factors which influence the stability of such systems are weak but numerous nonbonding van der Waals (vdW) interactions hence, in the present work the dispersion corrects for the vdW interaction have also been considered, for the

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first time. In order to finding convenient materials for hydrogen storage which satisfy DoE requirements [21] the relatively easiness of performing computations using standard density functional based tight binding program packages deserve richly some comments.

2. Computational methods

The Structural optimizations of CNTs bundles and hydrogen molecules are carried out using the recently developed DFTB+ code [22]. The DFTB+ uses the density functional based tight binding method based on a second-order expansion of the Kohn-Sham total energy in density functional theory with respect to charge density fluctuations. At second-order expansion a transparent, parameter-free, and readily calculable expression for generalized Hamiltonian matrix elements can be derived.

The DFTB approach, unlike the typical approximate Hartree-Fock/DFT methods, uses a tabulated set of integrals derived from *ab initio* DFT calculations [23], leading to a substantial speed-up of the method since explicit integration is not required in the method. Furthermore, unlike conventional tight-binding method it is possible to produce parameterizations capable of accuracy close to LDA/GGA with minimal adjustable parameters and also transferable between different systems. The basis functions of the DFTB method are also available, allowing the reconstruction of actual wavefunctions from the calculations. Further details of the method have been fully reviewed for instance in [22-25]. In this work the Slater-Koster (S-K) type parameter set [26] was implemented. Furthermore, the dispersion corrections for the nonbonding van der Waals interaction were implemented via the Slater-Kirkwood type model [27]. The accuracy of our method was shown by previous theoretical study [28], hence reinforcing the reliability of theoretical method used in the present study.

Table 1. Calculated binding energies E_b (in eV per adsorbed molecule) for the adsorption of a H_2 molecule on the CNTs bundles for the four configurations of figure 3.

Configuration	C1 (INT)	C2 (IC)	C3 (G)	C4 (S)
Binding Energy (eV)	2.04	-2.01	-0.05	0.01

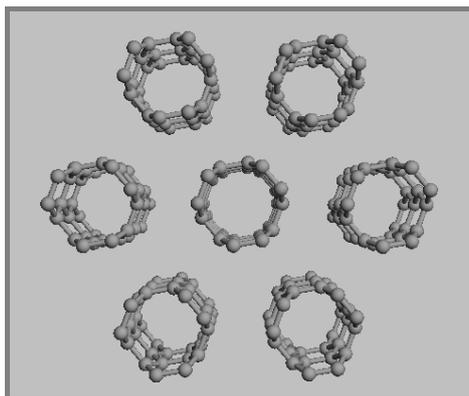


Fig. 1. Schematic representation of a pristine (3, 3) CNTs bundles.

Geometries of the CNTs bundles and hydrogen are optimized separately prior to the optimization of the whole system. Structural optimizations were performed using the conjugate gradient algorithm. For simplicity we chose single-walled (3, 3) CNT bundles including 252 carbon atoms as the model system (Fig. 1). The bundles consist of 7 individual carbon nanotubes parallel to each other in a hexagonal arrangement. Periodic boundary conditions and supercell approximations with a lateral separation of 17 Å between tube bundles centers are used to make sure that the nanotubes bundles plus H_2 do not interact with their periodic images. The unit is periodic in the direction of the tube and the length is 6.2039 Å for the CNTs bundle structures

being studied. Along the tubes axes, $1 \times 1 \times 4$ Monkhorst–Pack k -points were used for the Brillouin zone integration.

We have also tested the stability of the energetically favorable system with density functional based tight binding molecular dynamics (DF-TBMD) simulation. The DF-TBMD simulations are done by DFTB+ in the canonical regime. The structure under study is in contact with Andersen thermostat [29] having fixed temperature 300 K. The MD time step is 1.0 fs.

3. Results and discussion

To study the H_2 adsorption on the CNTs bundle we start with atomic structures of CNTs bundles. For SWNTs, the carbon network can be constructed in different ways, described by two parameters (n, m), which determine the tube diameter and chirality and therefore the periodicity along the tube axis. The most common conformation is the armchair configuration [30]. Thus, we have considered an armchair (3, 3) CNTs bundle which consists of seven tubes, as depicted in fig. 1. We examine the adsorption of a H_2 at four distinct sites of the CNTs bundle. Four possible configurations, named C1–C4, were selected for the molecule interacting with the tubes: C1 denotes adsorption of a H_2 inside the nanotubes (INT), C2 in the interstitial channels between three nanotubes (ICs), C3 in the grooves between adjacent nanotubes (G) and C4 on the graphene outside surface of the bundle (S). All considered configurations are represented in figure 2. The optimized CNTs bundle was used for the molecule adsorption. After full structural optimization of the systems we find that configuration C2 is the most stable configurations, which corresponds to the adsorbed molecule in the interstitial channels between three nanotubes of the bundle (ICs). The binding energy is calculated from

$$E_b = E_{CNTbundle-H_2} - E_{CNTbundle} - E_{H_2} \quad (1)$$

where $E_{CNTbundle-H_2}$ is the total energy of the CNTs bundle with an adsorbed hydrogen molecule, $E_{CNTbundle}$ is the total energy of the pure CNTs bundle, and E_{H_2} is the total energy of the isolated hydrogen molecule.

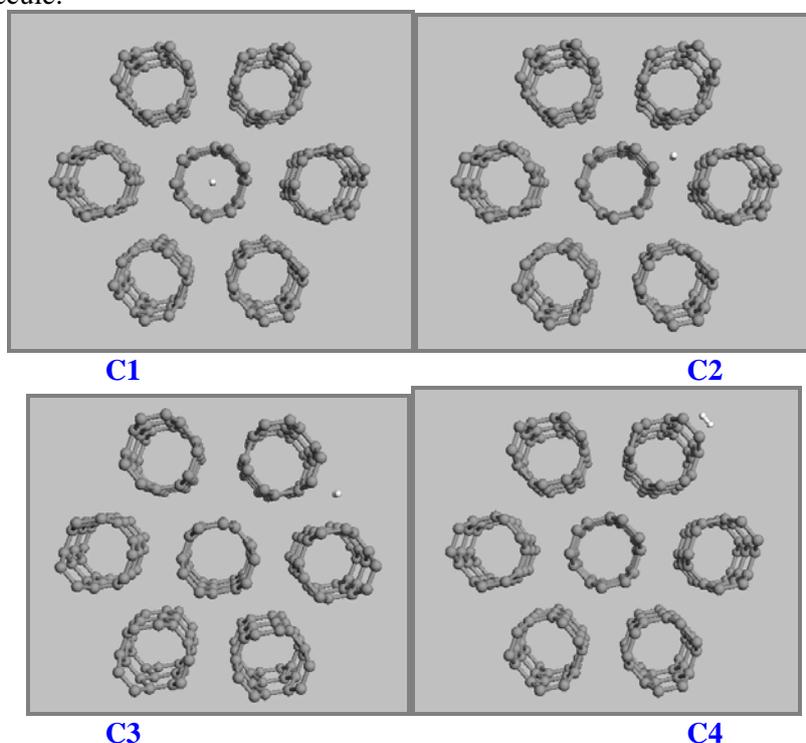


Fig. 2. Model for four different adsorption states for a hydrogen molecule inside the nanotubes (INT; C1), in the interstitial channels between three nanotubes (IC; C2), in the grooves between adjacent nanotubes (G; C3) and on the graphene outside surface (S; C4) of the (3, 3) CNTs bundle. (White ball : H , Gray ball : C).

For the energetically favorable configuration the calculated binding energy E_b and C–H equilibrium distance are about -2.01 eV (-46.41 kcal/mol) and 1.118 Å, respectively. The results show that H_2 is dissociated and then new bonds between the H and C atoms were formed. It can also be seen that the adsorption of H_2 on the tubes, results in a distortion of the tubes structure. The small distance of adsorbed H_2 from the plane and the negative adsorption energy of -2.01 eV indicate strong interaction of H_2 with the CNTs bundle [31-35].

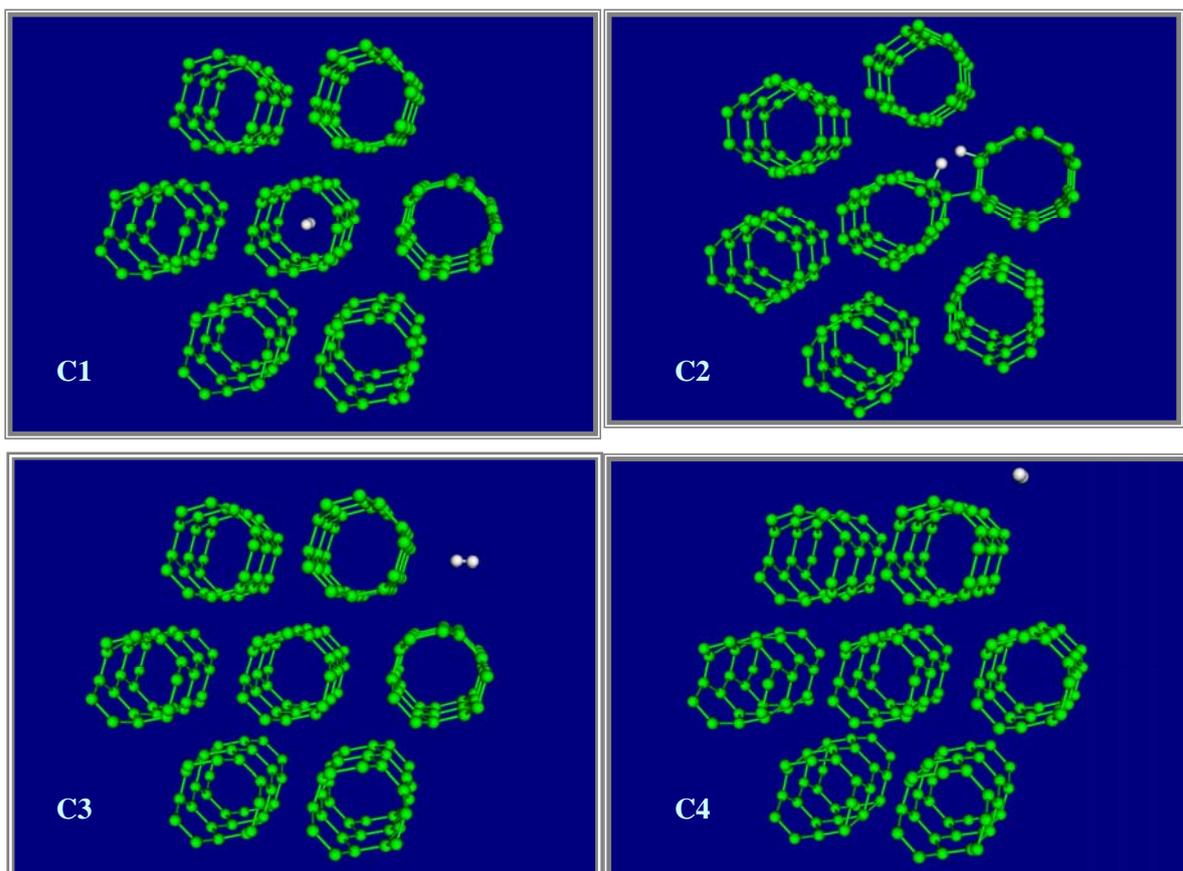


Fig. 3. The optimized geometric structures of the considered configurations of figure 2.

The calculated binding energy and C–H equilibrium distance for all of considered configurations are summarized in Table 1. The present results show that the binding energies are positive for C1 and C4 configurations while they are negative for C2 and C3 configurations, which is in agreement with the results of Refs. [14] and [15]. For the C1, C3 and C4 configurations the bond length of H_2 changed to about 0.7486 Å, which is basically the same as for an isolated H_2 molecule (0.7430 Å). The small change of the H–H bond is an indication of the weak interaction between the hydrogen molecule and the CNTs bundle. Figure 3 shows the schematics representation of the optimized structures for all of considered configurations.

We have also performed Mulliken charge analyses to evaluate the amount of electron transfers between nanotubes and hydrogen molecule. Charge analysis indicates that there is about 0.17 e transfer from the hydrogen atoms to the CNTs for the C2 configuration while, there is about 0.01 e transfer from the CNTs to the hydrogen molecule for the other configurations.

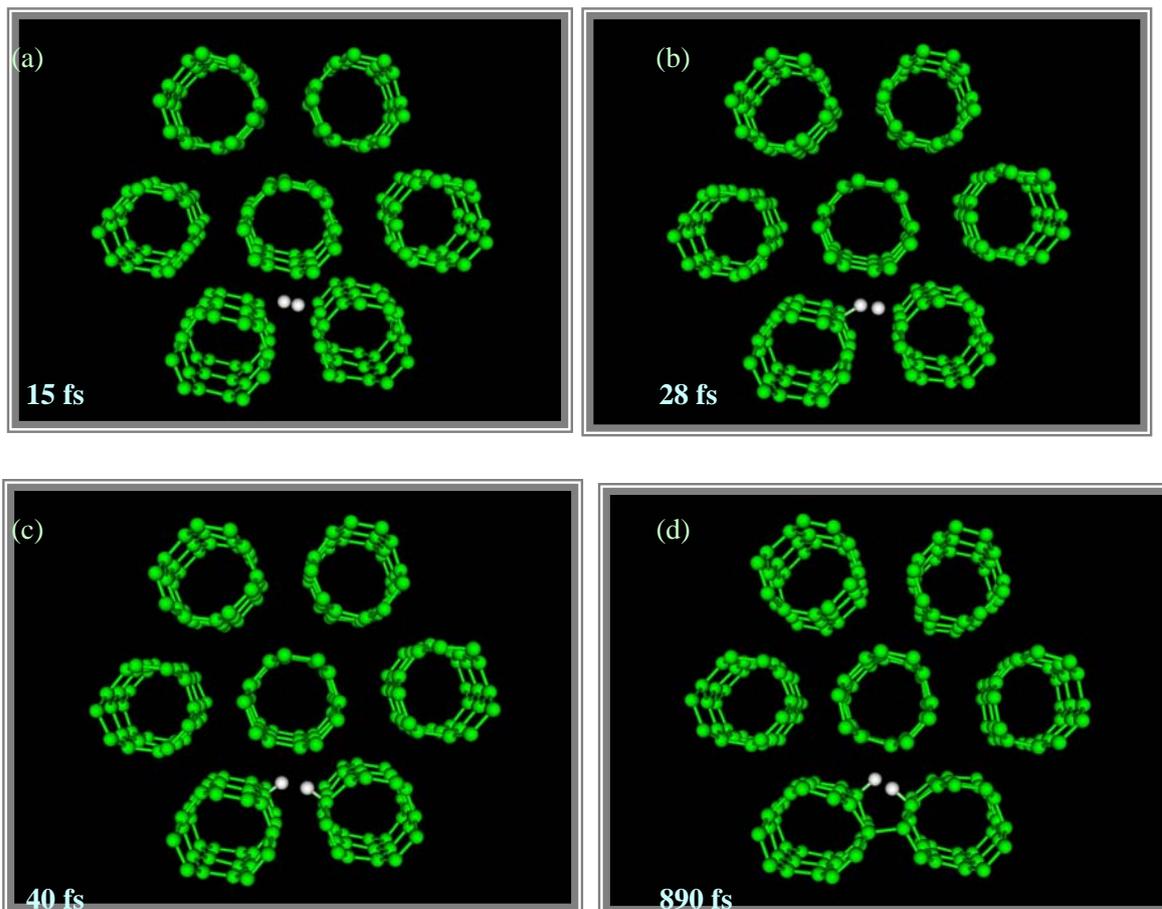


Fig. 4. Snapshots of DFT-based tight binding molecular dynamics simulations of C2 configuration structures at 300 K: (a) 15 fs, (b) 28 fs, (c) 40 fs and (d) 890 fs.

In order to investigate the chemisorption of H_2 molecule on the outer surface of tubes walls, we have performed DF-TBMD simulation for the C2 configuration. The mechanism of H–H bond dissociation is illustrated in Fig. 4. We put the system in contact with a thermostat at room temperature. The calculated results show that the H–H bond became long, it reaching almost 1.867 Å after 15 fs, and thus they are very weak and easy to break. As it can be seen from the figure, at 28 fs an H atom bonds with a C atom of the tube via the covalent bond. After 40 fs the remaining H atom bonds with another C atom from the adjacent tube. Atomic movements during MD simulations lead to the new bond between two C atoms of the adjacent tubes after 890 fs and hence, results in a distortion of the CNTs structure.

4. Conclusions

We have theoretically studied the adsorption of a single hydrogen molecule by the CNTs bundles using density functional based tight binding calculations. We have considered an armchair (3, 3) CNTs bundle which consists of seven tubes. To study the H_2 adsorption on the CNTs bundle, four distinct sites of the CNTs bundle were selected for the molecule interacting with the tubes.

We found that the interstitial channels between three nanotubes site is the energetically favorable site for H_2 adsorption. The results also showed that, when H_2 molecule was adsorbed on the CNTs walls, the H–H bond was dissociated and then a new bond between H and C atoms was formed. Furthermore, the formation of C–H bond is studied by density functional based tight

binding molecular dynamics simulation which has been carried out at room temperature. We hope that the ideas put forward here will facilitate bridging the gap between theory and hydrogen storage experiments.

Acknowledgements

We thank Dr. Saeed Yeganegi and Moammad Reza Mozaffari for many fruitful discussions. This work was su

References

- [1] L. Schlapbach, A. Züttel, *Nature* **414**, 353 (2001).
- [2] Y. Kojima, Y. Kawai, S. Towata, T. Matsunaga, T. Shinozawa, M. Kimbara in Symposium GG, Materials and Technology for Hydrogen Storage and Generation, GA., Nazri, C. Ping, R. C. Young, M. Nazri, J. Wang (Eds.), *Mater. Res. Soc. Symp. Proc.* **884E**, GG6.5 (2005).
- [3] D. Mori, N. Kobayashi, T. Shinozawa, T. Matsunaga, H. Kubo, K. Toh, M. Tsuzuki, *Jpn. Inst. Met.* **69**, 308 (2005).
- [4] D. Mori, N. Kobayashi, T. Matsunaga, K. Toh, Y. Kojima, *Materia Japan* **44**, 257 (2005).
- [5] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature* **386**, 377 (1997).
- [6] 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**, 2307 (1999).
- [7] M. Hirscher, M. Becher, M. Haluska, U. Dettlaff-Weglikowska, A. Quintel, G. S. Duesberg, Y. M. Choi, P. Downes, M. Hulman, S. Roth, I. Stepanek, P. Bernier, *Appl. Phys. A* **72**, 129 (2001).
- [8] M.S. Dresselhaus, K.A. Williams, P.C. Eklund, *MRS Bull.* **24**, 45 (1999).
- [9] W. Teizer, R.B. Hallock, E. Dujardin, T.W. Ebbesen, *Phys. Rev. Lett.* **84**, 1844 (2000).
- [10] M. Muris, N. Dufau, M. Bienfait, N. Dupont-Pavlovsky, Y. Grillet, J. P. Palmari, *Langmuir* **16**, 7019 (2000).
- [11] A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, S. Suzuki, Y. Achiba, *Chem. Phys. Lett.* **336**, 205 (2001).
- [12] S. Alapatra, A.Z. Ambano, S.E. Eber, A. D. Migone, *Phys. Rev. Lett.* **85**, 138 (2000).
- [13] M. Muris, N. Dupont-Pavlovsky, M. Bienfait, P. Zeppenfeld, *Surf. Sci.* **492**, 67 (2001).
- [14] M. Muris, M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlosky, M. Johnson, O. E. Vilches, T. Wilson, *Appl. Phys. A* **74**, S1293 (2002).
- [15] T. Wilson, A. Tyburski, M.R. Depies, O.E. Vilches, D. Becquet, M. Bienfait, *J. Low Temp. Phys.* **126**, 403 (2002).
- [16] S. Talapatra, A.D. Migone, *Phys. Rev. Lett.* **87**, 206106 (2001).
- [17] A.J. Zambano, S. Talapatra, A.D. Migone, *Phys. Rev. B* **64**, 075415 (2001).
- [18] A. Kuznetsova, Jr. J. Yates, J. Lin, R. E. Smalley, *J. Chem. Phys.* **112**, 9590 (2000).
- [19] Q. Wang, J. K. Johnson, *J. Phys. Chem. B* **103**, 4809 (1999).
- [20] M.W. Cole, V.H. Crespi, G. Stan, C. Ebner, J.M. Hartman, S. Moroni, M. Boninsegni, *Phys. Rev. Lett.* **84**, 3883 (2000).
- [21] Proceedings of the 1998 US DoE Hydrogen Program Review, 1, NREL/CP-570-2315, August 1998.
- [22] B. Aradi, B. Hourahine and T. Frauenheim, *J. Phys. Chem. A* **111**(26), 5678 (2007).
- [23] G. Seifert, D. Porezag and T. Frauenheim, *Int. J. Quantum Chemistry* **58**, 185 (1996).
- [24] T. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai and R. Scholz, *Phys. Stat. Sol. (b)* **271**, 41 (2000).
- [25] T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Amkreutz, M. Sternberg, Z. Hajnal, A. Di Carlo and S. Suhai, *J. Phys.: Condensed Matter* **14**, 3015 (2002).
- [26] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Phys. Rev. B* **58**, 7260 (1998).

- [27] M. Elstner, P. Hobza, T. Frauenheim, S. Suhai and E. Kaxiras, *J. Chem. Phys.* **114**, 5149 (2001).
- [28] M. D. Ganji, *Diamond & Related Materials* **18**, 662 (2009).
- [29] H.C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- [30] Talapatra S. and Migone A.D., *Phys. Rev. B* **65**, 045416 (2002).
- [31] I. Cabria, M. J. Lopez, J. A. Alonso, *Eur. Phys. J. D* **34**, 279 (2005).
- [32] M. D. Ganji, *Nanotechnology* **19**, 025709 (2008).
- [33] H. Pan, Y. P. Feng, J. Lin, *App. Phys. Lett.* **90**, 223104 (2007).
- [34] M. D. Ganji, *Phys. Lett. A* **372**, 3277 (2008).
- [35] M. D. Ganji, *Phys. E A* **41**, 1433 (2009).