

Normal modes of vibration of carbon nanotubes doped with nitrogen: towards conducting properties

J.R. Soto*, J. Austrich, R.M. Valladares, A. Valladares,
M.L. Marquina, R. Espejel, and A. Calles
*Facultad de Ciencias, Universidad Nacional Autónoma de México,
Apartado Postal 70-646, 04510 México D.F., México.*

Recibido el 9 de junio de 2006; aceptado el 6 de noviembre de 2006

The conducting properties of carbon nanotubes can be changed by nitrogen doping. There exists an enormous interest in modifying the conducting properties of organic and inorganic single and multiwall nanotubes, through doping, since their modified transport properties can be exploited in electronic nano-devices such as diodes, transistors, etc. In this work we study the normal modes of vibration of the armchair (4,4) nanotube: pristine and with nitrogen doping. We used the Density Functional Theory approach including periodic boundary conditions to obtain the *ab initio* Hessian tensor.

Keywords: Nanotubes; electronic properties; nitrogen doping; density functional theory.

Las propiedades conductoras de los nanotubos de carbón pueden cambiarse si se dopan con impurezas de nitrógeno. Existe un gran interés por modificar las propiedades conductoras de los nanotubos simples y multicapa, orgánicos e inorgánicos, mediante el dopaje, ya que sus propiedades modificadas de transporte pueden aprovecharse en nano-dispositivos electrónicos como diodos, transistores, etc. En este trabajo se estudian los modos normales de vibración del nanotubo *armchair* (4,4): puro y con impurezas de nitrógeno. Se empleó la aproximación de la Teoría de Funcional de la Densidad, incluyendo condiciones de frontera periódicas, para obtener el tensor Hessiano de primeros principios.

Descriptores: Nanotubos; propiedades electrónicas; dopado con Nitrógeno; teoría de funcional de la densidad.

PACS: 73.63.Fg; 78.66.Tr; 71.15.Mb

1. Introduction

Since the discovery of carbon nanotubes [1], their experimental and theoretical properties have been a subject of intense research. Carbon nanotube conductivity will play a very important role in the fabrication of nanodevices such as transistors, diodes, sensors, biosensors, batteries, etc. The carbon nanotubes with boron or nitrogen dopants exhibit semiconducting properties such that they can be used as part of nanotransistors at high temperatures. The greater part of nanotubes synthesized behave as p-type semiconductors.

The group of M. Terrones *et al.* [2] has tailored and characterized carbon nanotubes with nitrogen replacing some carbon atoms, these being the first n-type semiconducting nanotubes. Nitrogen is present in these nanotubes as a pyridine substructure in these CN_x structures. The purpose of the present work is the theoretical characterization of the structural, electronic and vibrational properties of carbon nanotubes doped with nitrogen and compare them with their corresponding pristine carbon nanotube properties.

2. Theoretical details

The electronic calculations that we performed for the nanotube systems were based on the Density Functional Theory (DFT) using the hybrid functional of Perdew, Burke and Ernzerhof (PBE-1997)[3]. Periodic boundary conditions were incorporated into the calculation such as the Gaussian03 package allows us for a one-dimensional periodic system. Actually, this procedure only allows to do gradient and optimization calculations. No symmetry restriction has been

used to optimize the nanotube structure in each case. The force constants were calculated making finite differences of gradients for the optimized structure.

For the pure carbon nanotube, we used symmetry properties in order to calculate the Hessian. In the case of the nitrogen doped nanotube, the Hessian components corresponding to the three nitrogen atoms of the pyridine plus their first carbon neighbors were calculated. These components are substituted in the Hessian matrix of the pristine nanotube and the row/column of the replaced carbon atom due to the pyridine doping was eliminated.

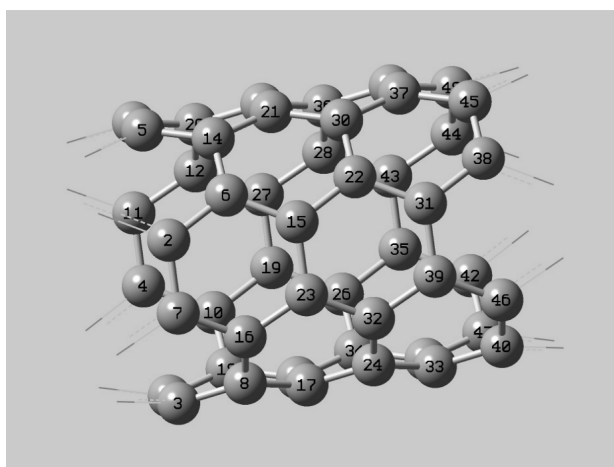


FIGURE 1. Armchair (4,4) carbon nanotube.

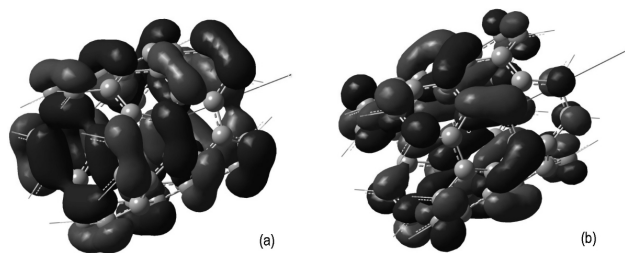


FIGURE 2. DFT molecular orbitals for the nanotube. a)HOMO, b)LUMO.

3. Results and discussion

We choose an armchair (4,4) pristine carbon nanotube as a first example; its optimized structure is shown in Fig. 1. The (n,n) armchair nanotubes have especially high symmetry and exhibit a mirror symmetry plane normal to the tubule axis. These nanotubes are quasi-zero-gap semiconductors. In Figs. 2a and 2b we show the results for the DFT HOMO and LUMO orbitals of this nanotube, respectively. The HOMO-LUMO gap for the pristine carbon nanotube was 0.93 eV. This agrees with the experimental fact that the system is semimetallic.

We performed the gradient and row/column calculations of the Hessian for the optimized structure. Figure 3 shows the diagonal cartesian force constants as a function of the distance. In this figure we observe that it is only necessary to consider neighbors within a radius of 4 Å in order to obtain the predominant force constant components. Then, we selected a supercell with the proper size for modelling the nanotube normal modes of vibration.

We obtained the normal modes of vibration by diagonalization of the Hessian. Figures 4a-d show some representative modes. As we can see in these figures, the normal modes of vibration are mainly radial or tangential in character, with respect to the nanotube axis. The ending atoms do not show a different behavior confirming a right 1-D translational invariance application.

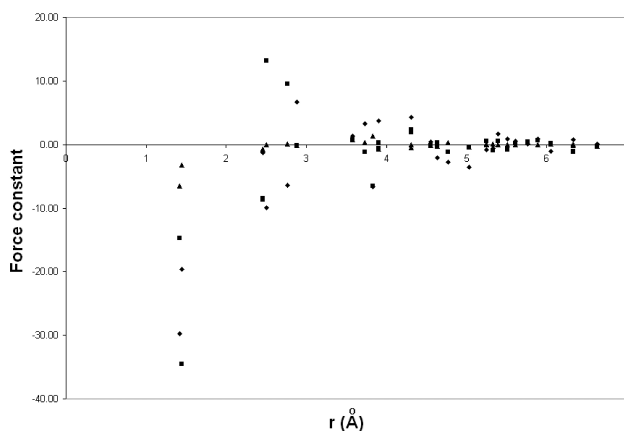


FIGURE 3. Diagonal cartesian force constants of the armchair nanotube (4,4): rhombus F_{xx} , squares F_{yy} , and triangles F_{zz} .

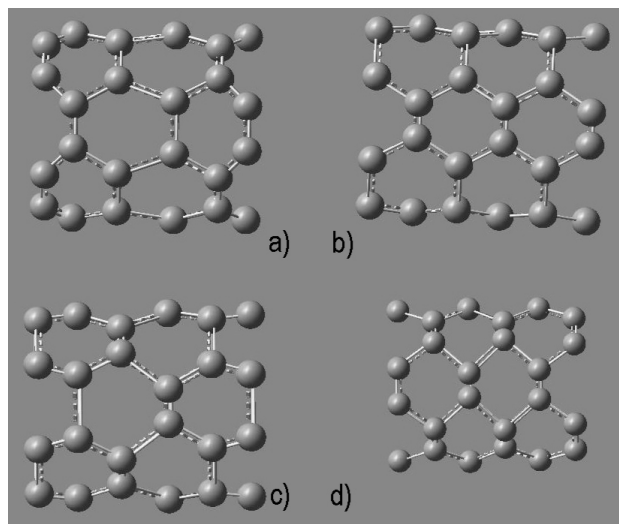


FIGURE 4. Representative normal modes of vibration. Armchair (4,4).

We chose pyridine type doping for the nitrogen doped nanotube structure. In Fig. 5 we show the optimized structure for the doped nanotube. This optimized structure shows two relevant features: the pyridine is not within the nanotube curvature, and the form of the tube is slightly oblate.

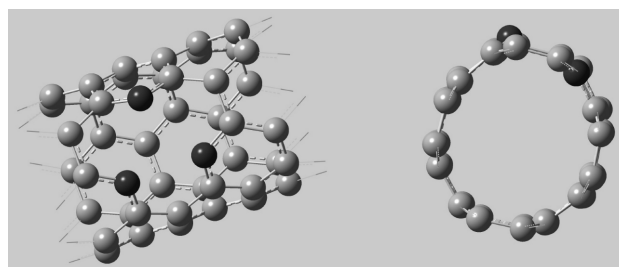


FIGURE 5. Armchair (4,4) nanotube doped with nitrogen pyridine.

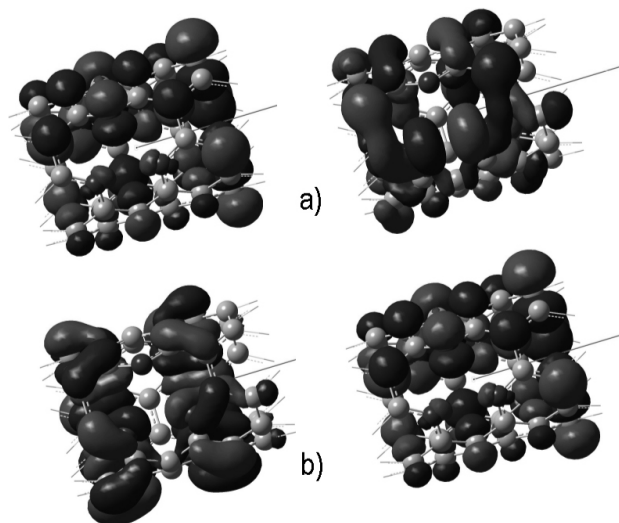


FIGURE 6. DFT molecular orbitals for the armchair (4,4) nanotube doped with nitrogen pyridine. a)HOMO, b)LUMO.

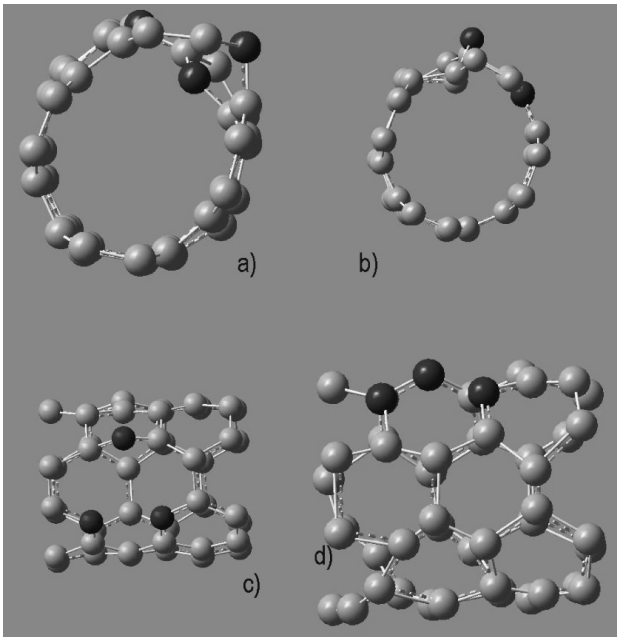


FIGURE 7. Representative normal modes of vibration. Armchair (4,4) nanotube doped with nitrogen pyridine.

Figures 6(a,b) show the HOMO and LUMO orbitals for the optimized doped nanotube structure. Due to pyridine doping, a decrease in the HOMO-LUMO gap to 0.25 eV can be observed when compared with the pristine nanotube gap. This fact is consistent with the increase of the electronic density of states near the Fermi level as shown in Ref. 2.

In order to quantify the charge polarization on the nanotube due to the nitrogen doping, we calculated the Mulliken charge distribution: there is a negative charge concentration on the pyridine of -0.54 / N atom versus a positive charge around $+0.26$ / C atom on the six nearest neighbors. The rest of the charge is spread on the other nanotube atoms of the supercell. We can conclude that this system is like a n-type semiconductor of quasi-zero gap, because the existence of many free electrons on the Fermi surface, again in coincidence with Ref. 2.

The columns of the Hessian corresponding to the doped nanotube are calculated and after the diagonalization, we obtained the normal modes of vibration shown in Figs. 7(a-c).

4. Conclusions

In this work we obtained the pristine and doped nanotube with nitrogen pyridine armchair (4,4) structures and their respective normal modes of vibration, using DFT *ab initio* calculations. The CN_x structure was stable, although this kind of doping implies that four carbon atoms are replaced by three nitrogen atoms. We showed also that this nanotube is a n-type semiconductor with a very small gap.

It is important to stress that the periodic boundary conditions permit optimized structures with no deformation at the nanotube ends. The phonon spectrum for doped nanotubes is relevant, because it can help to characterize their structural properties.

* Corresponding author: Fax (52)5556160326, e-mail: jr-soto@correo.unam.mx

1. S. Ijima, *Nature* **354** (1991) 56.

2. R. Czerw *et al.*, *Nanoletters* **1** (2001) 457.

3. J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **78** (1997) 1396.