Energetics and electronic structure of C$_{70}$-peapods and one-dimensional chains of C$_{70}$

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Abstract. We report total-energy electronic structure calculations that provide the energetics of encapsulation of C$_{70}$ fullerenes in carbon nanotubes. The encapsulation processes for C$_{70}$ in tubes thicker than (17, 0) are all exothermic. We find that the lying arrangement is energetically favourable for the thin nanotubes, whereas the standing arrangement is favourable for thick nanotubes. To explore the stable molecular arrangements in the nanotubes, we further study the energetics and electronic structures of one-dimensional chains of C$_{70}$. It is found that the standing intermolecular arrangement is the most stable structure for the chain due to the large intermolecular interaction. The electronic structures of the chains strongly depend on the mutual orientation of adjacent molecules. We find flat dispersion bands around the Fermi level of the standing chains and a possibility of spin polarization on the one-dimensional chain of C$_{70}$. 
1. Introduction

Carbon nanotubes [1] are known to be nanometre scale containers which can encapsulate foreign atoms and molecules inside due to their tubular structures [2]–[5]. In the early stages, lead atoms were indeed encapsulated inside nanotubes with multiple shells (multi-walled carbon nanotubes). In addition to the metal atoms, fullerenes have also been encapsulated inside single-walled carbon nanotubes (SWCNT) recently. High-resolution transmission electron microscope images clearly show the encapsulations of various fullerenes [6]–[11], e.g. C60, C70, C80, and C84, and metallofullerenes [12], e.g. Gd@C82 and Sc2@C84, inside the SWCNT. These unusual structures are occasionally called carbon peapods, which can be classified as a new class of crystalline carbon with novel structural hierarchy: the structures of the peapods are characterized by an interesting combination of one- and zero-dimensional constituent units, i.e. carbon nanotubes and fullerenes. In the hierarchical solid, the electronic structures and energetics of the systems are expected to exhibit an interesting interplay between their atomic arrangements and the spaces inside and outside the constituent units.

Our previous calculations have shown that the energetics of the peapods strongly depends on the interwall spacing between the fullerene and the nanotube which is determined by the tube radius and the size and the orientation of the fullerenes [13]–[15]. For the optimum spacing, the peapods are energetically stable and the energy gain for the encapsulation reaction is about 1.5 eV per fullerene molecule [13]–[15]. The electronic structures of the hierarchical solids are known to reflect the electronic states of the constituent units. For instance, in the solid C60, the electronic energy bands are characterized by the electron states of an isolated C60 molecule [16]. The electronic structures of peapods, thus, reflect those of the encapsulated fullerenes and nanotubes. In the case, however, the space inside and outside the units has also been found to affect the electronic structures of the peapods [13]–[15]. In hierarchical solids possessing large interunit spacings, the space induces peculiar delocalized electron states below the vacuum level with nearly free electron character (NFE state) [17]–[20]. The NFE states play crucial roles in the encapsulation of fullerenes and control the electronic states near the Fermi level [13]–[15]: it has been found that the energy gap of the C60-peapods strongly depends on the interunit spacing. Hybridization between NFE states and π states of fullerenes causes downward shift of the π states and results in a decrease of the energy gap. In addition to the space, the one-dimensional chain structure of the fullerenes also affects the electronic structures of the resultant peapods.
In one-dimensional chains consisting of large fullerenes with strong anisotropy, the electronic structures of the $\pi$ electron bands are strongly modulated by the orientation of the fullerenes due to an anisotropic distribution of the wavefunction for each electron state.

We report here total-energy calculations performed for one-dimensional chains of $C_{70}$ which are encapsulated zigzag carbon nanotubes. The electronic structure and energetics of the $C_{70}$-peapods are found to depend on their orientation in the nanotubes due to the ellipsoidal shape of the molecule. Furthermore, we also report detailed analyses on the electronic structures and energetics of the one-dimensional $C_{70}$ chains for various intermolecular spacings and configurations. The optimized intermolecular distances are found to lie in the range of 9.9–11.1 Å depending on the intermolecular orientation. The electronic structures of the chain strongly depend on the mutual orientation of the $C_{70}$. It is found that peculiar flat dispersion bands emerge around the energy gap for the chain in which the long axis ($C_5$ axis) of the $C_{70}$ is normal to the chain direction. Due to the localized nature of the lower unoccupied bands, we find the possibility of spin polarization on the one-dimensional chain of fullerenes.

2. Methods

All calculations have been performed using the local spin density approximation (LSDA) in the density-functional theory [21, 22]. For the exchange–correlation energy among electrons, we use a functional form [23] fitted to the Monte Carlo results for the homogeneous electron gas [24]. Norm-conserving pseudopotentials generated by using the Troullier–Martins scheme are adopted to describe the electron–ion interaction [25, 26]. In constructing the pseudopotentials, the core radii adopted for C 2s and 2p states are both 1.5 Bohr. The valence wavefunctions are expanded in the plane-wave basis set with a cut-off energy of 50 Ryd which is known to give enough convergence of total energy to allow discussion of the relative stability of various carbon phases [25]. We carry out the calculation for $C_{70}$ chains encapsulated in $(n, 0)$ nanotubes ($n = 17, 18, \text{ and } 19$) and isolated $C_{70}$ chains in this paper. We adopt a supercell model in which a peapod or a $C_{70}$ chain is placed with its wall separated by 6.5 Å from another wall of an adjacent peapod or a $C_{70}$ chain. To explore the possibility of long-range modulation of the $C_{70}$ chain arrangements, we have taken account of the double periodicity of the $C_{70}$. The conjugate-gradient minimization scheme is utilized both for the electronic structure calculation and for the geometry optimization [27]. In the geometry optimization for the peapods, we impose a commensurability condition relating the one-dimensional periodicity of the nanotube and that of the chain of $C_{70}$s. Consequently, the lattice parameter $c$ becomes 12.78 Å along the tube direction which corresponds to triple the periodicity of the zigzag nanotube. Integration over the one-dimensional Brillouin zone is carried out using two or four $k$ points.

3. Results and discussion

3.1. Energetics of $C_{70}@(n, 0)$

In table 1, we show reaction energies for the encapsulation reactions of $C_{70}$ in $(17, 0)$, $(18, 0)$, and $(19, 0)$ nanotubes. The reaction energy $\Delta E$ is defined by the following process:

\[ C_{70} + (n, 0) \rightarrow C_{70}@(n, 0) + \Delta E. \]

Since $C_{70}$ possesses an ellipsoidal shape, we consider two different orientations of the $C_{70}$ in the nanotubes: in a standing arrangement the long axis ($C_5$ axis) of $C_{70}$ is perpendicular to the
Table 1. Reaction energies $\Delta E$ (see the text) per $C_{70}$ in the encapsulation reaction for the $(n, 0)$ zigzag nanotubes. ‘Standing’ and ‘lying’ denote the peapods in which the long axis of $C_{70}$ is perpendicular and parallel to the tube axis, respectively.

| $n$ | Standing (eV/unit cell) | Lying (eV/unit cell) |
|-----|-------------------------|----------------------|
| 17  | $-0.470$                | $-1.846$             |
| 18  | $-1.302$                | $-1.596$             |
| 19  | $-1.310$                | $-0.910$             |

chain direction, whereas in a lying arrangement the axis is parallel to the chain direction. For the $(17, 0)$ nanotube, it is found that the reactions for both orientations are exothermic; the reaction energy, $|\Delta E|$, for the lying arrangement is larger than that for the standing arrangement by about $1.37$ eV. The energetics is totally due to the interwall spacing between $C_{70}$ and the nanotubes. The interwall spacing in the standing arrangement is $2.78$ Å which is insufficient to distribute the $\pi$ electrons, resulting in an increase of their kinetic energy. For the lying arrangement, on the other hand, the spacing is about $3.0$ Å which is close to the interlayer distance of the graphite and the interunit spacing of the $C_{60}@(10, 10)$. In the case of the $C_{60}$-peapods, the encapsulation for the $(10, 10)$ nanotube gives the largest $|\Delta E|$ [14]. The results indicate that the lying arrangement is energetically favourable for $C_{70}$ encapsulated in thin nanotubes with a diameter of about $13.5$ Å.

For the $(19, 0)$ nanotubes, the reaction energy $|\Delta E|$ of the standing arrangement is larger than that of the lying arrangement by $0.4$ eV/$C_{70}$. In the present calculations, since the centre of mass of the $C_{70}$ is located at the tube axis, the interunit spacing increases monotonically with increasing tube radius. However, in the thick nanotubes, it is expected that the $C_{70}$ in the lying arrangement may be located near the wall of the nanotube with an appropriate wall–$C_{70}$ distance of about $3$ Å. Indeed, our previous calculations have shown that the optimum position of the $C_{60}$ in the thick nanotube is dislodged from the centre of the nanotube to keep the preferable interwall distance of about $3$ Å [14]. In this case, the energy $\Delta E$ approaches not zero but a finite value of about $-0.4$ eV. Therefore, on the basis of the energetics of the $C_{60}$ chain encapsulated in a thick nanotube, it is expected that a realistic value of the energy $|\Delta E|$ for the $C_{70}$-peapod with the lying arrangement is larger than that obtained in the present calculation by about half an electron volt. Taking account of this correction, for the nanotubes thicker than the $(19, 0)$, it is likely that the reaction energies for both arrangements are almost identical to each other, and the orientation of the $C_{70}$ may be determined by the intermolecular interaction between adjacent $C_{70}$. Therefore, it is important to explore the energetics of the one-dimensional chains of the $C_{70}$ in various intermolecular arrangements.

3.2. Energetics of $C_{70}$ chains

Figure 1 shows fully optimized geometries of a one-dimensional chain of $C_{70}$ for various molecular arrangements. We consider three intermolecular arrangements: a standing arrangement, a lying arrangement, and an alternating arrangement in which standing molecules alternate with lying ones. In figure 2, we show the total energies of the three different
molecular arrangements as a function of the intermolecular distance. The stable intermolecular distances are found to be 9.9, 11.1, and 10.6 Å for the standing, the lying and the alternating arrangements, respectively. The calculated values of the optimized intermolecular distance show good agreement with that obtained by the x-ray diffraction analysis for the one-dimensional chains of the C\textsubscript{70} encapsulated in the nanotubes (10.5 ± 0.5 Å [12]). The standing arrangement is the most energetically stable among the three arrangements. In this arrangement, due to the ellipsoidal shape of the C\textsubscript{70}, large flat areas consisting of a hexagonal C–C network induce a large intermolecular interaction. On the other hand, the lying and alternating arrangements are less stable than the standing arrangement, and the total energies of the lying and the alternating arrangements are higher than that of the standing arrangement by 37 and 25 meV/C\textsubscript{70}, respectively. This result indicates that the C\textsubscript{70} encapsulated in thick nanotubes, such as the (19, 0) nanotube, are more likely to show the standing arrangement than the others. Furthermore, an interface between two different arrangements, the standing and the lying, is hardly expected to appear.

In the case of the standing arrangement, due to the ellipsoidal shape of the C\textsubscript{70} molecule, the energetics of the chain is also expected to depend on the mutual orientation of long axes between adjacent molecules. Figure 3 shows a contour plot of the total energy of the C\textsubscript{70} chain as functions of the intermolecular spacing and of the mutual orientation angle between the long axis of adjacent C\textsubscript{70}. As shown in figure 3, the most stable angle is found to be $\theta = 0^\circ$, for

Figure 1. Atomic arrangements of total-energy minimized C\textsubscript{70} chains with (a) standing, (b) lying and (c) alternating arrangements.
which the long axes of adjacent molecules are in parallel. In this mutual orientation of the C70 molecules, all the atoms in each molecule keep as far away from the corresponding atom in the adjacent molecules as possible. In addition to $\theta = 0^\circ$, we also find that $\theta = 90^\circ$ gives a metastable orientation. The calculated total energy of the orientation is higher than that for the $\theta = 0^\circ$ arrangement by 4 meV/C70. Since atomic arrangements with this mutual orientation result in a smaller overlap between the flat areas of adjacent C70, the energy gain due to the intermolecular interaction is smaller than that for the $\theta = 0^\circ$. On the other hand, the orientation of about $\theta = 50^\circ$ gives a saddle point at which the atom in the molecule possesses a corresponding atom (bond) in the adjacent molecule—similar to the AA stacking structure of graphite. It is worth estimating the energy barrier for the rotation of the molecule around the chain axis. Figure 4 shows the total energy of the standing chain as a function of the mutual rotation angle. The calculated energy barrier is found to be 8 meV. The results suggest that the C70 molecules in the standing arrangement are still rotating around the short (chain) axis at low temperature.

3.3. Electronic structures of C70 chains

In this section we study the electronic structures of the one-dimensional chains of C70 to elucidate the dependence of the electron states on the mutual configuration between adjacent molecules for four different arrangements, i.e. the standing ($\theta = 0^\circ$), the standing ($\theta = 90^\circ$), the lying, and the alternating intermolecular arrangements. In our previous works [13]–[15], we have reported that the space between fullerenes and nanotubes controls the $\pi$ electron states of fullerenes. However, due to the imposed commensurability condition relating the one-dimensional periodicity of the nanotube and that of the chain of fullerenes in the calculations, the detailed electronic structures of the one-dimensional chain of fullerenes and the resultant peapods have remained unclear.
Figure 3. A contour plot of the total energy per C\textsubscript{70} for the C\textsubscript{70} chain with the standing arrangement as functions of the intermolecular spacing and the mutual orientation angle. The values on the contours denote total energies (in eV). The energies are measured from that of an isolated C\textsubscript{70} molecule.

Figure 4. Total energies per C\textsubscript{70} for the standing chains with $c = 9.9$ Å as a function of the mutual orientation angle. The energies are measured from that of an isolated C\textsubscript{70} molecule.

Figure 5 shows the electronic energy bands of the C\textsubscript{70} chains with the standing ($\theta = 0^\circ$), the standing ($\theta = 90^\circ$), the lying, and the alternating arrangements with fully optimized geometries. In an isolated C\textsubscript{70} molecule, there are triply bunched highest occupied (HO) states and triply bunched lowest unoccupied (LU) states. A previous theoretical calculation has shown that the three LU states of C\textsubscript{70} are only distributed at the C sites on pentagons [28]. Therefore, it is
plausible that the electronic structures of the chain may depend strongly on the mutual orientation of adjacent molecules.

In the lying chain, the HO and LU states show dispersions of about 0.2 and 0.4 eV and become valence and conduction bands, respectively, with a band gap of about 1.5 eV (figure 5(a)). This large dispersion of the LU states is totally due to the significant overlap of the wavefunctions between adjacent molecules, which are indeed distributed around the pentagon sites (figure 6(a)). In addition to the dispersive energy bands, a nearly flat dispersion band also emerges in the LU states. The state is also localized at the pentagon sites but is slightly dislodged from the polar regions of the molecule (figure 6(b)).

It is found that, in sharp contrast to the lying chain, the remaining three chains possess small dispersion bands near the conduction band bottom. In the standing (θ = 0°) chain, two of three states show dispersion of 0.15 eV whereas the remaining state exhibits nearly flat dispersion (figure 5(b)). Furthermore, in the standing (θ = 90°) and the alternating chains, the band dispersions of the LU states are also narrower than for the lying chain (figures 5(c) and (d)). In these intermolecular arrangements, the pentagon sites of adjacent molecules are significantly separated from each other. The large separation causes localization of the LU states, which results in a small band dispersion of the states. The distribution of wavefunctions of the LU state in the standing (θ = 0°) arrangement clearly shows their localized nature (figure 6(c)). The small dispersions also induce an increase in the fundamental energy gaps of these chains. The calculated values of the energy gap for the standing (θ = 0°), standing (θ = 90°), and alternating arrangements are 1.60, 1.57, and 1.61 eV, respectively; these gaps are wider by about 0.1 eV than that of the lying chain. This orientation dependence may be observed in the absorption spectra of the C70-peapods: the onset and sharp structures of the spectra strongly depend on the molecular arrangements in the nanotubes.

3.4. Carrier doping in the C70 chain

It is found that flat dispersion bands emerge near the conduction band bottom for the standing and alternating chains. The unusual character also affects the electronic properties of the peapods.
by doping the electrons up to these energy bands: in the standing arrangements, the mobility of the electrons at the bottom of the conduction band is expected to be lower than that for the lying arrangement. Indeed, the calculated effective masses at the bottom of the conduction band (electron masses) for the standing \((\theta = 0^\circ)\) and the standing \((\theta = 90^\circ)\) chains are \(0.79 \, m_e\) and \(5.16 \, m_e\) (\(m_e\) is the bare electron mass)—larger than that of the lying chain \((0.40 \, m_e)\). The large effective mass and flat dispersion bands of the LU states of the standing \((\theta = 90^\circ)\) chain imply a possibility of spin polarization of electrons injected into the states. Here we examine the electronic structure of the chain with one additional electron per \(C_{70}\). Figure 7 shows the calculated spin density \(n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})\) for the standing \((\theta = 90^\circ)\) chain. The distribution of the spin density clearly shows the spin polarization. The calculated number of polarized spins is one per \(C_{70}\). The results suggest that the electron-doped \(C_{70}\)-peapods exhibit interesting physical properties due to the simultaneous existence of both \(\pi\) electrons on nanotubes and localized electron spins on the \(C_{70}\).

It is important to examine the possibility of long-range spin ordering of the polarized electron spin on the \(C_{70}\). Here, we examine the total energies of the ferromagnetic (FM) and antiferromagnetic (AF) spin arrangements. It is found that the calculated total energy of the FM spin arrangement is lower than that of the AF arrangement by \(8 \, \text{meV} / C_{70}\). Thus the polarized
electron spin on the C$_{70}$ exhibits FM long-range ordering due to the substantial overlap of the LU states between adjacent molecules.

4. Summary

We have studied the energetics of one-dimensional C$_{70}$ chains which are encapsulated zigzag carbon nanotubes. We have found that the energy gain on the encapsulation of C$_{70}$ in the nanotube depends on the tube radius and orientation of the C$_{70}$: the lying orientation of the C$_{70}$ is energetically favourable over the standing orientation in the thin nanotubes, i.e. (17, 0) nanotubes, whereas the standing orientation of the C$_{70}$ is favourable in thick nanotubes, i.e. (19, 0) nanotubes. The results indicate that the orientation of the fullerenes with strong anisotropy is controllable by changing the tube radius.

Since the C$_{70}$ molecule possesses an ellipsoidal shape, various intermolecular arrangements are expected to arise. In the present work, we have explored the energetics and electronic structures of one-dimensional chains of the C$_{70}$ molecules. The standing arrangement with parallel mutual orientation is found to be more energetically stable than the lying and the alternating ones. The results corroborate the assertion that the standing arrangement of C$_{70}$ in thick nanotubes is favourable if one takes account of not only the C$_{70}$–tube interaction but also the C$_{70}$–C$_{70}$ interaction. The mutual orientation of the C$_{70}$ modulates the electronic energy bands near the conduction band bottom of the C$_{70}$ chains. In the lying arrangement, the LU states are found to exhibit significant dispersion of about 0.5 eV. On the other hand, in the standing and the alternating arrangements, it is found that the LU states lose their dispersion and that flat dispersion bands emerge at the bottom of the conduction band due to the localized nature of the states at the atomic sites on the pentagons. The localized character of the states is found to induce spin polarization on the chain by injecting electrons into the states.

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