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Computational study of molecular properties of aggregates of C_{60} and (16, 0) zigzag nanotube

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Abstract

Molecular properties for two aggregates of C_{60} and a (16, 0) zigzag nanotube: (a) C_{60} encapsulated in the nanotube, (b) C_{60} attached to the outer wall of the nanotube, are studied using the self-consistent charge density-functional tight-binding method with additional dispersion correction. The binding energy for the encapsulated fullerene is −108.3 kcal/mol and for the attached fullerene, only −20.3 kcal/mol. The harmonic vibrational frequencies of the aggregates are found to be almost identical to those obtained for the non-interacting system. Very small extent of the changes upon interaction may pose a challenge to study the aggregated structures using experimental spectroscopic methods.

1. Introduction

The physical properties of complexes of single-wall carbon nanotubes (CNT) with other molecules are a topic of many recent studies [1–6]. One of the most interesting structures among them are carbon peapods [7,8], consisting of a chain of fullerenes encapsulated inside a single- or multi-wall nanotube. These systems have often very intriguing molecular and electronic properties, distinct from those of the isolated components [5,9], which may be relevant for fabricating novel molecular nanodevices [10,11]. They also offer a unique opportunity to study quasi one-dimensional systems at the molecular level [12].

The most common peapod structure is the C_{60}@CNT system. It was studied in detail using a variety of experimental [5,13–15] and computational techniques [6,9,16–21]. Despite of a considerable attention it has received, a number of questions still remains unanswered. In the present study we attempt to describe the differences in physical properties between two related molecular systems: C_{60} encapsulated inside a nanotube and C_{60} attached to the outer wall of a nanotube. We study equilibrium structures, binding energies, and vibrational frequencies of these two aggregate systems composed of a C_{60} fullerene and a segment of a (16, 0) zigzag nanotube. Our main aim is to investigate the character and extent of changes in molecular properties of carbon nanostructures that occur in the self-assembling processes. We expect that such a theoretical study can provide valuable information for researchers attempting to reveal experimentally the properties of aggregates of carbon nanostructures.

2. Calculations

Our molecular models consist of a C_{60} fullerene and a segment of a (16, 0) zigzag nanotube that can be described by a chemical formula $C_{128}H_{32}$. As usual, we use hydrogen

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atoms to saturate the valence of the terminal carbon atoms. Binding energies, equilibrium structures, and harmonic vibrational frequencies are computed using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method [22,23]. SCC-DFTB is a fast, approximate quantum mechanical technique that can be treated as an approximated density functional theory. SCC-DFTB combines low numerical cost with relatively good accuracy [24], and therefore, can be considered as a valuable tool in the analysis of large molecular systems. It is important to note that the SCC-DFTB method does not account for the dispersion forces. Therefore, to incorporate these long-range dispersive interactions—crucial for a proper description of interactions between carbon nanostructures—in the SCC-DFTB formalism, we used an additional empirical formula with a damped R^{-6} term [18]. The additional part of the SCC-DFTB Hessian corresponding to the dispersion interactions has been derived and coded. For future reference, we denote the SCC-DFTB method with included dispersion interactions as SCC-DFTB-D. Results of additional calculations, performed using the UFF force field, are available as Auxiliary Materials.

We have found that it is very difficult to optimize fully the fullerene-nanotube aggregates. One imaginary frequency (16 i cm^{-1}) has been found for model B, despite of a substantial effort devoted to removing this imaginary mode. The vibrational vector corresponding to the imaginary frequency can be described as mutual rotations of the fullerene and the nanotube. We believe that the possible influence of the imaginary mode on binding energies and other vibrational frequencies is rather small.

3. Results

We have performed our analysis for two stable complexes of C_{60} and a (16,0) carbon nanotube: (a) fullerene encapsulated inside the nanotube (model A), (b) fullerene attached to the outer wall of the nanotube (model B). Equilibrium geometries and harmonic vibrational frequencies have been calculated for both models using the SCC-DFTB-D method. Binding energies computed for both structures are given in Table 1.

The SCC-DFTB binding energy (including dispersion) for model A is −108.3 kcal/mol. This value is different from the previous results obtained for a similar system using other methods, which ranged between −11.8 kcal/mol [6] and −75.0 kcal/mol [21]. The first value has been obtained by a pseudopotential DFT local density approximation calculations, which is known to inadequately describe dispersion forces [25]. The second value has been obtained with a Lennard-Jones-type potential developed particularly for carbon. The molecular mechanics method, while giving more reasonable values, unfortunately lacks the universality and the precision of *ab initio* or semiempirical methods. For model B the SCC-DFTB binding energy is only −20.3 kcal/mol. The deformation energies of the fullerene and the nanotube are negligible in both cases. Noticeably smaller binding energy for the fullerene attached to the outer wall of the nanotube can be explained by weaker dispersive interactions for this structure.

Table 1
Binding energies (in kcal/mol) of C_{60} and the (16,0) CNT calculated using the SCC-DFTB-D method

	Binding energy	C_{60} deformation energy	CNT deformation energy	Interaction energy
Model A	−108.3	+0.5	+0.9	−109.7
Model B	−20.3	+0.1	+0.3	−20.7

A decomposition of the binding energy into the deformation and interaction components is also given.

The optimized geometries of model A and model B are shown in Fig. 1. Fig. 2 gives a schematic representation of mutual positions of C_{60} and CNT in the aggregate structures. Optimized geometric parameters for the aggregates

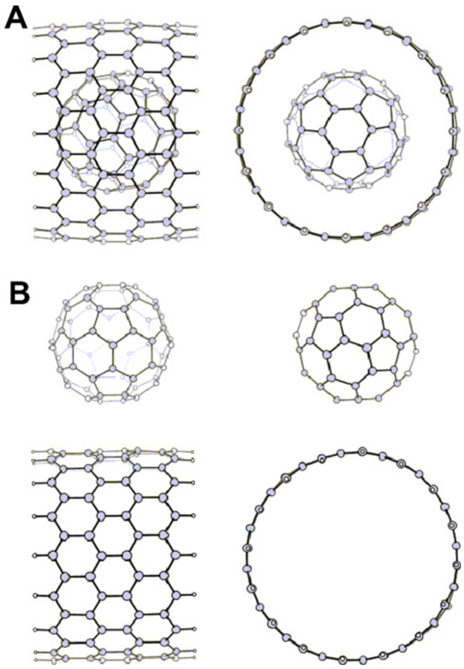

Fig. 1. Molecular models of C_{60} encapsulated in a (16,0) nanotube (model A) and C_{60} attached to the outer wall of a (16,0) nanotube (model B).

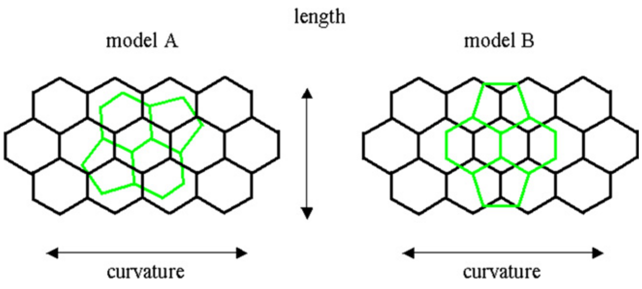

Fig. 2. Schematic representation of the mutual positions of the nanotube (dark line) and the nanotube (light line) in model A and model B.

Table 2
Optimized values of geometric parameters (in Å) of C_{60} and CNT in pristine species and in aggregates

	Longitudinal diameter	Latitudinal diameter	Radial diameter
SCC-DFTB-D			
Pristine C_{60}	–	–	7.11
C_{60} in model A	7.13	7.09, 7.07	–
C_{60} in model B	7.10	7.24	6.62
Pristine CNT	–	–	12.57
CNT in model A	–	–	12.63
CNT in model B	–	12.65	12.48

and pristine species are given in Table 2. The geometry of C_{60} is deformed in the aggregates from a perfect sphere to an ellipsoid. This effect is almost negligible for model A but it is very distinct for model B, where the diameter of C_{60} along the radius connecting the fullerene and CNT is reduced from 7.11 Å to 6.62 Å. The change of geometry of the nanotube upon the interaction is much smaller than for the fullerene. The change of the nanotube length is negligible. The diameter of the nanotube in model A is slightly enlarged. For model B, the nanotube is slightly deformed and its cross section has a shape of an oval. The distance between the wall of the nanotube and the wall of the fullerene for model A is approximately 2.8 Å. For model B, the shortest distance between the nanotube and the fullerene is 2.53 Å.

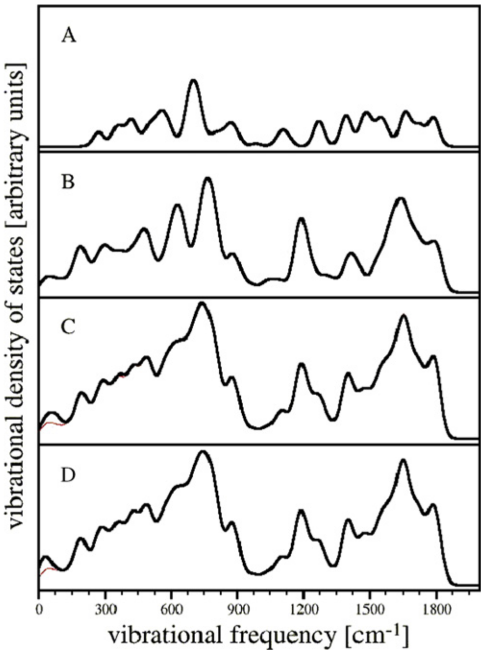

Fig. 3. SCC-DFTB-D vibrational densities of states: (A) C_{60}, (B) (16,0) zigzag nanotube, (C) C_{60} encapsulated at the (16,0) zigzag nanotube (model A), and (D) C_{60} attached to the outer wall of the (16,0) zigzag nanotube (model B). Additionally, for models A and B, the cumulative density of states for non-interacting fullerene and nanotube is given (thin red line almost identical to the VDoS of interacting species). (For interpretation of the references in colour on this figure legend, the reader is referred to the web version of this article.)

The calculated vibrational densities of states (VDoS) are shown in Fig. 3 for pristine C_{60} and CNT, and for their aggregates. For the aggregate structures, we give an additional curve corresponding to the cumulative sum of VDoS for the non-interacting fragments to visualize the degree of changes in vibrational frequencies upon encapsulation. These additional curves overlap almost perfectly with the aggregate's VDoS suggesting that the vibrational frequencies of the fullerene-nanotube aggregates are very similar to the superimposed vibrational frequencies of the pristine species.

To investigate the impact of intermolecular interactions on the change of the positions of the vibrational levels, we have performed detailed analysis of the SCC-DFTB-D harmonic vibrational modes of the fullerene-nanotube aggregates. We have projected the aggregate vibrational modes onto the vibrational modes of the isolated species. This procedure has allowed us to distinguish the origin of each of the vibrational modes and has revealed to us the coupling strength between the vibrational modes of C_{60} and CNT. We have found that for more than 84% of the aggregate modes, the overlapping with some modes of the pristine fullerene or nanotube is 99% (or larger). In approximately 96%

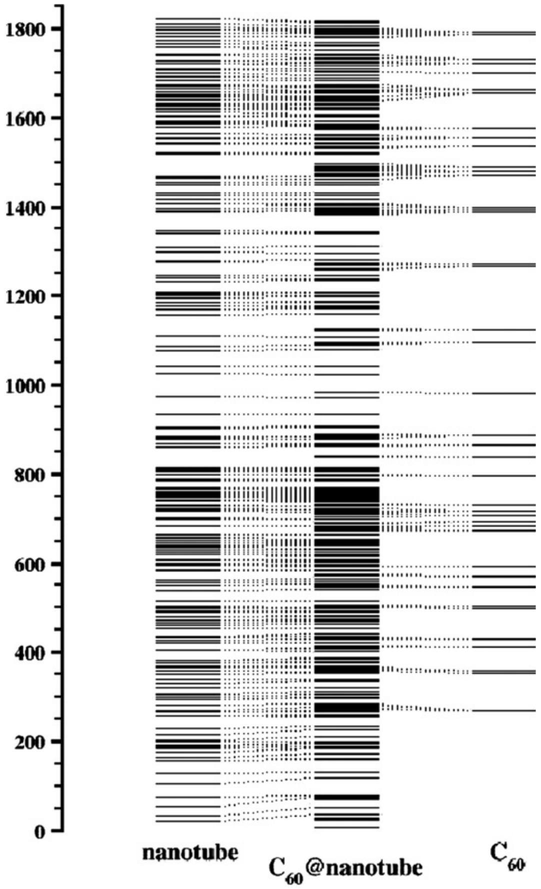

Fig. 4. Correspondence of vibrational modes of C_{60} encapsulated in a (16,0) nanotube (model A) to the vibrational modes of pristine fullerene and nanotube. The vibrational modes have been calculated using the SCC-DFTB method.

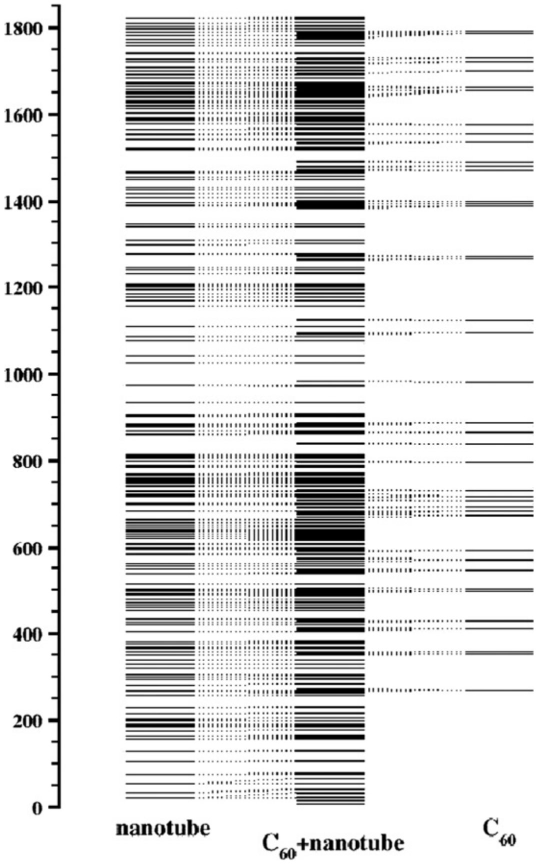

Fig. 5. Correspondence of vibrational modes of C_{60} attached to the outer wall of a (16,0) nanotube (model B) to the vibrational modes of pristine fullerene and nanotube. The vibrational modes have been calculated using the SCC-DFTB method.

of the cases, the dominance of only the nanotube or the fullerene vibrational modes was larger than 90%. These results suggest that the coupling between the vibrations of the fullerene and the nanotube is in general very small. This allows us for decomposing the harmonic vibrational modes of the fullerene-nanotube aggregates into the levels corresponding solely to vibrations of C_{60} or vibrations of CNT. The results are shown in Fig. 4 for model A and in Fig. 5 for model B. In both cases, the symmetry of C_{60} has been lowered by the interaction with the nanotube; the vibrational multiplets of C_{60} have been split into a series of close-lying vibrational levels. Large portion of the aggregate's vibrational levels has been displaced with respect to the positions of the corresponding levels in the pristine fullerene and the nanotube. The displacements are not large. For model A, the largest positive displacements are 14 cm^{-1} (fullerene modes) and 22 cm^{-1} (nanotube modes); the largest negative displacements are 16 cm^{-1} (fullerene modes) and 8 cm^{-1} (nanotube modes). For model B, the corresponding values are considerably smaller. The largest positive displacements are 6 cm^{-1} (fullerene modes) and 13 cm^{-1} (nanotube modes); the largest negative displacements are 16 cm^{-1} (fullerene modes) and 3 cm^{-1} (nanotube modes). The decomposition presented in Figs. 4 and 5 is possible only because of weak coupling between C_{60} and CNT leading to small mixing of their vibrational modes.

Another interesting aspect of the vibrational analysis described above is determination of the fullerene bouncing and rotational modes for model A. The vibrational modes corresponding to the hindered rotations are located at 16 cm^{-1}, 16 cm^{-1} and 24 cm^{-1}. The longitudinal bouncing mode is located at 17 cm^{-1}, and the latitudinal bouncing modes are located at 71 cm^{-1} and 74 cm^{-1}. These results suggest that the interaction potential is very flat and the fullerene molecule can almost freely rotate and translate along the nanotube.

4. Conclusion

We have examined binding energies, equilibrium structures, and harmonic vibrational frequencies of fullerene-nanotube complexes using the SCC-DFTB method with dispersion correction. Two different aggregates of C_{60} and a (16,0) zigzag nanotube have been considered: C_{60} encapsulated in the nanotube and C_{60} attached to the outer wall of the nanotube. The SCC-DFTB binding energy of C_{60}@(16,0) system of −108.3 kcal/mol is much lower than previous results obtained using different methods. The vibrational analysis has shown that the vibrational spectra of the fullerene-nanotube aggregates are very similar to those obtained by superimposing the vibrational spectra of the pristine nanotube and the fullerene. The mixing of the vibrational modes of the fullerene and the nanotube is small; the results obtained using the SCC-DFTB-D method show that approximately 96% of aggregate's vibrational modes corresponds either to the vibrational modes of the pristine nanotube or to the vibrational modes of the pristine fullerene. The displacement of the vibrational levels calculated with SCC-DFTB-D is rather small; the maximal displacement is only 22 cm^{-1}. Small splittings of the vibrational multiplets of C_{60} and the small displacement of the vibrational levels found in this study may be valuable information for experimentalists trying to identify various fullerene-nanotube aggregate structures via spectroscopic methods. Unfortunately, this study shows that this can be a very difficult task due to very small effects of the dispersive interactions on the molecular structure and vibrational frequencies of the aggregates.

To complete the task of the characterization of the vibrational properties of the fullerene-nanotube aggregates, we plan to study in our next paper the impact of dispersive interactions on the infrared and Raman intensities. The SCC-DFTB method with additional dispersive corrections seems to be a powerful technique to study such large molecular systems.

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