Physics Letters A 380 (2016) 2781–2785

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Stable double helical iodine chains inside single-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form 19 May 2016
Accepted 23 May 2016
Available online 23 June 2016
Communicated by R. Wu

Keywords:
Peapod
Nanotube
Iodine chain

ABSTRACT

The helicity of stable double helical iodine chains inside single-walled carbon nanotubes (SWCNTs) is studied by calculating the systematic interaction energy. Our results present clear images of stable double helical structures inside SWCNTs. The optimum helical radius and helical angle increase and decrease with increasing diameter, respectively. The tube's diameter plays a leading role in the helicity of encapsulated structures, while the tube's chirality may induce different metastable structures. This study indicates that the observed double helical iodine chains in experiments are not necessarily the optimum structures, but may also be metastable structures.

1. Introduction

The interior space of single-walled carbon nanotubes (SWCNTs) can be used for encapsulating various molecules [1–3]. This opens new roads to perform further research on quasi-one dimensional (1D) systems [4,5]. Since the first successful encapsulation of fullerene C_{60} molecule [6], the stable structures and novel properties of guest molecules in SWCNTs have continuously been a hot topic for experimental and theoretical researchers [7–12]. The atomic structure of a SWCNT can be described by its chiral indices (n, m) which specify its perimeter vector on the graphene net [2,3]. The diameter and chirality of a tube are important parameters in the study of the structures and properties of encapsulated guest molecules [13,14]. For example, G.T. Pickett et al. found that the packaged hard spheres inside the cylindrically confined space exhibit different chiral structures for different confinement diameters [15]. Using a similar hard sphere model, ten different ordered phases of encapsulated C_{60} molecules inside SWCNTs were found by the calculation of a simulated annealing method [16]. Subsequently, four ordered phases, including a linear chain phase, zigzag phase, double helical phase and two-molecule layers phase, were confirmed in double-walled carbon nanotubes (DWCNTs) [17]. In addition, smaller and larger fullerenes (C_{20}, C_{28} and C_{70}, C_{78} etc.) as well as non-fullerene molecules (H_8SiO_{12} and $C_{10}H_{16}$) also exhibit different ordered phases when they are confined within different tubes [18–22]. Previous works have demonstrated that these ordered phases only depend on the tube's diameter and are insensitive to the tube's chirality. Orientational behavior analysis indicates that the tube's diameter plays a crucial role in the stable orientations of encapsulated guest molecules, while the tube's chirality has a weak influence on their preferred orientation for very small tubes [23–31]. Additionally, SWCNTs filled with atomic nanocrystals have attracted particular. *Ab initio* investigation shows that the energetics and structural, electronic, and optical properties of a hybrid Xe@SWCNTs system are sensitive to both the tube's diameter and chirality [32]. Moreover, various encapsulated atomic crystals, such as 3*d* metal nanowires, multi-coordination BaI_2 crystals, layered KI crystals, and metastable $AgCl_{1-x}I_x$ crystals, among others, have been studied in both experimental and theoretical works [33–39]. It is noteworthy that double helical iodine chains (I-chains) have been successfully prepared inside SWCNTs with diameters ranging from 13 to 14 Å [40]. The first-principle calculation shows that the stability of this double helical structure is determined by the systematic charge transfer, which is similar to the stability mechanism of the C_{60}@SWCNTs peapod system [10]. Different periods, such as 1.5 nm, 5 nm, 12.5 nm, and even larger values, have been observed using the High Resolution Transmission Electron Microscope (HRSTEM). The authors suggest that these different periods are caused by the differing chirality of the tube's wall. However, it is difficult to verify this conjecture using experimental techniques. The influence of a tube's diameter and chirality

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http://dx.doi.org/10.1016/j.physleta.2016.05.042
0375-9601/

on its stable structure is still unclear. Up to now, few reports on the double helical I-chains inside SWCNTs have been published in theoretical studies. Thus, a comprehensive and detailed theoretical study is necessary to clarify these open questions.

In this work, we perform a detailed study of the stable double helical I-chains inside SWCNTs by calculating the systematic interaction energy using van der Waals interaction potential. We focus on the helicity (including the helical radius r and helical angle ϕ) of encapsulated double helical I-chains inside SWCNTs with diameters ranging from 13.57 Å to 33.92 Å. In order to analyze the influence of a tube's diameter and chirality on the helicity of encapsulated I-chains, we select tubes in two categories: tubes that have different diameters but the same chirality, and tubes that have similar diameters and different chiralities. Our results show that the optimum helical radius, opt(r), exhibits a linear increase from 3.0 Å to 13.2 Å as the tube's radius (R_T) increases from 6.785 Å to 16.96 Å, which produces a constant separation (3.7–3.8 Å) between the I-chains and the tube's wall. Additionally, the optimum helical angle, opt(ϕ), decreases with increasing R_T. In our comparative analysis, we find that the helicity of encapsulated double helical I-chains mainly depends on the tube's diameter, while the different metastable structures are induced by the tube's chirality. Our study indicates that the observed structures in experiments are not necessarily the optimum structures of encapsulated double helical I-chains, but may instead be the metastable structures. This work presents a clear image and the corresponding details of encapsulated double helical I-chains inside SWCNTs.

2. The model and simulation method

For our simulation, the standard one-parameter graphene sheet model of a SWCNT is constructed with the center of mass of the helical structure located on the center of the tube. As shown in Fig. 1, the tube is fixed in the (x, y, z) Cartesian coordinate system with its center of mass on the origin o. The tube's long axis coincides with the z-axis. Because the length of the tube is very long (>600 Å) compared to the lengths of all the I-chains considered in this work, we can ignore the tube's edge effect in the calculation. The growth of two I-chains begin on the positive (r, $\varphi = 0$) and negative ($-r$, $\varphi = 0$) x-axis, respectively. The growth direction of the I-chains is along the positive and negative directions of z-axis with a helical radius $r \geq 2$ Å. Thus, the minimum distance between two centrosymmetric atoms (such as $Atom_1$ and $Atom_2$) or I-chains is 4 Å, which is comparable to the value of the I–I bonding length ($d = 2.9$ Å) [40]. With the given d, the spatial positions of two arbitrary symmetrical iodine atoms are determined by the coordinates $(r\cos n\phi,\ r\sin n\phi,\ n(d^2 - (2r\sin(\phi/2))^2)^{1/2})$ and $(-r\cos n\phi,\ -r\sin n\phi,\ n(d^2 - (2r\sin(\phi/2))^2)^{1/2})$, respectively, where $n = 1, 2, 3 \ldots N$ ($N = \Pi/\phi$) and N is the total number of atoms of single chain structure; and r and ϕ correspond to the helical radius and helical angle, respectively. Using the above z-coordinate, the interval of ϕ is expressed by equation (1).

$$0 \leq \phi \leq 2\arcsin(d/2r) \tag{1}$$

The length ($L = N(d^2 - (2r\sin(\phi/2))^2)^{1/2}$) of a complete period is determined by the corresponding r and ϕ. Similar to the encapsulated fullerene molecules [27–31], the interaction between the I-chains and the SWCNT is also a van der Waals interaction that can be described by the Lennard-Jones 12–6 potential. The nanotube field potential $V(R_T, r, \phi)$ for a given R_T, r, and ϕ can be obtained by summing over all pair interactions

Table 1
The L–J 12–6 potential parameters for I–I and C–I used in this work.

Type	I–I	C–I
D_0	0.339	0.1886
R_0	4.50	4.1755

Table 2
The detailed structural properties and calculated results from this work are presented here. Columns I and II show the tube's chirality and radius, respectively. Columns III–VI show the optimum helical radius, the separation between the I-chains and the tube's wall, the optimum helical angle, and the period of the encapsulated double helical I-chains.

(n, m)	R_T/Å	opt(r)/Å	Space/Å	opt(ϕ)/°	L/Å
(10, 10)	6.785	3	3.785	52	3.66
(11, 9)	6.795	3	3.795	52	3.66
(15, 4)	6.795	3	3.795	52	3.66
(12, 8)	6.83	3	3.83	52	3.66
(11, 11)	7.465	3.7	3.765	43	4.11
(12, 12)	8.14	4.4	3.74	36	5.04
(13, 13)	8.82	5.1	3.72	33	2.93
(14, 14)	9.5	5.7	3.8	29	3.08
(15, 15)	10.175	6.4	3.775	26	2.07
(16, 16)	10.855	7.1	3.755	23	4.4
(17, 17)	11.535	7.8	3.735	21	4.58
(18, 18)	12.215	8.5	3.715	19	6.6
(19, 19)	12.89	9.2	3.69	18	3.53
(20, 20)	13.57	9.8	3.77	18	1.3
(21, 21)	14.25	10.5	3.75	15	11.36
(22, 22)	14.925	11.2	3.725	14	11.74
(23, 23)	15.605	11.9	3.705	13	13.95
(24, 24)	16.285	12.5	3.785	13	8.23
(25, 25)	16.96	13.2	3.76	12	13.37

$$V(R_T, r, \varphi) = \sum_{N_{\lambda 1}}\sum_{N_{\lambda 2}} v\left(|\rho_{\lambda 1} - \rho_{\lambda 2}|\right) + \sum_{N_\tau}\sum_{N_{\lambda 1}} v\left(|\rho_\tau - \rho_{\lambda 1}|\right) + \sum_{N_\tau}\sum_{N_{\lambda 2}} v\left(|\rho_\tau - \rho_{\lambda 2}|\right), \tag{2}$$

where τ and λ ($\lambda 1$ and $\lambda 2$) index the atoms of the nanotube and the atoms of I-chains, respectively; and ρ_i and N_i ($i = \tau$ and λ) stand for the coordinate and the number of corresponding atoms, respectively. Because the total number of atoms ($2N$) of the double helical I-chains is a variable that depends on the values of r and ϕ, we average the total interaction energy to a single iodine atom by using equation (3) for a simple analysis.

$$V(R_T, r, \phi)_{atom} = V(R_T, r, \phi)/2N \tag{3}$$

The Lennard-Jones 12–6 potential is given in equation (4).

$$v(r) = D_{IJ}\left(-2(R_{IJ}/r)^6 + (R_{IJ}/r)^{12}\right) \tag{4}$$

The potential parameters R_{IJ} and D_{IJ}, which correspond to the van der Waals distance and energy, respectively, are listed in Table 1 [41]. This interaction potential has been successfully used to study various interacting molecular systems, such as the typical C_n-peapod structures [42–48].

As is well known, different diameters correspond to different chiral indices (n, m) of the tubes. Our calculation begins at the armchair (10, 10) tube and ends at (25, 25) tube with the R_T ranging from 6.785 Å to 16.96 Å. In addition, three chiral tubes, including (11, 9), (15, 4) and (12, 8), have been used for a comparative analysis. The detailed structural information can be seen in Table 2. We perform the simulation in the following steps. For a given R_T, the r of the I-chains increases from 2.0 Å to R_T with a step size $\Delta r = 0.1$ Å. The ϕ increases from 1° with a step size $\Delta\phi = 1°$ to the maximum defined in equation (1). For each step of r or ϕ, a complete period of the helical structure is obtained