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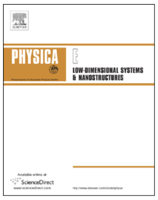

Structural and electronic properties of *trans*-polyacetylene under local strain

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HIGHLIGHTS

- The influence of a local bending or compression of the space between neighboring carbon atoms on the band gap of *trans*-PA was studied.
- Making use of an effective difference equation the band structure of *trans*-PA has been calculated.
- Under the local strain the threshold voltage for the current flow through the bent molecule crucially varied.
- Our results indicate that the energy gap of the strained molecule modified significantly which affects the electronic properties of the molecule.

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ABSTRACT

A theoretical study is presented to investigate the structural and electronic properties of *trans*-polyacetylene (*trans*-PA) molecule under local strain. The influence of a local bending or compression of the space between neighboring carbon atoms on the band gap of the molecule was studied. Making use of an effective difference equation based on tight-binding procedure the band structure of *trans*-PA has been calculated. Our results indicate that the energy gap of the strained molecule modified significantly which affects the electronic properties of the molecule. We found that the size of the molecular gap is proportional to the bending angle so that for the bending perpendicular to π-orbitals plane the band gap reduced drastically and for the parallel one the band gap gradually increased. Furthermore, the current–voltage characteristics of the strained *trans*-PA molecule are studied. We found that under the local strain the threshold voltage for the current flow through the bent molecule decreased (increased) depending on the bending is perpendicular (parallel) to the molecule plane.

1. Introduction

There have been intensive studies on *trans*-PA molecule, experimentally and theoretically, especially for its unique electronic structure and transport properties due to the quasi-one dimensional nature and the existence of an equilibrium band gap, resulting to potential applications in molecular electronics [1–7]. The semiconducting band gap 1.4 eV [3,8] is the unique feature of *trans*-PA structure based on which *trans*-PA molecule is expected as promising material for both electronic and optoelectronic applications. From the theoretical point of view, one may consider *trans*-PA as the one-dimensional version of graphene, at least with respect to the fractionalization of the electric charge [2,5,6]. From the experimental and technological sides, the advent of the semiconductor nanotechnology [9] with new possibilities of developing semiconductor devices made from *trans*-PA molecule [10] strongly motivated the study of the main factors may affect the electronic structure and transport properties of the molecule. The electronic structures of *trans*-PA can be modified by doping and disorder [11–16], external fields [17], structural defects such as solitons [1,18–21] and mechanical strain. Strain arises when the molecule is compressed or stretched out of equilibrium. Mechanical strain often gives rise to surprising effects on electronic properties of carbon-based materials. For example, it can turn the metallic nanotube into semiconductor and vice versa [22–26]. Along with the uniquely strong mechanical properties of the sp^2 and sp^3 bonded carbon materials [27], the interplays between mechanical and electronic properties may be useful in various applications [28]. Much attention has paid to the mechanical strain influence on graphene systems since the naturally or intentionally tensional strain may be inevitable in graphene-based electronic devices. It is founded that the band gap of a graphene nanoribbon is sensitive to strain [29,30]. Nevertheless, the influence of the

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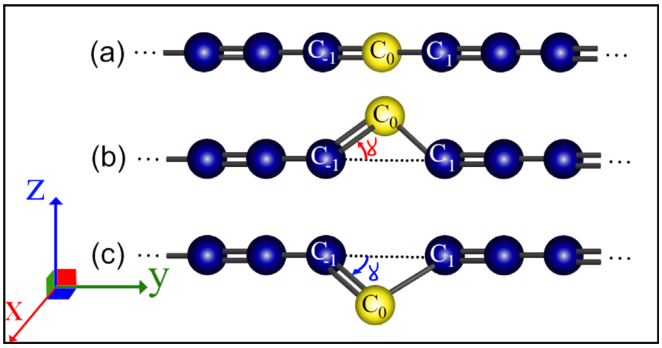

Fig. 1. Plots show the schematic illustrations of *trans*-PA molecule. (a) A segment of the pristine molecule without bending. It is assumed that the π-orbitals are in y–z plane. (b) and (c) illustrate the bent molecules depending on the bending is parallel or perpendicular to the π-orbitals plane, respectively. The angle of the bend γ is measured relative to y axis.

strain on the electronic properties of *trans*-PA molecule has received less attention. The aim of our present work is to study theoretically the electronic and structural properties of strained polyacetylene molecule. *Trans*-PA has a quasi-one-dimensional structure and translational symmetry damages, for example bending of the molecule, are unavoidable. Therefore, a realistic study of the electronic properties of *trans*-PA molecule requires that the inherent defects such as bending of the molecule have been taken into account. Local strain, as bending, can be induced on *trans*-PA structure either by a soliton or naturally. In this paper the influence of a local bending or compression of the space between neighboring carbon atoms on the band gap and subsequently the electronic structure of the molecule is studied. It should be noted that compression by an equal length and bending by an equal angle of a single band and a double one leads to the same physical properties. We consider two kinds of bends, the perpendicular and the parallel to π-orbitals plane. As depicted in Fig. 1, we assume that the π-orbitals plane is parallel to y–z plane. We have found that the band gap of the molecule reduced drastically when the bending is perpendicular to the π-orbitals plane. However, for the bending parallel to the plane the band gap gradually increased. Following the modified band gap, the electron transport through the molecule is seriously affected. The model and description of the computational methods for investigating the strained-dependent transport properties of the molecule are introduced in Section 2. The results and discussion are presented in Section 3, followed by conclusions in Section 4.

2. Model and Hamiltonian

To describe the model structure of *trans*-PA molecule under strain, let the molecule is placed on y–z plane subjected to strain (compression) along the y-direction, as shown in Fig. 1. Under local strain the molecule may bend perpendicular or parallel to π-orbitals plane, the y–z plane. We consider the both bending models as a local bending of the space between neighboring carbon atoms C_{-1} and C_{+1} along the molecular chain so that γ is the bending angle relative to y-axis. Within the framework of the SSH model [1,20] the Hamiltonian of the strained *trans*-PA molecule may be decomposed as,

$$\hat{H}_m = \hat{H}_e + \hat{H}_{e-ph} + \hat{H}_{ph}, \tag{1}$$

where the electron and electron–phonon part of the strained molecule Hamiltonian are given by,

$$\begin{aligned}\hat{H}_e + \hat{H}_{e-ph} = {} & \sum_n \varepsilon_n \hat{c}_n^{+} \hat{c}_n - \sum_n \left[t_0 + \alpha y_n \right] \left(\hat{c}_n^{+} \hat{c}_{n+1} + \hat{c}_{n+1}^{+} \hat{c}_n \right) \\ & - \varepsilon_\gamma t_0 \left(\hat{c}_{-1}^{+} \hat{c}_0 + \hat{c}_0^{+} \hat{c}_{-1} \right),\end{aligned} \tag{2}$$

in which $\hat{c}_n^{+}(\hat{c}_n)$ creates (destroys) a π-electron at site n on the molecular chain. ε_n is the on-site energy and here reference energy is chosen such that the on-site energy to be zero. With u_n the displacement of the nth carbon atom from its equilibrium position, $y_n = (u_n - u_{n+1})$ is the bond alternation. According to SSH model, t_0 and α are the hopping integral of an undimerized molecule and the electron–phonon weak coupling constant, respectively so that αy_n modulates the hopping integrals along the molecular-symmetry axis. For perfectly dimerized molecule and in the weak coupling regime, u_n and band gap of *trans*-PA molecule are given as $u_n = (-1)^n u_0$ and $2\Delta_0 = 8\alpha u_0$, respectively. Based on the SSH model hypothesizes, for $2\Delta_0 = 1.4\,\text{eV}$, we take $\alpha = 4.1\,\text{eV/Å}$, $t_0 = 2.5\,\text{eV}$. These correspond to an equilibrium dimerization amplitude $u_0 \approx 0.04\,\text{Å}$, such that $\alpha y_n = 2(-1)^n \alpha u_0$. In Eq. (2) γ is the angle of the bend and ε_γ is the relative change of the transfer integral t_0, that can result from two kinds of bends; the perpendicular or the parallel to π-orbitals plane, for which $\varepsilon_\gamma^{\perp} = \frac{\alpha a}{4t_0}\gamma^2$ and $\varepsilon_\gamma^{II} = (\frac{\alpha a}{4t_0}\gamma^2 - \frac{t_0 - t_\sigma}{t_0})\gamma^2$, respectively [31]. Here $\alpha = 1.44\,\text{Å}$ is the lattice constant and t_σ is the transfer integral for the σ-bond. We consider only the π-band, because the σ-one is completely filled up and it does not take part in the effects under consideration. In Eq. (1) the phonon part of the strained molecule Hamiltonian in the harmonic approximation is given by,

$$H_{ph} = \sum_n \left[\frac{1}{2} M \dot{u}_n^2 + \frac{1}{2} K_0 y_n^2 \right] + \frac{1}{4} K_0 a^2 \gamma^2 + \vartheta(\gamma^4), \tag{3}$$

where M and $K_0 = 21\,\text{eV/Å}^2$ are the mass of a CH-group and the elasticity of the bond, respectively. The strained *trans*-PA molecule through which we are interested to explore the several features of the electronic transport phenomena, attached to two semi-infinite one-dimensional metallic leads. Since the electron conduction is mainly determined by the central part of the junction lead-molecule-lead, the electronic structure of this part should be resolved in details. It is therefore reasonable to decompose the total Hamiltonian of the system as,

$$H = H_L + H_m + H_c + H_R. \tag{4}$$

The Hamiltonian of the left (L) and right (R) electrodes is described within the single-band tight-binding approximation and is written as,

$$H_\beta = \sum_{i_\beta} \varepsilon_{i_\beta} \hat{b}_{i_\beta}^{+} \hat{b}_{i_\beta} - \sum_{<i_\beta, j_\beta>} \left(t_{i_\beta, j_\beta} \hat{b}_{i_\beta}^{+} \hat{b}_{j_\beta} + \text{H. c.} \right), \tag{5}$$

where $\hat{b}_{i_\beta}^{+}(\hat{b}_{i_\beta})$ creates (destroys) an electron at site i in metallic lead β (L or R) and the hopping integrals t_{i_β, j_β} are equal to $t = 1\,\text{eV}$ for the nearest neighbors and zero otherwise. Here, $\varepsilon_{i_\beta} = \varepsilon_0$ is the on-site energy. With $\varepsilon_0 = 0$ we have set the zero of energy at the Fermi level. Finally, H_c in Eq. (4) describes the coupling between the metallic leads and the molecule and is given as,

$$H_c = \sum_{i \in L} \left(t_L \hat{b}_i^{+} \hat{c}_{-N} + t_L^{*} \hat{c}_{-N}^{+} \hat{b}_i \right) + \sum_{i \in R} \left(t_R \hat{b}_i^{+} \hat{c}_N + t_R^{*} \hat{c}_N^{+} \hat{b}_i \right). \tag{6}$$

Here $t_{L(R)}$ denotes the tunneling coupling between the π-electron state of the carbon atom of number $-N$ (N) from the left (right) and the electron states in the left (right) metallic electrode. It is necessary to mentioned that the electrode-to-molecule coupling strength ($t_{L(R)}$) through Eq. (6) has significant impact on the electron transport through molecule. As emphasized in some valuable works [32,33], the stronger coupling strength give rises to