Interference Blockade in the Conductance of Organic Molecules

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Abstract. – The conductance of cis/trans isomers of stilbene molecules connected to armchair single wall carbon nanotubes is studied in the Landauer formalism combined with a density-functional based approach. For a given arrangement of the electrodes, dramatic differences in the transmission between both isomers are found. For a given isomer, the conductance can be varied by orders of magnitude by changing the molecule-electrode relative orientation. Both effects can be explained by a simple, physically transparent interference rule, which suggests a straightforward conductance control in such molecular systems by different switching mechanisms.

Introduction. - In recent years rapid progress in the field of molecular electronics has been made. Novel experimental approaches allow the investigation of the electronic transport properties of small molecular groups or even single molecules connected to macroscopic or mesoscopic electrodes [1]. Effects like negative differential resistance (NDR) [2,3,4] and rectification [5,6,7] have been demonstrated. Common to this class of systems is the subtle interplay between electronic and structural properties in determining the electronic transport. This makes the search for molecules that exhibit controllable conformational changes highly desirable. Thus, recent experiments on conjugated organic molecules have shown reversible conductance switching which can be related to reorientation of single molecules induced by voltage pulses [8], to internal structural modifications induced by charge transfer within the molecular complex [9,10] or to conformational changes due to interactions with the local environment [11].

Stilbene ((1,2)-diphenyl-ethylene) is a prototypical example of a system with a controllable transition between two stable states. This molecule undergoes a cis-trans isomerization around the central ethylenic bond under, e.g. the influence of a laser field [12], which suggests a natural way to realize a switching mechanism. Many experimental and theoretical investigations have been carried out in order to understand the electronic and structural properties of the molecule, the mechanism leading to isomerization as well as its optimal control [12,13,14]. Less theoretical attention has been paid, however, to the electronic transport properties of...
the isomers and, especially, to the possibility of identifying them via their fingerprints in the conductance spectrum.

In this Letter we investigate electron transport in cis/trans stilbene within a pure carbon molecular device, in which the molecule is covalently bonded to two carbon nanotubes (CNT) acting as electrodes. The possibility to develop a carbon based nanoelectronics has been investigated theoretically [16] and in recent transport experiments [10]. We will show that for some specific molecule-electrode orientations the conductance of both isomers is drastically suppressed around the Fermi energy and that this effect can be clearly related to quantum interference of the electronic waves (“interference blockade”). The appearance or disappearance of the blockade effect can be simply controlled by the Fermi wave vector $k_F$ of the electrodes and the difference in the geometrical pathways $\Delta x$ of the electronic wave functions around the phenyl rings. The following simple relation holds for the studied molecular junctions:

$$k_F \Delta x \approx n \pi.$$  

(1)

Blockade occurs for odd $n$ (“off-state”) while nearly ideal transmission is found for even $n$ (“on-state”). Switching between both conductance states can be controlled either by a conformational change, e.g. by cis/trans isomerization or by reorientation of the whole molecule with respect to the electrodes, in accord with recent experimental observations on similar systems [8, 10, 11].

**Theoretical Method.** - Our computational approach [17] combines a density-functional-based tight-binding (DF-TB) formalism with numerical Green function techniques to investigate electronic transport within the Landauer theory. The basic quantity to be calculated in the following is the two-terminal conductance $g = \frac{e^2}{\pi \hbar} T(E_F)$, which is proportional to the transmission probability $T(E_F)$ at the equilibrium Fermi energy $E_F$ in the linear response regime and at zero temperature [18]. The transmission can be expressed as:

$$T(E) = 4 \text{Tr}[3m \Sigma_L G \Sigma_R G^\dagger].$$  

(2)

Here, $G$ is a retarded molecular Green function including self-energy interactions $\Sigma_{L,R}$ with the left (L) and right (R) electrodes. The self energies are given by $\Sigma_{L,R} = V_{L,R} g_{L,R} V_{L,R}$, where $V_{L,R}$ are electrode-molecule coupling terms and $g_{L,R}$ is the retarded Green function of the electrodes, which is obtained using recursive techniques [19]. In calculating these quantities in the DF-TB scheme we use a nonorthogonal basis set including the 2s2p carbon valence orbitals and the 1s orbitals of hydrogen.

Upon coupling to the electrodes the molecular orbitals are broadened and partially shifted, so that instead of looking at the electronic eigenvalue spectrum of the isolated molecules, it is more useful to analyze the projected density of states (PDOS), obtained from the total DOS of the device by a partial trace:

$$\nu_l(E) = -\frac{1}{\pi N_l} \text{Tr}_l [G(E)S].$$  

(3)

In this expression the index $l$ runs over some appropriate subset containing $N_l$ atomic sites and the overlap matrix $S$ takes into account the non-orthogonality of the basis set.

**Electronic Transport.** - The molecular devices are shown in the upper panel of Fig. 1. Two armchair (5,5) CNTs [20] with open ends are bridged by a single stilbene isomer. In
the free molecules the \textit{trans} state is almost planar, while in the \textit{cis} configuration the phenyl groups undergo a combination of twisted and torsional rotations around the C=C double bond, leading to a more compact structure. As shown in Fig. 1 the CNTs are oriented in a way that their axes are parallel to each other.

In order to improve the molecule-electrode contact anchoring groups are usually used, e.g. thiol groups on gold surfaces \cite{21}. Here, we want to study a carbon based setup, so that CH radicals are used as anchoring groups \cite{22}. In addition, we limit our discussion to the case of a single contact point between the molecule and the CNT surfaces (if not stated otherwise, when speaking of \textit{trans} and \textit{cis} stilbene we refer always to the (CH)$_2$-stilbene system). To simulate the device’s atomic structure we use a cluster consisting of the molecule and eight unit cells of the CNT on either side of it. Structural optimization is performed by using conjugate-gradient techniques. Hereby, only the molecule and the surface unit cell of the tubes are allowed to relax. The bond length of the CH-CNT single contact was determined to lie around 1.42 Å depending on the device geometry, a value intermediate between single and double bond, which guarantees a strong covalent bond to the electrodes.

In Fig. 1 the conductance \( g \) in units of \( 2e^2/h \) is plotted as a function of the incoming electron energy. We found a drastic difference in the transmission around the Fermi energy. While for \textit{trans}-stilbene two large resonances are seen with almost perfect transmission \( T \approx 1 \) the \textit{cis} state shows almost no transmission in the same spectral window. This is quite surprising as both isomers posses electronic states near the Fermi level, as will be shown in the following. Moreover, it should be noted, that the large level broadening due to strong molecule-electrode coupling precludes Coulomb blockade effects.

In Fig. 2 we show the PDOS \( \nu_l \), as defined in Eq. 3. The index \( l \) runs over molecular sites and over CNT surface sites, separately. The vertical arrows indicate the position of the molecular orbitals of the isomers previous to contacting them to the CNTs. The indicated lowest unoccupied (LU) molecular orbital (MO) LUMO and the LUMO+1 are \( \pi \)-orbitals with
Fig. 2 – Density of states (in arbitrary units), projected onto the molecule (solid line) and onto the CNT surface atoms (dashed line) for the trans and cis configurations shown in Fig. 1, upper panel. The HOMO, LUMO and LUMO+1 of the isolated molecules (including the CH-radicals) are shown as a guide for the eye. Due to the strong electrode-molecule coupling the molecular resonances are shifted and broadened.

a large contribution from the C-atoms belonging to the anchoring groups. The LUMO and LUMO+1 of the cis isomer are almost degenerate. The amount of splitting depends however on the position of the CH-radicals along the phenyl ring. The large resonances near the Fermi energy in both isomers are clearly related to molecular orbitals, because the surface CNT-PDOS is rather featureless in this energy region. Side peaks around -0.5 eV and between 1–1.5 eV are mainly determined by CNT states which derive from surface dangling bonds. These states are originally much closer to the Fermi level, but upon relaxation they move away from the midgap due to the slight restructuring of the CNT surface. Moreover, the highest occupied MO (HOMO) cannot be clearly identified because it lies in an energy window where bulk states are also present, so that both states can strongly mix.

The main point to be emphasized here is, however, that cis stilbene shows a prominent resonance (the nearly degenerated LUMO and LUMO+1 states) near the Fermi energy, which nevertheless does not show up in the transmission. Thus, the strong conductance suppression cannot be related to an intrinsic molecular property and, hence it must be related to the interfacial topology.

To analyze this in more detail, we have considered several possible single contact geometries of trans-stilbene which are schematically shown in Fig. 3. Note that we keep the left electrode fixed and change only the contact points on the right side. The transmission at the Fermi energy (presented in the lower panel of Fig. 3) as a function of the contact point shows an oscillating behavior with strong conductance suppression by about 3 orders of magnitude at positions (b) and (d).

A qualitative understanding of this interference blockade follows from the different paths around the right phenyl ring, an electron can take. For position (c) e.g., there is no difference between the clockwise and counterclockwise paths, whereas for position (b) a path difference of about $\Delta x \approx 3$ Å (two side lengths of the hexagon) does exist. This leads to a phase
difference of approximately \( k_F \Delta x \approx 3 \approx \pi \) (where we have used the calculated Fermi wave vector of \( k_F \approx 1 \text{Å}^{-1} \)), which makes the paths interfere almost completely destructively. Thus, by moving around the phenyl ring we are basically inducing a change in the phase of the electronic waves, leading finally to Eq. (1). It should be noted that the dramatic but periodic conductance variation is clearly related to the existence of only two possible paths for the electrons along the molecular frame. It is remarkable that the qualitative explanation given above is quite insensitive to structural relaxation. The absolute values of the transmission are of course influenced by the latter, but not the general trend shown in Fig. 3.

Fig. 3 – Transmission at the Fermi energy for trans isomer for different (single) contact points (schematically shown in the upper panel) of the right CNT-electrode to the molecule. Arrows indicate the position of the CH-radical. A change of the contact point modifies the relative phase of electrons moving around the phenyl rings.

If the above arguments have some generality they should hold also for cis stilbene. By modifying the contact points (i.e. the position of the CH-group on one of the phenyl ring according to the scheme of Fig. 3), it should therefore be possible to "switch on" the molecular resonances of the cis isomer. This is indeed the case, see Fig. 4. The contact points for the trans and cis isomers correspond to the cases (d) and (c) of Fig. 3, respectively. While the transmission in the trans system is suppressed, the LUMO/LUMO+1 resonances (not well resolved due to strong coupling) of the cis isomer are now clearly visible in the conductance.

Finally, we note that the influence of internal molecular symmetries as well as contact effects, on the electronic transport, have been recently addressed experimentally \([5, 23]\) and theoretically \([3, 4, 7, 24]\). The molecular junction studied here combines both aspects, as the CH-radicals not only modify the symmetry of the stilbene molecule but, at the same time, they determine the contact point to the electrodes.
Summary. - Electronic transport through stilbene isomers within a carbon based device has been investigated. A perfect interference blockade has been found. Also, we have shown that similarities in the electronic structure of both isomers do not necessarily imply similar conductance spectra, the interfacial effects being decisive in controlling electron transport. As a result, both isomers can be distinguished via transport experiments only if the contact geometries are appropriately chosen. Moreover, apart from conductance switching via photoisomerization the blockade effect suggests an alternative switching mechanism by a controlled manipulation of the molecule-electrode interface.

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