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# Microwave emulations and tight-binding calculations of transport in polyacetylene

Thomas Stegmann<sup>a</sup>, John A. Franco-Villafañe<sup>b,a</sup>, Yenni P. Ortiz<sup>a</sup>, Ulrich Kuhl<sup>c</sup>, Fabrice Mortessagne<sup>c</sup>, Thomas H. Seligman<sup>a,d</sup>

<sup>a</sup> Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Avenida Universidad s/n, 62210 Cuernavaca, Mexico

<sup>b</sup> Instituto de Física, Benemérita Universidad Autónoma de Puebla, Apartado Postal J-48, 72570 Puebla, Mexico

<sup>c</sup> Université de Nice – Sophia Antipolis, Laboratoire de la Physique de la Matière Condensée, CNRS, Parc Valrose, 06108 Nice, France

<sup>d</sup> Centro Internacional de Ciencias, 62210 Cuernavaca, Mexico

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## ABSTRACT

A novel approach to investigate the electron transport of *cis*- and *trans*-polyacetylene chains in the single-electron approximation is presented by using microwave emulation measurements and tight-binding calculations. In the emulation we take into account the different electronic couplings due to the double bonds leading to coupled dimer chains. The relative coupling constants are adjusted by DFT calculations. For sufficiently long chains a transport band gap is observed if the double bonds are present, whereas for identical couplings no band gap opens. The band gap can be observed also in relatively short chains, if additional edge atoms are absent, which cause strong resonance peaks within the band gap. The experimental results are in agreement with our tight-binding calculations using the nonequilibrium Green's function method. The tight-binding calculations show that it is crucial to include third nearest neighbor couplings to obtain the gap in the *cis*-polyacetylene.

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## 1. Introduction

The aim of further miniaturization of electronic devices has led in recent years to the question, if it is possible to shrink down the individual active element to a single molecule. This question stimulated the research field of molecular electronics, see [1] and references therein for an overview. One approach is based on carbon nanotubes, which for certain geometric parameters (i.e. tube diameter or number of windings) show a band gap and hence, can be used as transistors [2–5]. A recent milestone has been the realization of a carbon nanotube computer [6]. However, a drawback of this approach is that after the growth of the nanotubes the metallic carbon nanotubes have to be separated from the semi-conducting ones. An alternative approach could be to use individual polyacetylene chains, see a sketch in Fig. 1 (a,b), which are predicted to have a band gap [7–12]. However, most of the experimental work has been done with thin films of polyacetylene chains [13,14]. Transport experiments with *individual* polyacetylene chains have, to the best of our knowledge, not been performed yet. However, new developments in microwave experiments allow to emulate exper-

imentally a tight-binding model, which has proven successful in studies of graphene [15,16]. These microwave experiments, which are performed here for the first time on molecular structures, can measure the transport of microwaves through one or two dimensional tight-binding systems. The microwave transmission corresponds to the ballistic single electron transport in mesoscopic physics or in molecules. Electron–electron interaction, which is present to some extent in real molecules, cannot be emulated by the microwave experiment.

In this paper we explore the transport in polyacetylene like systems. In long chains a transport gap is observed, which is expected due to the dimerization of the chain, i.e. the chain is composed of unit cells of two carbon atoms (dimers). Additional edge atoms add edge localized resonance states within the gaps, which become important for short chains but are negligible for long chains.

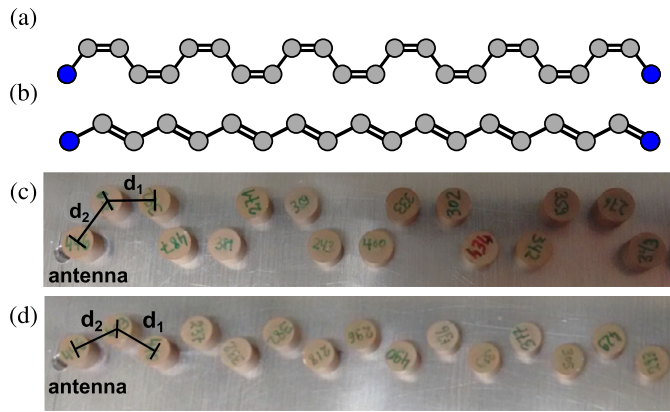
## 2. System: polyacetylene chains

The setup, which we use to emulate both the *cis*- (armchair) and *trans*- (zigzag) isomers of polyacetylenes of various lengths, is shown in Fig. 1 (c,d). The studied chains consist of  $N_d$  dimers, which we here define via the double bonds, with  $N_c$  additional edge atoms at the chain ends, which do not belong to dimers. The

E-mail address: info@thomastegmann.de (T. Stegmann).

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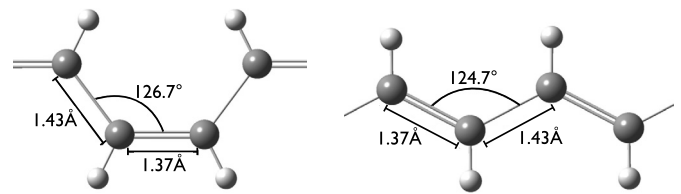
**Fig. 1.** Structure of polyacetylene chains in *cis*-geometry (a) with  $N_d = 11$  dimers and  $N_c = 2$  additional edge atoms, which are not part of the dimers, and in *trans*-geometry (b) with  $N_d = 9$  dimers and a single edge atom ( $N_c = 1$ ) at the left chain end. The resonators correspond to carbon atoms, the hydrogen atoms are not shown. The blue shaded resonators at the chain ends indicate the resonators to which the contacts (or antennas) are coupled to study the transport. The *cis*-chain corresponds to the armchair shape, whereas the *trans*-chain corresponds to a zigzag shape. In (c) and (d) photos of the microwave experiment to emulate polyacetylene chains for the *cis*- and *trans*-geometry are shown, respectively. On the left hand side the antenna on the bottom plate is seen, whereas the antenna on the right hand side is mounted to the top plate (not shown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

chains have altogether  $N = 2N_d + N_c$  atoms. For example, a *cis*-chain consisting of  $N_d = 11$  dimers with  $N_c = 2$  additional edge atoms, one at each end of the chain, is shown in Fig. 1(a). A *trans*-chain of  $N_d = 9$  dimers with a single edge atom on the left can be seen in Fig. 1 (b).

### 2.1. DFT studies

At first, we have calculated the optimal structure of the molecule by means of density functional theory (DFT). The key idea of DFT is that the ground-state of an interacting many-body system is a unique functional of the electron density [17,18]. The ground-state is found by minimizing its energy with respect to the electron density. In order to perform the minimization of the ground-state energy functional, an atomic basis and an exchange-correlation potential have to be selected. The atomic basis is used to construct attempts to the ground-state, while the exchange-correlation potential is taking into account the Coulomb interaction between the electrons. It is known exactly only for the free electron gas, but accurate approximations have been developed. This reduces the interacting many-body problem to a system of non-interacting particles in an effective potential. Here, we use the 6-311g(d) basis set [19], which consists of Gaussian functions, and the B3LYP hybrid exchange-correlation functional [20]. The calculations are performed by the DFT program GAUSSIAN09 [21]. A detailed introduction into DFT can be found for example in [22,23].

Polyacetylenes are chains of carbon atoms. The dangling bonds of the carbon atoms are saturated by hydrogen atoms which are taken into account in our DFT studies, see Fig. 2. However, as their contribution to the conductance can be neglected, the hydrogen atoms will not be considered in the microwave experiment nor in the tight-binding model, see Fig. 1. In both cases, the most stable structure is found for dimerized chains, where the nearest-neighbor distance of the carbon atoms alternates between two different values. For the *cis*-chain, the horizontal bonds have a length of  $1.37\text{\AA}$  while the diagonal bonds have a length of  $1.43\text{\AA}$  with an angle of  $126.7^\circ$ , see Fig. 2 (left). For the *trans*-chain, the bond lengths are  $1.37\text{\AA}$  and  $1.43\text{\AA}$  with an angle of



**Fig. 2.** Stable structure of the polyacetylene molecule, optimized by the DFT method. The left part shows the *cis*-configuration (armchair) and the right part the *trans*-configuration (zigzag) with the corresponding angles and distances between the carbon atoms. The larger gray spheres correspond to the carbon atoms and the smaller white spheres to the hydrogen atoms, which saturate the dangling bonds of the carbon atoms.

$124.7^\circ$ , see Fig. 2 (right). Our findings agree with other *ab initio* studies of these molecules [24,25]. This dimerization, which is also known as Peierls distortion [26], is indicated in Fig. 1 and Fig. 2 by alternating single and double bonds between the carbon atoms. Homogeneous chains, where the nearest-neighbor distance of all carbon atoms is the same, do not give the energetically optimal structure.

### 2.2. Microwave experiment

Using the techniques, developed to investigate the band structure of graphene [15,16] and to emulate relativistic systems [27,28], we have performed an analogous experiment with microwave resonators to study the transport properties of the chains. A set of identical dielectric cylindrical resonators (5 mm height, 4 mm radius, refractive index  $n \approx 6$ ) is placed between two metallic plates. The nearest neighbor distance of the resonators is  $d_1 = 12.0\text{ mm}$  for the long bonds and  $d_2 = 11.5\text{ mm}$  for the short bonds, giving the same distance ratio  $d_1/d_2$  as in the DFT calculations. Close to the chain ends, see the blue shaded resonators in Fig. 1, antennas are placed through which microwaves (transverse electrical (TE)-modes) can be injected and detected. The individual resonators have an isolated resonance at  $\nu'_0 = 6.65 \pm 0.005\text{ GHz}$ . We restrict our investigation to frequencies around  $\nu'_0$ , where each resonator contributes only one resonance. From now on we will use the normalized frequency  $\nu = \nu' - \nu'_0$ , where the resonance frequency of the resonators is at 0 MHz. Photos of the experimental setup (without the metallic plate on top) are shown in Fig. 1 (c,d), and a detailed description can be found in [16].

### 2.3. Tight-binding model

Theoretically, we model the polyacetylene chains by the tight-binding Hamiltonian

$$H = \sum_{|i-j| \leq d} t_{|i-j|} |i\rangle \langle j|, \quad (1)$$

which provides a qualitative good description of the electronic transport in polyacetylene chains [7,8,12,29,30]. A more complete understanding can certainly be gained by taking into account electron correlations [31,32], yet the tight-binding model is often a good starting point for studies of molecular electronics [1].

The location of the isolated spectral peaks for the smallest *cis*- and *trans*-chains in our experiments are used to fit the onsite energies and the coupling parameters, i.e. the part of the spectrum for the smallest molecules which is uniquely determined by our measurement is used to fix the non-zero couplings for each of the two chains. This is in keeping with the standard technique of extracting a Hamiltonian from a "polyad" for molecules [33,34]. Note, that we actually have polyads here because similar other spectra will appear for different frequency ranges, yet they are well separated from the spectra we study. The thus obtained coupling strengths  $t_i$

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