

Vibrational properties of noncovalently oligothiophene-functionalized graphene nanomaterials

M Boutahir, A H Rahmani, H Chadli and A Rahmani

Laboratoire d'Etude des Matériaux Avancés et Applications (LEM2A), Université Moulay Ismail, FSM-ESTM, BP 11201, Zitoune, 50000 Meknes, Morocco

E-mail: a.rahmani@fs-umi.ac.ma

Abstract. In this paper, the non resonant Raman spectra of hybrid nanostructures obtained by confinement of oligothiophene derivatives in two sheets of graphene are calculated in the framework of spectral moments method, together with a bond-polarizability model. Minimum energy calculations are performed, using a convenient Lennard-Jones expression of the van der Waals intermolecular potential, to derive the optimum configurations of oligothiophene with graphene. Parallel configuration of thiophene molecules with respect to the graphene plane was considered.

1. Introduction

The worldwide demand for energy has grown enormously over the recent years and it is likely to grow even more in the near future [1, 2, 3]. Because of the limited supply of our main energy sources (fossil fuels)[4], the development of renewable energy sources such as solar energy is a great priority.

Organic solar cells are a promising low-cost alternative to silicon solar ones [5], but the main handicap is the low power conversion efficiency of these devices. One of the alternatives to solve this handicap is the introduction of carbon nanotubes (NTs) or graphene to form an interpenetrating blend with the polymer. Since the discovery of photoinduced charge transfer between organic conjugated polymers (as donor) and nanotubes or graphene (as acceptor), these latter have been used to fabricate photovoltaic devices in combination with different polymers to the aim of increasing the power conversion efficiency [6, 7, 8].

The process consists of combining species with carbon nanotubes and graphene to create a new hybrid system. Three methods are currently used for that purpose. The first one is a functionalization of polymers at the surface of the tubes [9]. The second method is the noncovalent adsorption or wrapping of various functional molecules [10]. The third one consists of encapsulating oligomers inside nanotubes or between two sheets of graphene in order to keep their original physical properties [11, 12, 13]. The advantage of the last method is that the nanotubes and graphene protect the internal organic molecules from photo degradation and attacks by external



reactive species, there by preventing undesirable alteration of the organic molecules [14].

Thiophene and its polymerized derivatives are considered as the reference compounds of conjugated polymers widely used in organic electronic devices and recently in novel hybrid graphene materials for solar cell. In fact, new 1D hybrid nano-systems are elaborated with oligomers either encapsulated into the hollow core of single-wall carbon nanotubes or non-covalently functionalized at the surface of graphene sheet. The non-covalent functionalization of graphene with conjugated polymers molecules provides an elegant approach to elaborate hybrid systems with original physical properties. Several experimental works dealt with the encapsulation of oligothiophene derivatives (oTh) into NTs(oTh@NT) [15, 13, 16]. Indeed, these systems are particularly interesting as the π -conjugation of the thiophene molecules provides nonlinear optical properties and intrinsic electrical conductivity [17, 18, 19, 20, 21].

In this work, we investigate the non resonant Raman spectra of hybrid nanostructures obtained by confinement of oligothiophene derivatives in multi-layered graphene. We study two hybrid systems, bithiophene in two sheets of graphene (2T@G) and quater-thiophene between two sheets of graphene (4T@G). The calculations have been performed in the framework of the bond-polarization theory using the spectral moment's method (SMM)[22].

2. Models and computational method

The dynamical matrix of our hybrid system is built block by block from the dynamical matrices of each subsystems: The graphene and oligothiophene forms the tridiagonal block of the dynamical matrix of the hybrid systems. While the interactions of graphene-oligothiophene and graphene-graphene forms the off-diagonal block.

The dynamical matrix of the oligomers molecules is calculated using DFT as implemented inside the Spanish initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package [23].

The C-C interactions in graphene sheets are represented by the force constant model introduced by Saito et al [24]. This model was previously used by our group to study the nonresonant Raman spectra of SWNTs as a function of their lengths[22]. Whereas, the interactions between oligomer-graphene are described according to the van der Waals potential. We choose a Lennard-jones type

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

with parameters: $\epsilon = 2.964$ meV and $\sigma = 0.3407$ nm for carbon atoms. $\epsilon = 10.7$ meV and $\sigma = 0.3560$ nm for sulfur atoms. $\epsilon = 0.67$ meV and $\sigma = 0.1069$ nm for hydrogen atoms.

The Sulfur-Carbon and Carbon-Hydrogen parameters were calculated using the rule of mixtures of Lorentz -Berthelot: $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$ et $\sigma_{AB} = (\sigma_A + \sigma_B)/2$.

3. Results

The Raman spectra of graphene are dominated by the tangential mode (TM) located at 1588cm^{-1} . Many experimental and theoretical Raman studies have shown that the TM frequency follows a dependence as a function of the number of sheet of graphene. This dependence is well reproduced by Saito empirical force field[24].

The Raman spectrum of a free bithiophene(2T) molecule have been intensively studied in the literature [25]. Our calculated frequencies are close to those obtained in Ref[25]. From the low frequency region of the spectra of 2T(resp. 4T) molecule (Figure2(resp. Figure3)), we found a double peaks around 8 and 20cm^{-1} (resp. 8cm^{-1}) corresponding to a libration modes. The spectra is dominated by the region between 600 and 1600cm^{-1} with intense bands associated to the C-S-C deformation (677cm^{-1} (2T) and 697cm^{-1} (4T)), the C-H bending (1050cm^{-1} (2T) and 1055cm^{-1} (4T)), the C-C inter-ring stretching(1271cm^{-1} (2T) and 1284cm^{-1} (4T)), and C=C stretching(1504cm^{-1} (2T) and 1503cm^{-1} (4T)).

These results support that the dynamical matrices of graphene and 2T or 4T are expected to be reliable and can be used to build the tridiagonal block of the dynamical matrix of the new hybrid systems (2T@G and 4T@G).

In this preliminary work, an isolated molecule (nT) is inserted between two sheets of graphene with a supercell contains more than 192 atoms each. A supercell size close to 19.7\AA , along OX axis, and 25.5\AA , along OY one, is considered in order to avoid the interactions between molecules when we made the periodic conditions (figure1). Minimum energy calculations are performed, using a convenient Lennard-Jones expression of the van der Waals intermolecular potential, to derive the optimal distances between molecule (nT) and graphene sheets. In this parallel configuration, we found that the graphene-nT distance is close to $3.49\text{\AA} \pm 0.05$ and graphene-graphene distance is close $6.88\text{\AA} \pm 0.05$ (table1). The graphene-graphene distance in graphite is close to 3.4\AA which is smaller than the graphene-nT one in multi-layered system graphene-nT-graphene.

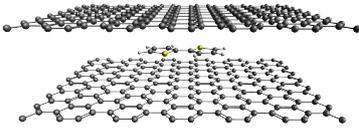


Figure 1. Structure of 2T@G.

Table 1. optimized structural of 2T and 4T between two sheets of graphene.

nT	nT-graphene distance (nm)	graphene-graphene distance (nm)
2T	0.349 ± 0.005	0.688 ± 0.005
4T	0.347 ± 0.005	0.687 ± 0.005

Now we investigate the Raman spectra of the two hybrid systems 2T@G and 4T@G obtained after minimizations. The figure2 displays the ZZ-polarized Raman spectra of 2T molecule (bottom) and 2T@G (top). Raman lines can be divided into three frequency ranges; (i) below 600cm^{-1} (panel a), (ii) an intermediate range between 600cm^{-1} and 1500cm^{-1} (panel b), (iii) above 1500cm^{-1} where the tangential modes are located (panel c).

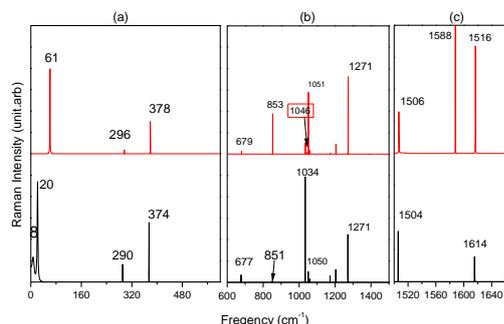


Figure 2. The ZZ-polarized Raman spectra of 2T molecule (bottom) and 2T@G hybrid (top).

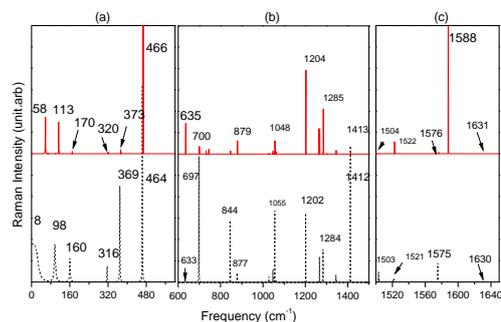


Figure 3. The ZZ-polarized Raman spectra of 4T molecule (bottom) and 4T@G hybrid (top).

The modes located in the lower frequency range are very sensitive to the confinement of thiophene into graphene, because major changes of frequencies and intensities are observed. First, we observe that the libration modes (8cm^{-1} and 21cm^{-1}) of 2T disappear in the Raman spectrum of 2T@G. We observe also a frequency shift of the other modes of 2T@G with respect to the corresponding modes of 2T.

In the intermediate range, Raman spectra of 2T@G show a several lines which originate from the splitting of the 2T degenerate modes due to van der Waals interactions from 677 to 679cm^{-1} and from 1050 to 1051cm^{-1} as well as from 1504 to 1506cm^{-1} . Moreover, a new mode appears at 1046cm^{-1} which is associated to C-H bending as shown in the Figure4, where we present the eigendisplacement vector of this coupled mode. These behaviours could be associated to the competition between intramolecule interactions and molecule-graphene ones.

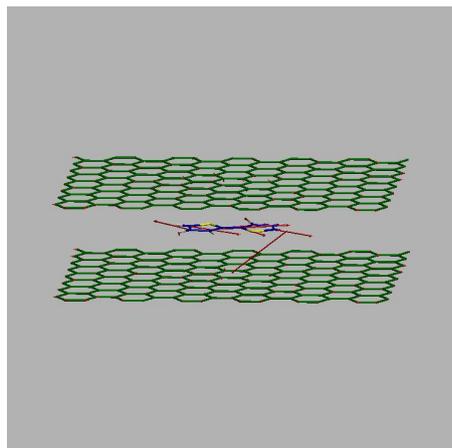


Figure 4. Calculated atomic motions of 1046cm^{-1} mode.

In the TM range, we observe an upshift of the modes in 2T@G with respect to the corresponding modes of 2T. The G-band of graphene is the same in 2T@G around 1588cm^{-1} .

For the other system (4T@G), the figure3 displays the ZZ-polarized Raman spectra of 4T molecule (bottom) and 4T@G (top). As in (2T@G) the mode of libration (8cm^{-1}) of 4T molecule disappears in the Raman spectrum of 4T@G, and we find an upshift of the other modes of 4T@G

with respect to those of 4T molecule.

In the intermediate range, like in 2T@G Raman spectra of 4T@G show several lines due to van der Waals interactions. An upshift of the all modes by (2cm^{-1} or 3cm^{-1}) in 4T@G with respect to those in 4T molecule.

We note that the G-band of graphene, around 1588cm^{-1} , is not affected by the encapsulation in 4T@G hybrid.

4. Conclusion

In this study, the optimal configuration of the isolated nT-oligomers inside two sheets of graphene are derived using a convenient Lennard-Jones potential. In these multilayer graphene-nT-graphene hybrids, we found that the nT-graphene distance is greater than the graphene-graphene one in graphite. For the obtained configurations of 2T@G and 4T@G, the nonresonant Raman spectra have been calculated using the bond-polarizability model combined with the spectral moment's method. We showed that the major changes is obtained in the low frequency range where the libration modes in the 2T and 4T are disappeared in the Raman spectra of the hybrids. The Study with nT-nT interactions inside graphene multilayers is in progress.

5. ACKNOWLEDGMENT

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