Thermal effects on photogeneration of free carriers in organic conductors

5 AUTHORS, INCLUDING:

Pedro Henrique de Oliveira Neto
University of Brasília
28 PUBLICATIONS 154 CITATIONS

SEE PROFILE

Luiz Roncaratti
University of Brasília
27 PUBLICATIONS 298 CITATIONS

SEE PROFILE

Ricardo Gargano
University of Brasília
102 PUBLICATIONS 601 CITATIONS

SEE PROFILE

Geraldo Magela e Silva
University of Brasília
90 PUBLICATIONS 509 CITATIONS

SEE PROFILE

Thermal effects on photogeneration of free carriers in organic conductors

Pedro H. de Oliveira Neto, Wiliam F. da Cunha, Luiz F. Roncaratti, Ricardo Gargano *, Geraldo M. e Silva

Institute of Physics, University of Brasília, CP04455, Brasília, DF, CEP 70919-970, Brazil

ABSTRACT

We performed numerical simulations of two parallel interacting conjugated polymer chains subjected to photoionization. Within the SSH model modified to include thermal effects, an electron is removed from one chain and later absorbed by the other chain. It was obtained that the system relaxes into a free polaron in each chain. For higher electron absorption the system initially relaxes into a pair of half-polarons that spontaneously suffers monomolecular recombination. The time response of the system agrees with experimental results. Although thermal effects are important to carrier creation mechanism, the obtained photogeneration creation time is temperature independent, as suggested experimentally.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Conjugated polymers have energy gap of a typical photo-luminescent material. This leads to interesting properties from the technological point of view. As thermal effects play an important role over the dynamics of charge carriers in these materials, temperature is crucial in the account of polymeric optoelectronic device properties. In the last years a large number of applications of conjugated polymers in optoelectronics has attracted great interest from the scientific community [1–4] due to the good performance of the polymer based devices. For these applications, the mechanisms of carrier photogeneration, as well as important effects of temperature on these processes are fundamental, but remain poorly described.

Concerning the theoretical description of charge carrier creation mechanisms, the model of excitons, which stated that recombination of these quasi-particles was responsible for the charge carrier generation [5–8], initially competed with experimental evidences that polarons were directly created [9,10]. Soci et al. used an ultrafast ($t > 100$ fs) time-resolved photoinduced absorption probe via infrared active vibrational mode (IRAV) and fast ($t > 100$ ps) transient photoconductivity measurements in highly ordered sample of poly (p-phenylene vinylene) (PPV) to suggest a direct polaron creation [11]. Also, the dynamics of these particles would be governed by bimolecular recombination. In a theoretical study of intrachain carrier photogeneration, An et al. suggest two kinds of answer: one is a mixed state of polaron–exciton and oppositely charged polaron pair possessing bond configuration and the other one is the neutral polaron–exciton [12]. Another recently obtained result in a theoretical work proposed by Meng et al. suggests similar results for a pair of coupled chains [13]. Since a neutral

polaron–exciton is a quasi-particle that has the same lattice distortion of a polaron without its charge localization, the two results clearly imply the absence of free charge carriers, as it would be expected from the experimental results [11]. Using pump–probe technique with a time measurement resolution smaller than 25 fs in a isolated sample of poly (9,9-dioctylfluorene) (PFO) embedded in an inert matrix, Virgili et al. [14] suggest free intrachain charge carrier generation as a result of higher-lying optical state excitation and not neutral structures as Meng and An have obtained [12,13]. The previous results show that the carries photogeneration in conjugated polymers, usually explained by intrachain exciton decay, has not been totally understood. The lowest excitation contribution and the distinguishability between intrachain and interchain processes must be clarified.

Another key controversial aspect is related to the temperature dependence on the carrier creation. Firstly, the model proposed for molecular crystal (i.e., the Onsager model) considers photoexcitation as being highly localized, generating initially localized electron–hole bond pairs. These, in turn, dissociate due to phonon scattering, generating charge carriers. This model is also used to treat conjugated polymer and predicts a strong temperature dependence of charge carrier creation process [15,16]. Nevertheless, there are strong experimental evidence in the sense that the time of charge carrier creation in conjugated polymers is temperature independent [17].

In this Letter the numeric simulation of two parallel chains subjected to photoionization is presented. The approach used consists on the use of an empirical tight-binding model of the SSH type, modified to include temperature effects with Langevin terms. This procedure is known to yield excellent results when charge carrier dynamics is concerned [18,19]. Our intent is to simulate a charge transference between chains. To do that we considered a pair of chains interacting very weakly. With the purpose to simulate a physical photoionization we numerically excited an electron from

* Corresponding author.
  E-mail addresses: gargano@fis.unb.br, gargano@unb.br (R. Gargano).

a state in chain one to a state in chain two. Although this represents a numerical photoexcitation, physically this represents a photoionization due to the weak coupling.

In all cases the photoionized electron was taken out from the highest occupied molecular orbital. This electron is then absorbed by the other chain in different unoccupied molecular orbitals. This arrangement features an interchain electron transfer. Simulation of transitions to the first, second and third unoccupied levels have been performed. Additionally, we carried out simulations using different temperatures. The result shows that, depending on the excitation, the system may take two different configurations. For the first excited state, direct formation of free charged polarons is presented. In the case of higher excited states, the system initially finds itself in a bond state of half-polarons. It is obtained that at finite temperature this state spontaneously dissociates into a free polaron. The response time for the system agrees with the experimental evidence. It is important to emphasize that in this context, by a 'half-polaron' we mean a quasi-particle that has half the lattice distortion and charge localization of a polaron. These structures are commonly originated from meta-stable states that occurs for very short time. Another important result associated with temperature is that, although thermal effects influence carrier formation, increasing temperature does not generates appreciable modifications on the creation time. This fact rescues the experimentally observed temperature independence of charge carrier generation time [17].

2. Methodology

The Hamiltonian is $H = H_1 + H_2 + H_{int}$, where H_1 and H_2 are SSH-type Hamiltonians [20],

$$H_j = -\sum_{n,s} t_{jn,n+1}\left(C_{jn+1,s}^\dagger C_{jn,s} + H \cdot c\right) + \sum_n \frac{K}{2}y_{jn}^2 + \sum_n \frac{p_{jn}^2}{2M}, \quad (1)$$

$C_{jn,s}$ being the annihilation operator of a π-electron with s spin in the nth site of chain j; K is the harmonic constant; M is the mass of a CH group; $y_{jn} \equiv u_{jn+1} - u_{jn}$ where u_{jn} is the displacement coordinate; p_{jn} is the momentum conjugated to u_{jn} and $t_{j\,n,n+1}$ is the hopping integral, given by

$$t_{jn,n+1} = [1 + (-1)^n\delta_0](t_0 - \alpha y_{jn}). \quad (2)$$

α is the electron–phonon coupling; t_0 is the transfer integral between the nearest neighbor sites in the aundimerised chains; and δ_0 is the Brazovskii–Kirova symmetry breaking parameter.

$$H_{int} = -\sum_{s,n} t_\perp \left(C_{1n,s}^\dagger C_{2n,s} + C_{2n,s}^\dagger C_{1n,s}\right), \quad (3)$$

where $t_\perp$ is the transfer integral between sites labeled by same index n. The parameter were chosen for a polyacetylene chain in 'cis' configuration [20], $t_0 = 2.5$ eV, $M = 1349.14$ eV $\times$ fs^2/Å^2, $K = 21$ eV Å^{-2}, $\delta_0 = 0.05$ and $\alpha = 4.1$ eV Å^{-1}. This values are the same used in other theoretical works [12,13,24] and the results are expected to be valid for other conjugated polymers.

It is a well known fact that interchain coupling is a major problem as far as the efficiency of luminescence systems is considered [21]. In order to bypass this kind of problem, the use of block copolymers and polymer blends have been suggested to reduce the aggregation and thus improve luminescence [22,23]. In this sense our intent is to investigate two weakly interacting parallel chains since this is the most useful kind of system from the technological point of view. For that it was adopted $t_\perp = 1.0 \times 10^{-6}$ eV.

The strategy used to numerically solve the problem, is first to prepare a stationary state fully self-consistent with the degrees of freedom of both electrons and phonons. We then time evolve the system considering the time-dependent equations of motion

finding the following equations for one particle wave functions $\psi_{k,s}$ which are the solutions to the time-dependent Schrödinger equation

$$i\hbar\dot{\psi}_{jk,s}(n,t) = -t_{jn,n+1}\psi_{jk,s}(n+1,t) - t_{jn-1,n}^*\psi_{jk,s}(n-1,t)$$
$$- t_\perp\psi_{\hat{j}k,s}(n,t), \quad (4)$$

where j and $\hat{j}$ are chain indices running from 2 to 1 and 1 to 2, respectively.

The equation of motion used to evolve the lattice is provided in a classical approach and it is

$$F_n(t) = M\ddot{u}_n$$
$$= -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[B_{n,n+1} - B_{n-1,n}$$
$$+ B_{n+1,n} - B_{n,n-1}], \quad (5)$$

without the j-index to simplify the notation. Here

$$B_{n,n'} \equiv \sum_{k,s}' \psi_{k,s}^*(n,t)\psi_{k,s}(n\prime,t) \quad (6)$$

is the term that couples the electronic and lattice problems. Note that the primed summation characterizes a sum over the occupied states only. In our study we have simulated an electron withdrawn from one of the chains and subsequent absorption of this electron by the other chain. Once the system is made of two weakly interacting parallel chains, we remove an electron from an occupied molecular orbital and consider an unoccupied virtual molecular orbital in the sum of equation (6).

Introducing the expansion

$$\psi_k(t_j) = \sum_l C_{lk}\phi_l(t_j),$$

with $C_{lk} = \langle\phi_l|\psi_k\rangle$, where the eigenfunction and eigenvalues of the electronic part of the Hamiltonian at a given time t_j are $\{\phi_l\}$ and $\{\varepsilon_l\}$, respectively. The solution of the time-dependent Schrödinger equation is then put in the form [24]

$$\psi_{k,s}(n,t_{j+1}) = \sum_l \left[\sum_m \phi_{l,s}^*(m,t_j)\psi_{k,s}(m,t_j)\right] \exp\left(-i\frac{\varepsilon_l\Delta t}{\hbar}\right)\phi_{l,s}(n,t_j).$$
$$(7)$$

Eqs. (5) and (7) are solved by discretizing the time variable with a very small value in the electronic time scale.

To include temperature effects, a canonical Langevin equation was used by introducing, as the fluctuation term a stochastic signal $\zeta(t)$, and a dissipation term γ in Eq. (5) to move the sites positions in a phenomenological representation of thermal disturbance, i.e.:

$$M\ddot{u}_n = -\gamma\dot{u}_n + \zeta(t) + F_n \equiv \widetilde{F}_n(t). \quad (8)$$

Here $\zeta(t)$ is a 'white' noise in the sense that $\langle\zeta(t)\rangle \equiv 0$ and $\langle\zeta(t)\zeta(t')\rangle = B\delta(t - t')$; the relationship between ζ, γ and the temperature T of the system is given by the well known Fluctuation Dissipation Theorem,

$$B = 2k_BT\gamma M. \quad (9)$$

Indeed, we can make use of the Langevin approach since the SSH model already assumes a classical treatment for the lattice part of the system.

3. Results

Trough all simulations we consider 100 site chains with periodic boundary conditions. Photoionization is simulated by an electron withdrawn from one of the chains, i.e., from the HOMO (highest occupied molecular orbital) level. The electron absorption level in the other chain is the LUMO (lowest unoccupied molecular

orbital), LUMO+1 and LUMO+2. The photoionization takes place at 6 fs of simulation time in all cases and it is considered the electron being transferred from chain 2 to chain 1. In this Letter we present results considering temperatures: 0 K, 150 K and 250 K. The dimerised configuration generates a bond length variable y_n of alternating sign. To better visualize the results, order parameters for charge density and bond length are defined as follows:

$$\bar{\rho}_n(t) = 1 - \frac{\rho_{n-1}(t) + 2\rho_n(t) + \rho_{n+1}(t)}{4},$$
$$\bar{y}_n(t) = (-1)^n \frac{-y_{n-1}(t) + 2y_n(t) - y_{n+1}(t)}{4}. \qquad (10)$$

These definitions provide a clear visualization of the charge distribution and pattern of bonds.

Fig. 1 shows the charge density ($\bar{\rho}_n$) time evolution of chains 1 and 2 in the same set of axes for better comparison. The graphic presents the data of the case $T = 0$ K, that is, in absence of temperature effects. Initially it is noted the almost immediate charge transference between chains and then no perturbation on the charge density for approximately 420 fs after the photoionization. It is well known that this kind of perturbation leads to almost instantaneous lattice deformation (≈ 80 fs), however, the mean effect on charge density vanishes, as can be seen in the picture. In this simulation only a lattice oscillation was observed. This oscillation, however, led to no effects on the charge density. A similar result is observed in An et al. [12] work where the response time of the system presents a chain length dependence. After this transient state a positive ($+e$) charged polaron is observed on chain 1, and symmetrically, a negative ($-e$) charged polaron appears on chain 2. As can be seen from the figure, these polarons are in different chains. Another consensus feature is that free polaron pair formation does not take place at systems composed of strongly coupled chains [13]. The reason is that coupling leads to simultaneous excitation from both chains when submitted to photoexcitation. In other words, the charge transfer necessary to carrier formation does not occur in that case, and thus the system remains with strongly coupled neutral states of quasi-particles.

In Fig. 1 we observe the charge transfer in the beginning of the simulation even though the 420 fs delay to the lattice relaxation. The charge carrier photogeneration in conducting polymers is experimentally observed to be four times shorter than that. The present discrepancy from the obtained result is due to the systems great symmetry. Since there are no impurities and periodic boundary conditions were used, there is no preferential position for charge accumulation and consequent polaron formation. After 420 fs the numerical fluctuations provide the loss of translational

symmetry necessary to polaron creation. In fact, this behavior is observed in systems of coupled trans-polyacetylene chains [25]. The experimental time response is recovered when a broken symmetry is present in the simulation, as will be shown in the next case.

In Fig. 2 we have the time evolution of order parameter $\bar{y}_n$ on chain 2 submitted at 250 K. We observe a relaxation faster than 100 fs in this case, and the correspondent formation of a characteristic polaron. This time response is similar to that of a soliton pair formation in trans-polyacetylene [20]. An analogous result is obtained in chain 1. Thermal effects are noted through all the lattice furnishing a random motion to the polaron that can be observed during all simulation time. Unlike the previous case, the response time of the system is reasonably close to the expected experimentally, for thermal effects provide the necessary symmetry breaking to the charge carrier formation. We performed the same type of simulation with several different values of temperature and it was noted that the response time remains typically unaffected. A detailed analysis, however, allows us to conclude that the system response for 250 K is approximately 20 fs faster than for 50 K. This fact strengthens the thesis that photogeneration time in conjugated polymers is nearly temperature independent. The results here presented agree with experimental evidence since most of the experiments are performed with a time resolution poorer than 20 fs and in a temperature variation range smaller than 100 K.

Time evolution for charge density of chain 1 for a LUMO+1 absorption is presented in Fig. 3 for temperatures 150 K (a) and 0 K (b). In both cases, we observe the formation of two half-polarons. In the case of absence of temperature, both structures remain consistently separated through all simulation (Fig. 3b). On the other hand, in the presence of thermal effects, the combination of two half-polarons to a single characteristic polaron is observed at approximately 150 fs in Fig. 3a. The combination of two charged quasi-particles belonging to one molecule is usually called monomolecular recombination. Since there is a small coupling between chains, chain 2 relaxes generating a polaron of charge $-e$ analogously to the previous case. As it was proposed by Soci et al. [11], this configuration of opposite charged carriers in different molecules recombines in a polaron annihilation phenomenon (bimolecular recombination). In this sense, monomolecular recombination is also responsible for the free charge carriers formation that are annihilated in bimolecular processes afterwards. The same result is not observed in the absence of temperature, which suggests that thermal effects play an important role in the monomolecular recombination process. As we repeated our simulation for
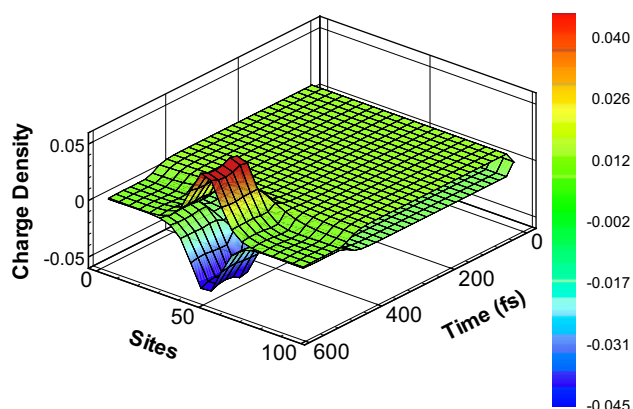

Fig. 1. The picture represents the time evolution of the charge density $\bar{\rho}_n(t)$ for both chains. Observe the almost instantaneous interchain charge transfer, as well as, the formation of a free polarons in each chain at approximately 400 fs.
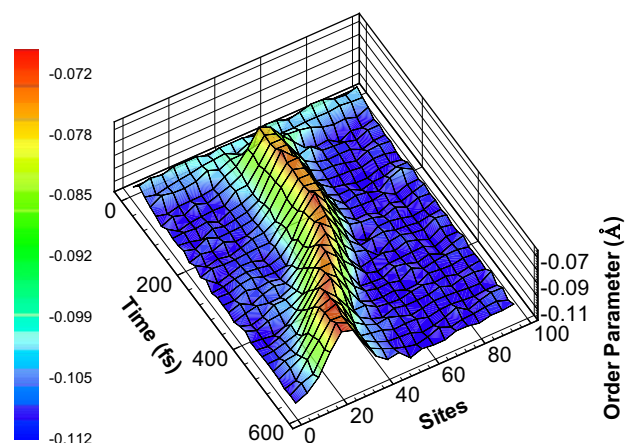

Fig. 2. It is shown the bond order parameter ($\bar{y}_n$) time evolution for chain 2 at 250 K. The polaron formation takes place at approximately 50 fs. Note that this time response is much faster than in the 0 K regime.
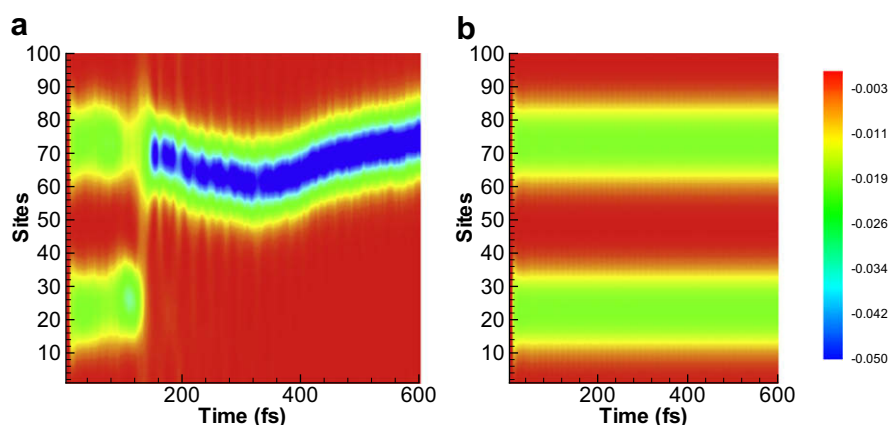
Fig. 3. Charge density time evolution of chain 1 a LUMO+1 absorption for temperatures: (a) 150 K and (b) 0 K. In (a) a monomolecular recombination occurs at 80 fs, and in (b), at 0 K, there is no recombination.

different temperatures, the same pattern was present. In other words, the recombination time is not affected by temperature change. Fig. 3 also suggests a typical Brownian motion for the carrier. It is important to point out that the thermal effects were imposed to the sites and the random walk of the carrier is a consequence and may be described by a generalized Langevin equation [26].

In Fig. 4 we present the energy level behavior around the valence band edge. The graphic corresponds to a 150 K simulation of excitation to LUMO+1. Initially there is no isolated level inside the gap, which means that the two half-polarons are bound. In the 0 K simulation, the energy levels were observed and the obtained results are analogous to those obtained in the first 60 fs of Fig. 4. The transient state lingers for about 140 fs when the characteristic polaron level shrinkage becomes clear. The relaxation time for the system confirms the one observed in Fig. 3 and agrees with Soci et al. [11]. An energy level fluctuation is also present. This fluctuation can be attributed to thermal effects, since it was not observed in the 0 K case.

When the system absorbs an electron at LUMO+2, the results are very close to those of LUMO+1. A pair of bonded half-polarons is observed through all the simulation at 0 K. As we consider temperature, a spontaneous association takes place with the subsequent formation of a free polaron. Recombination time is not

drastically changed with the temperature increase. Performing an accurate analysis we can see that the LUMO+2 system relaxes about only 20 fs faster than LUMO+1, suggesting that the presence of a higher energetic electron helps the recombination to be faster. Nevertheless, this time difference is, again, hard to detect since most experimental results are executed in a time interval higher than 20 fs.

4. Conclusions

In this work we studied the photogeneration mechanism of charge carriers in conjugated polymers. Specifically, the free polaron formation in weakly interacting parallel chains submitted to electron photoionization under the action of thermal effects was investigated. We used the numerical resolution of a modified SSH-type Hamiltonian. Our results indicate that when an electron is photoionized from one chain and absorbed by the neighboring chain, the system relaxes into one free polaron in each chain. This observation contrasts with previous works where, in the absence of temperature, the system relaxes into bonded states, thus not generating free polarons as suggested experimentally. This happens because the coupling does not allow charge transference. In the case of higher excited electrons absorption, the system relaxes into a pair of bonded half-polarons that spontaneously associate creating a free polaron when thermal effects are considered. Indeed our results suggest that photoionization is the major mechanism of charge carrier creation when considering the ultrafast optical or photocurrent experiments. In fact, neutral structures are observed whenever other kind of photoexcitation takes place. Since this polaron recombination happens at a single chain, it is referred as monomolecular recombination.

The obtained results strongly suggest that thermal effects are important to the mechanism of carriers creation. The symmetry breaking supplied by thermal effects is essential to obtain creation times in agreement with experimental results. However, it is also observed that further increase of temperature has virtually no effect in the polaron creation time. This fact suggests an independence of temperature efficiency in organic conductors which, in contradiction to the Onsager model, agrees with experimental evidence.
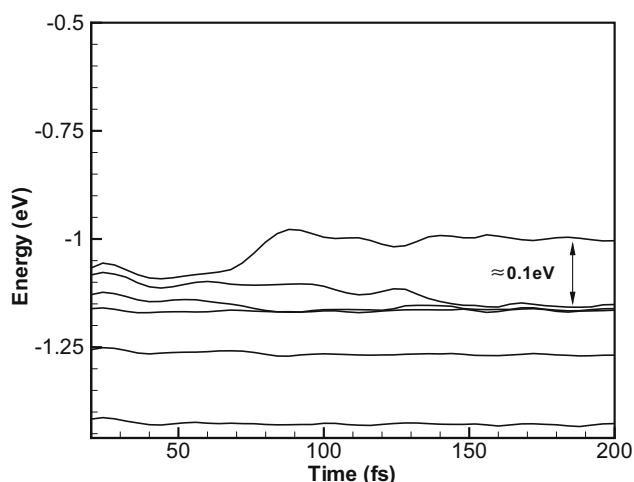
Fig. 4. A highlight in valence band energy levels for the case of LUMO+1 absorbtion at 150 K. Note the typical polaron energy level formation at approximately 150 fs.

References

[1] T.A. Skotheim, J.R. Reynolds, Handbook of Conducting Polymers, CRC Press, 2007.

[2] P.M. Beaujuge, S. Ellinger, J.R. Reynolds, Nat. Mater. 7 (2008) 795.

[3] B. Neese, B. Chu, S.-G. Lu, Y. Wang, E. Furman, Q.M. Zhang, Science 321 (2008) 821.

[4] F. Huo, Z. Zheng, G. Zheng, L.R. Giam, H. Zhang, C.A. Mirkin, Science 321 (2008) 1658.

[5] J.M. Leng, S. Jeglinski, X. Wei, R.E. Benner, Z.V. Vardeny, F. Guo, S. Mazumdar, Phys. Rev. Lett. 72 (1994) 156.

[6] R. Kersting, U. Lemmer, M. Deussen, H.J. Bakker, R.F. Mahrt, H. Kurz, V.I. Arkhipov, H. Bässler, E.O. Göbel, Phys. Rev. Lett. 73 (1994) 1440.

[7] S. Barth, H. Bässler, Phys. Rev. Lett. 79 (1997) 4445.

[8] W. Graupner, G. Cerullo, G. Lanzani, M. Nisoli, E.J.W. List, G. Leising, S. De Silvestri, Phys. Rev. Lett. 81 (1998) 3259.

[9] D. Moses, H. Okumoto, C.H. Lee, A.J. Heeger, T. Ohnishi, T. Noguchi, Phys. Rev. B 54 (1996) 4748.

[10] Y. Nishihara, A. Fujii, M. Ozaki, K. Yoshino, E. Frankevich, Jpn. J. Appl. Phys 42 (2003) L538.

[11] C. Soci, D. Moses, Q.-H. Xu, A.J. Heeger, Phys. Rev. B 72 (2005) 245204.

[12] Z. An, C.Q. Wu, X. Sun, Phys. Rev. Lett. 93 (2004) 216407.

[13] Y. Meng, B. Di, X.J. Liu, Z. An, C.Q. Wu, J. Chem. Phys. 128 (2008) 184903.

[14] T. Virgili, D. Marinotto, C. Manzoni, G. Cerullo, G. Lanzani, Phys. Rev. Lett. 94 (2005) 117402.

[15] M. Pope, C.E. Swenberg, Electronic Process in Organic Crystals, Oxford, New York, 1982.

[16] E.A. Silinsh, Organic Molecular Crystals, Kluwer Academic Publisher, 1980.

[17] D. Moses, C. Soci, X. Chi, A.P. Ramirez, Phys. Rev. Lett. 97 (2006) 067401.

[18] P.H. de Oliveira Neto, W.F. da Cunha, R. Gargano, G.M. e Silva, J. Phys. Chem. A 113 (2009) 14975.

[19] P.H. de Oliveira Neto, W.F. da Cunha, G.M. e Silva, Eur. Phys. Lett. 88 (2009) 67006.

[20] A.J. Heeger, S. Kivelson, J.R. Schrieffer, W.P. Su, Rev. Mod. Phys. 60 (1988) 781.

[21] S.A. Jenekhe, J.A. Osaheni, Science 265 (1994) 765.

[22] M. Yan, L.J. Rothberg, E.W. Kwock, T.M. Miller, Phys. Rev. Lett. 1995 (1992) 75.

[23] B.J. Sun, Y.-J. Miao, G.C. Bazan, E.M. Conwell, Chem. Phys. Lett. 260 (1996) 186.

[24] P.H. de Oliveira Neto, W.F. da Cunha, R. Gargano, G.M. e Silva, Int. J. Quant. Chem. 108 (2008) 2442.

[25] P.H. de Oliveira Neto, G. Magela e Silva, Theochem 852 (2008) 11.

[26] S.H. Kim, T. Zyung, H.Y. Chu, L.-M. Do, D.-H. Hwang, Phys. Rev. B 61 (2000) 15854.