



LETTER

Temperature dependence of polaron stability in conjugated polymers

To cite this article: Y. L. Zhang *et al* 2015 *EPL* **111** 17009

View the [article online](#) for updates and enhancements.

You may also like

- [Electronic properties and polaronic dynamics of semi-Dirac system within Ladder approximation](#)
Chen-Huan Wu
- [Dynamic recombination of triplet excitons in polymer heterojunctions](#)
Ya-Dong Wang, , Jian-Jun Liu et al.
- [Bose polarons in ultracold atoms in one dimension: beyond the Fröhlich paradigm](#)
Fabian Grusdt, Gregory E Astrakharchik and Eugene Demler

Temperature dependence of polaron stability in conjugated polymers

Y. L. ZHANG, X. J. LIU^(a) and Z. AN^(b)

College of Physics, and Hebei Advanced Thin Films Laboratory, Hebei Normal University - Shijiazhuang 050024, China

received 19 May 2015; accepted in final form 7 July 2015

published online 29 July 2015

PACS 71.38.-k – Polarons and electron-phonon interactions

PACS 71.15.Pd – Molecular dynamics calculations (Car-Parrinello) and other numerical simulations

PACS 72.80.Le – Polymers; organic compounds (including organic semiconductors)

Abstract – Within a tight-binding electron-phonon interaction model modified to include thermal effects, the theoretical temperature dependence of polaron stability in conjugated polymers is investigated using a nonadiabatic evolution method. It was found that temperature effects lead to polaron states becoming delocalized, while many weakly localized polaron states are generated. It is worth noting that after thermal equilibrium of the system has been reached, energy transfer between the lattice and the electrons still slowly takes place through two different physical processes corresponding to lower and higher temperatures.

Copyright © EPLA, 2015

Introduction. – Due to the fact that conjugated polymers are easy to process and can be fabricated for mechanically flexible, large-area applications, they have been widely used in recent years. In conjugated polymers, the polaron is one of the predominant excitations and plays an important role in the properties and applications of optoelectronic devices, *e.g.*, light-emitting diodes, lasers, and photovoltaic cells. Many theoretical studies concerning external-electric-field effects on the dynamics of polarons in conjugated polymers have been carried out [1–8]. From this body of work, it is possible to conclude that polaron can travel as an entity along the polymer chain in low electric fields but dissociate in high electric fields. Furthermore, the role of electron-electron (e-e) interaction on polaron dynamical properties has been investigated using the SSH Hamiltonian in combination with the Hubbard model or extended Hubbard model by a number of research groups [9–11]. They have pointed out that the e-e interaction is an important factor which influences the stability of a polaron. Experimentally, Lin *et al.* have observed the disruption of a polaron in a strong electric field 15 mV/Å [12]. In addition, the effects of impurities, defects, and collision between charge carriers on polaron dynamics have also been studied and have produced interesting results [13–17].

Recently, several groups have studied the effects of temperature on the behavior of polarons, and found that temperature has an important influence on the mobility of the charge carriers in organic conjugated polymers. Thermal effects cause localized polaron states to become instable and delocalized, and even to disappear at higher temperatures. Therefore, temperature is an important factor when it comes to describing the lifetime of polaron structures and the dissociation field for polarons [18,19]. G. M. e Silva *et al.* [20] have treated the influence of temperature on charge transport in both intrachain and interchain processes in conjugated polymers. They found that in both cases increased temperature can raise carrier mobility through an untrapping mechanism. It is worth noting that in the presence of an electric field, there are two distinct regimes in the temperature dependence of the mobility of polarons in conjugated polymers. For electric fields of 1.0 mV/Å or higher, lattice thermal oscillations can increase the mean velocity of a polaron, while under weaker electric fields, mobility is damped by thermal oscillations [21]. Subsequently, G. M. e Silva and his groups have employed revised SSH model including an external electric field and temperature effects to investigate dynamical phase transitions related to the stability of polarons and bipolarons, recombination of intrachain (bi)polarons, scattering of polarons and bipolarons [22–26]. These dynamic studies are useful for gaining insight into temperature influence of the charge

^(a)E-mail: xjliu@mail.hebtu.edu.cn

^(b)E-mail: zan@hebtu.edu.cn

carrier motion in organic optoelectronic. Experimentally, Kanemoto *et al.* [27] proposed that the movement of a polaron generates an anisotropic ESR spectrum which decreases with increasing temperature. From the work outlined above, it may be seen that temperature is an important factor when it comes to polymeric optoelectronic properties, but that it remains poorly described.

In the present paper, in order to fully understand the polaron delocalization processes in a thermal bath, we study the effects of temperature on the stability of the polarons and energy variation of system in a polyacetylene chain. We have chosen the Su-Schrieffer-Heeger (SSH) model [28] modified to include thermal effects. The thermal effects are considered by adopting Langevin equations with white noise introduced through the lattices vibration [29,30]. The next section gives an outline of the model. Results and discussions are shown in the third section. Finally, a summary is given in the last section.

Model and numerical method. – The SSH model included a Brazoskii-Kirova-type symmetry-breaking term [31], and can be written as

$$H = - \sum_n [t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e](c_{n+1}^\dagger c_n + \text{h.c.}) + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2 + \frac{M}{2} \sum_n \dot{u}_n^2. \quad (1)$$

The first term of eq. (1) is the electronic Hamiltonian, and the latter two terms are the lattice Hamiltonian. t_0 is the transfer integral of electrons in a regular lattice, α is the electron-phonon coupling, u_n is the lattice displacement of the n -th site from its equidistant position, and t_e is the ground-state degeneracy parameter for nondegenerate polymers. c_n^\dagger and c_n are the operators that create and annihilate an electron at the n -th site. K is the elastic constant of the lattice, and M is the mass of a CH group.

The evolutional electron wave functions $\Phi_k(n, t)$ satisfy the time-dependent Schrödinger equation

$$i\hbar \dot{\Phi}_k(n, t) = -t_n \Phi_k(n+1, t) - t_{n-1} \Phi_k(n-1, t), \quad (2)$$

where $t_n = t_0 - \alpha(u_{n+1} - u_n) + (-1)^n t_e$, the electronic state $\Phi_k(n, t)$ can be expanded using instantaneous eigenstates $\Phi_k(n, t) = \sum_l C_{l,k}(t) \phi_l(n, t)$. The instantaneous eigenstates $\phi_l(t)$ can be obtained by diagonalizing the Hamiltonian matrix at that moment. The occupation of the instantaneous eigenstates can be obtained using $N_l(t) = \sum_k |C_{k,l}(t)|^2$.

The time evolution of the lattice is governed by the Newtonian equation

$$M\ddot{u}_n(t) = -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] + \alpha[\rho_{n,n+1}(t) + \rho_{n+1,n}(t) - \rho_{n,n-1}(t) - \rho_{n-1,n}(t)] - \lambda M \dot{u}_n + f_n(t), \quad (3)$$

where the density matrix is defined as $\rho_{n,n'}(t) = \sum_k \Phi_k(n, t) D_k \Phi_k^*(n', t)$, and $D_k (= 0, 1, 2)$ is the time-independent distribution function and is determined by the initial state. The latter two terms of eq. (3) describe temperature effects. λ is the friction constant, which is taken to be of the same order of magnitude as the experimental Raman spectral line width in polydiacetylene ($= 0.01\omega_Q$), where ω_Q is the bare optical phonon frequency [32,33]. Finally, $f_n(t)$ is thermal random force which is characterized by the statistical properties [34–36]

$$\langle f_n(t) \rangle = 0, \quad (4)$$

$$\langle f_n(t) f_{n'}(t') \rangle = 2k_B T M \lambda \delta_{n,n'} \delta(t - t'), \quad (5)$$

where k_B is the Boltzmann constant and T is the temperature.

The coupled differential equations (2) and (3) can be solved using a Runge-Kutta method of order 8 with step-size control [37]. The parameters used here are taken to be those for *cis*-polyacetylene, *i.e.*, $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21.0$ eV/Å², $t_e = 0.05$ eV, $M = 1349.14$ eVfs²/Å² [38]. In order to obtain an acceptable time to reach the target final temperature for the polymer chain, we have used a damping value $\lambda = 0.04\omega_Q = 0.01$ fs⁻¹. Although the parameters are chosen for polyacetylene, the results are expected to be qualitatively valid for other conjugated polymers.

Results and discussions. – In our simulations, a polymer chain consisting of 100 sites was considered. A pre-existing electron polaron was placed at the center of the chain at the initial time. In the dynamic simulations, stochastic forces $f_n(t)$ ($n = 1, 2, 3 \dots$) satisfying eq. (4) and (5) were introduced. A discrete time step (1 fs) was used, which means that the strength of the forces was taken to be unchanged over each femtosecond. In addition, the results shown below have been taken as the ensemble average over 20 simulations.

We are now in a position to study numerically the polaron dynamical characteristics as a function of temperature. Firstly, fig. 1 shows the time evolution of the staggered bond order parameter $\delta_n(t) \equiv (-1)^n (u_{n-1}(t) + u_{n+1}(t) - 2u_n(t))/4$ at temperatures of 5 K (a), 150 K (b), and 300 K (c). From the figure, one can see that the polaron performs a random walk along the polymer chain under the influence of the random thermal forces and that the stability of the polaron is strongly affected by thermal effects. At 5 K, the polaron lattice distortion can be clearly distinguished from the lattice fluctuations, and the polaron performs a slow random walk over the course of the simulation time. When the temperature is increased to 150 K, the polaron lattice distortion can be clearly distinguished from the lattice fluctuations within the initial 400 fs. However, the locality of the polaron becomes weaker with time after about 400 fs. Over our simulation time, the polaron performs a rapid random walk. At a higher temperature, 300 K, the behavior of the polaron is

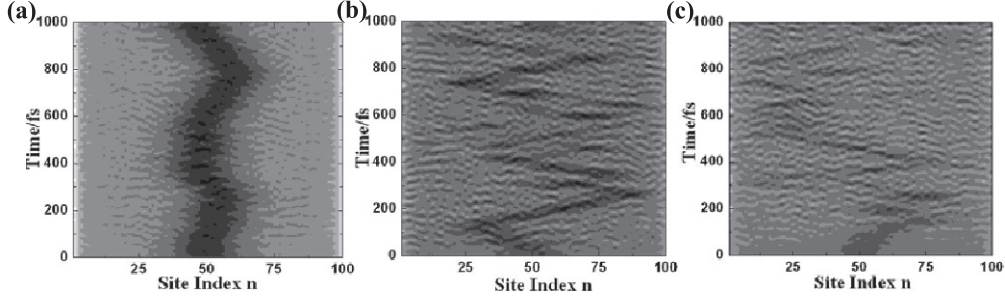


Fig. 1: Evolution of the staggered bond order parameters δ_n with time at different temperatures: (a) $T = 5$ K, (b) $T = 150$ K, (c) $T = 300$ K.

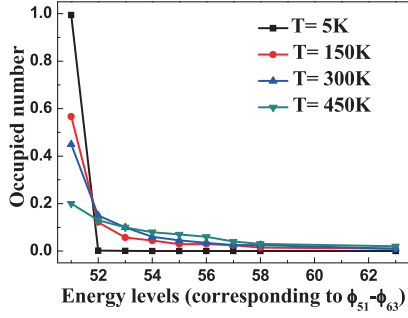


Fig. 2: (Colour on-line) The occupied number of energy levels from LUMO to LUMO+12 (corresponding to instantaneous eigenstates from ϕ_{51} to ϕ_{63}) in the conduction band at different temperatures.

dramatically different from the above two cases, as shown in fig. 1. In this case, the polaron lattice distortion can only be clearly distinguished from the lattice fluctuations in the initial 200 fs, and it is difficult to distinguish the polaron as a separate entity in the polymer chain during the time following. The pre-existing polaron is completely annihilated by the effect of temperature. These results show that the stability of the polaron becomes weaker with increasing temperature.

To gain a better understanding of the polaron stability at different temperatures, we investigated the occupied number of the eigenenergy levels in the conduction band at the final simulation time. They are obtained as the ensemble average values over 20 simulations at each temperature. It is useful to study the occupied numbers of the eigenenergy levels from LUMO to LUMO+12 (corresponding to instantaneous eigenstates from ϕ_{51} to ϕ_{63}) for all the temperatures, as the changes reflect the stability of polarons. For an electron polaron, the occupation of the LUMO energy level is 1, and the occupation of the higher energy levels (LUMO+1, LUMO+2, LUMO+3...) is 0, which corresponds to the case for 0 K. From fig. 2, it can be seen that the occupation of the LUMO is less than 1 with nonzero temperatures. For example, the occupied number of the LUMO is 0.96 at 5 K, which indicates that the electron has a 0.04 probability of being excited to higher energy levels (LUMO+1, LUMO+2, LUMO+3...) and redistributed across these

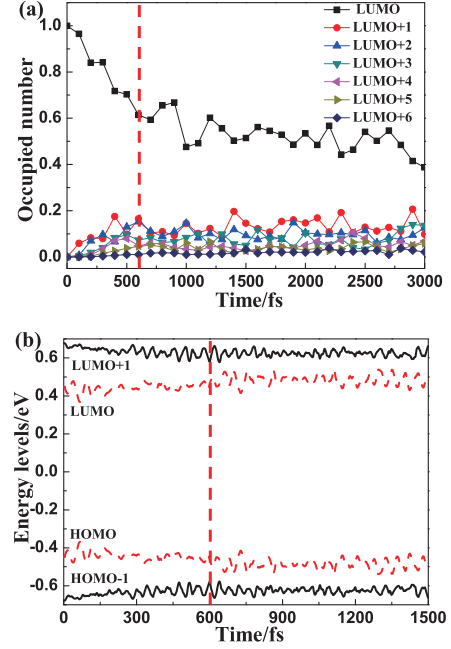


Fig. 3: (Colour on-line) Time dependence of occupied numbers (a) and localized electronic energy levels (b) for the negative polaron at $T = 300$ K.

levels. Similarly, at 150 K, 300 K and 450 K, the occupations of the localized LUMO energy level are 0.58, 0.45 and 0.2, and the probabilities of the electron being excited to the higher energy levels are 0.42, 0.55 and 0.8, respectively. Consequently, we can obtain that the temperature effects induce the electron to be excited from the localized LUMO energy level to the higher energy levels (LUMO+1–LUMO+49). With increasing temperatures, the occupied number of the localized LUMO energy level decreases, and the polaron becomes more delocalized.

To further elaborate the process of polaron delocalization at higher temperatures, fig. 3 shows the time evolution of the occupied number of several instantaneous eigenstates (a), and evolution of the localized electronic energy levels with time (b), at 300 K. From fig. 3(a), the time evolution of the occupied number of the instantaneous eigenstates (corresponding to energy levels LUMO–LUMO+6) is shown. One can see that

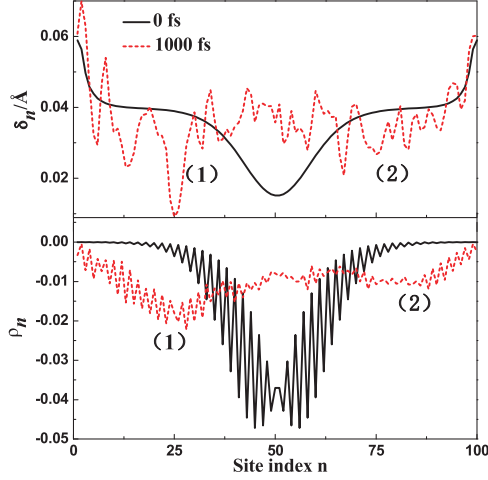


Fig. 4: (Colour on-line) The staggered bond order parameters δ_n (upper part) and charge densities ρ_n (lower part) at 0 fs and 1000 fs for 300 K. (1) and (2) mark the two obvious lattice distortions.

as time increases, the occupied number of the LUMO energy level decreases from 1 to 0.45. At the same time, the occupied numbers of the higher energy levels (LUMO+1–LUMO+6) all increase with time. For example, the occupied number of the energy level LUMO+1 increases from 0 to 0.15. Similarly, those of LUMO+2, LUMO+3, LUMO+4, LUMO+5 and LUMO+6 increase from 0 to 0.10, 0.06, 0.045, 0.035 and 0.025, respectively. The higher the energy levels, the smaller the occupied numbers, and the occupied numbers of higher energy levels (LUMO+7...) are not shown in fig. 3(a). The evolution with time of the occupied numbers for the energy levels can be divided into two parts. Over the initial 600 fs, the occupied number changes very quickly, which corresponds to a fast energy transfer process. On the other hand, the change in the occupied number is very slow after 600 fs, which indicates a slow transfer process.

In fig. 3(b), the time evolution of several of the main localized electron energy levels is shown. One can see that with increasing time, the localized electron energy levels (HOMO and LUMO) in the band gap gradually become delocalized while moving away from the gap. At the same time, the HOMO–1 and LUMO+1 levels become more localized and move down toward the midgap. Finally four weakly localized energy levels are formed in the energy gap. Similarly, the evolution of the energy levels with time also can be divided into two parts, i) the fast relaxation process in the initial 600 fs, ii) the slow relaxation process after 600 fs. The process of thermalization of the polymer does not occur instantaneously but rather by about 600 fs. Before thermalization, the system quickly absorbs energy from the thermal bath, which quickly induces electron excitation from the LUMO level to the higher energy levels, accompanied by a rapid relaxation process. After thermalization, the polymer reaches the target final temperature and approximately satisfies the dynamic equivalence. The

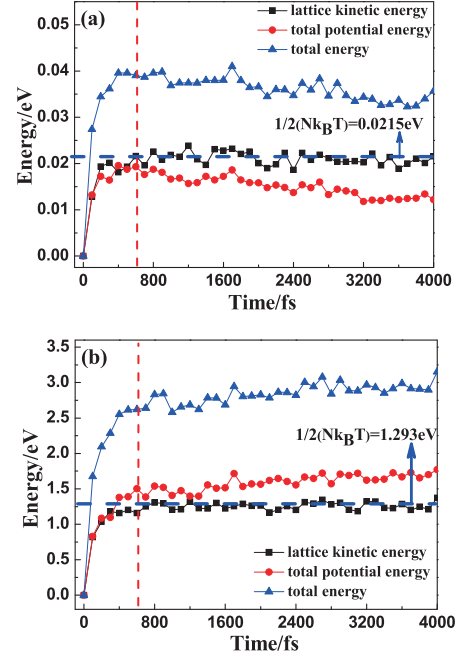


Fig. 5: (Colour on-line) Time evolution of energy at lower and higher temperatures: kinetic energy (squares), potential energy (circles), the total energy (triangles) for (a) 5 K, (b) 300 K.

energy exchange between the system and the thermal bath then becomes slow, which implies a slow evolution of the occupied numbers and the energy levels.

Figure 4 shows the staggered bond order parameters δ_n (upper part) and charge densities ρ_n (lower part) at times of 0 fs and 1000 fs at 300 K. One can see that the initial state is an electron polaron localized at the center of the chain. However, at 1000 fs, the well of the polaron distortion is difficult to find and many weakly localized distortions are formed, two of them are quite obvious and marked (1) and (2) in fig. 4. These distortions correspond to the formation of the four weakly localized energy levels in fig. 3(b).

To sum up, by taking into account the thermal effects, the translational symmetry of the electronic Hamiltonian is destroyed, and the localized electrons have a nonzero probability of being excited to higher energy levels. Because of the electron-phonon coupling, the higher energy levels occupied by an electron should become weakly localized. That is, the polaron state becomes delocalized, and many weakly localized polaron states are generated.

Next, we discuss the time evolution of the energy as affected by the temperature, which is important for gaining better understanding of the stability of the polarons. Figure 5 shows the evolution with time of the kinetic energy, potential energy as well as the total energy at temperatures of 5 K (fig. 5(a)) and 300 K (fig. 5(b)). From the figure, one can see that the lattice kinetic energy increases abruptly during the initial 600 fs and then remains approximately constant at all the later time for both 5 K and 300 K. This indicates that the thermalization of the

polymer chain occurs at about 600 fs. At that time, the polymer chain reaches the target final temperature and satisfies the classical equivalence $k_B T = Mv^2$. For 5 K, $(1/2)Nk_B T = 0.0215$ eV, and for 300 K, $(1/2)Nk_B T = 1.293$ eV. The evolution of the potential energy is different for $T = 5$ K and $T = 300$ K. For the lower temperature, 5 K, the potential energy and total energy of the polymer greatly increase before thermalization, and then decrease slowly after thermalization over the course of our simulation time. For the higher temperature, 300 K, the potential energy and total energy also increase sharply before thermalization, and then both slowly increase after thermalization.

The difference in the energy evolutions can be explained as follows. The polymer quickly absorbs energy from the thermal bath before thermalization of the system. The energies (including the lattice kinetic energy, the potential energy and the total energy) all increase abruptly at each temperature. After thermalization, the energy exchange between electrons and lattices still slowly continues. For the lower temperature of 5 K, the electrons easily transfer energy to the lattices, while due to maintaining dynamic equilibrium, the lattices lose energy to the thermal bath, the total energy of the polymer thus slowly decreases with time. On the contrary, for the higher temperature 300 K, the lattices easily lose energy to the electrons, and in order to maintain dynamic equilibrium, the lattices should absorb energy from the thermal bath. The result is that the total energy of the polymer slowly increases with time.

Summary. – In this work, the theoretical temperature dependence of polaron stability has been investigated. Due to lattice thermal oscillations, the polaron becomes delocalized, and many weakly localized polaron states are generated. The electrons and lattice still exchange energy in the presence of thermodynamic equilibrium states. At lower temperatures, the electrons lose energy, and the energy shifts to the lattice. At higher temperatures, the lattice loses energy, and the energy shifts to the electrons. These results and analysis provide a more detailed physical picture of the effects of temperature on polaron stability, and help to show their important role in charge carrier mobility in conjugated polymers. Finally it should be mentioned that the electron-electron (e-e) interaction is not included in the present work. Considering that the e-e interactions play a very important role in determining the behavior of the charge carriers in conjugated polymers, we will use the Su-Schrieffer-Heeger+Pariser-Parr-Pople (SSH+PPP) model [39–41] to investigate the effects of on-site and long-range e-e interactions on the polaron transport in a thermal bath in the future.

This work was supported by the National Natural Science Foundation of China (Grants No. 11074064, and No. 11304075), the Natural Science Fund of Hebei

Province of China (Grants No. A2012205045, and No. A2012108003), and the Key Project of Educational Commission of Hebei Province of China (No. ZD2014052). The authors wish to thank Prof. N. E. DAVISON for helpful discussions.

REFERENCES

- [1] HULTELL M. and STAFSTRÖM S., *Chem. Phys. Lett.*, **428** (2006) 446.
- [2] JOHANSSON A. A. and STAFSTRÖM S., *Phys. Rev. B*, **69** (2004) 235205.
- [3] LIU X. J., GAO K., FU J. Y., LI Y., WEI J. H. and XIE S. J., *Phys. Rev. B*, **74** (2006) 172301.
- [4] RAKHMANOVA S. V. and CONWELL E. M., *Appl. Phys. Lett.*, **75** (1999) 1518.
- [5] E SILVA G. M., *Phys. Rev. B*, **61** (2000) 10777.
- [6] RAKHMANOVA S. V. and CONWELL E. M., *Synth. Met.*, **110** (2000) 37.
- [7] BASKO D. M. and CONWELL E. M., *Phys. Rev. Lett.*, **88** (2002) 056401.
- [8] JOHANSSON Å. and STAFSTRÖM S., *Phys. Rev. Lett.*, **86** (2001) 3602.
- [9] MA H. B. and SCHOLLWÖCK U., *J. Phys. Chem. A*, **113** (2009) 1360.
- [10] DI B., AN Z., LI Y. C. and WU C. Q., *EPL*, **79** (2007) 17002.
- [11] ZHAO H., YAO Y., AN Z. and WU C. Q., *Phys. Rev. B*, **78** (2008) 035209.
- [12] LIN H. N., LIN H. L., WANG S. S., YU L. S., PERNG G. Y., CHEN S. A. and CHEN S. H., *Appl. Phys. Lett.*, **81** (2002) 2572.
- [13] YAN Y. H., AN Z. and WU C. Q., *Eur. Phys. J. B*, **42** (2004) 157.
- [14] LIMA M. P. and E SILVA G. M., *Braz. J. Phys.*, **35** (2005) 961.
- [15] LIMA M. P. and E SILVA G. M., *Int. J. Quantum Chem.*, **106** (2006) 2597.
- [16] AN Z., DI B., ZHAO H. and WU C. Q., *Eur. Phys. J. B*, **63** (2008) 71.
- [17] LIMA M. P. and E SILVA G. M., *Int. J. Quantum Chem.*, **106** (2006) 2603.
- [18] DA CUNHA W. F., DE OLIVEIRA NETO P. H., GARGANO R. and E SILVA G. M., *Int. J. Quantum Chem.*, **108** (2008) 2448.
- [19] LIU W., LI Y., QU Z., GAO K., YIN S. and LIU D. S., *Chin. Phys. Lett.*, **26** (2009) 037101.
- [20] DE OLIVEIRA NETO P. H., DA CUNHA W. F. and E SILVA G. M., *EPL*, **88** (2009) 67006.
- [21] RONCARATTI L. F., GARGANO R. and E SILVA G. M., *J. Phys. Chem. A*, **113** (2009) 14591.
- [22] RIBEIRO L. A., DA CUNHA W. F., DE OLIVEIRA NETO P. H., GARGANO R. and E SILVA G. M., *New J. Chem.*, **37** (2013) 2829.
- [23] RIBEIRO JUNIOR L. A., DA CUNHA W. F., DE ALMEIDA FONSECA A. L., GARGANO R. and E SILVA G. M., *Chem. Phys. Lett.*, **614** (2014) 151.
- [24] DA CUNHA W. F., RIBEIRO JUNIOR L. A., GARGANO R. and E SILVA G. M., *Phys. Chem. Chem. Phys.*, **16** (2014) 17072.

- [25] RIBEIRO L. A., OLIVEIRA NETO P. H., DA CUNHA W. F., RONCARATTI L. F., GARGANO R., DA SILVA FILHO D. A. and E SILVA G. M., *J. Chem. Phys.*, **135** (2011) 224901.
- [26] RIBEIRO JUNIOR L. A., DA CUNHA W. F. and E SILVA G. M., *J. Phys. Chem. A*, **118** (2014) 6272.
- [27] KANEMOTO K., FURUKAWA K., NEGISHI N., ASO Y. and OTSUBO T., *Phys. Rev. B*, **76** (2007) 155205.
- [28] HEEGER A. J., KIVELSON S., SCHRIEFFER J. R. and SU W. P., *Rev. Mod. Phys.*, **60** (1988) 781.
- [29] HÄNGGI P. and JUNG P., *Adv. Chem. Phys.*, **89** (1995) 239.
- [30] ZHANG Y. L., LIU X. J. and AN Z., *J. Phys. Chem. C*, **118** (2014) 2963.
- [31] TANDON K., RAMASESHA S. and MAZUMDAR S., *Phys. Rev. B*, **67** (2003) 045109.
- [32] TROISI A. and CHEUNG D. L., *J. Chem. Phys.*, **131** (2009) 014703.
- [33] RONCARATTI L. F., GARGANO R. and E SILVA G. M., *J. Phys. Chem. A*, **113** (2009) 14591.
- [34] IVIC Z., ZEKOVI S. and KOSTIC D., *Phys. Rev. E*, **65** (2002) 021911.
- [35] FLYTZANIS N., IVIĆ Z. and MALOMED B. A., *Europhys. Lett.*, **30** (1995) 267.
- [36] FLYTZANIS N., IVIĆ Z. and MALOMED B. A., *J. Phys.: Condens. Matter*, **7** (1995) 7843.
- [37] BRANKIN R. W., GLADWELL I. and SHAMPINE L. F., RKSUITE: software for ODEIVPS (www.netlib.org).
- [38] AN Z., WU C. Q. and SUN X., *Phys. Rev. Lett.*, **93** (2004) 216407.
- [39] TANDON K., RAMASESHA S. and MAZUMDAR S., *Phys. Rev. B*, **67** (2003) 045109.
- [40] ZHANG Y. L., LIU X. J., SUN Z. and AN Z., *J. Chem. Phys.*, **138** (2013) 174906.
- [41] LIU X. J., ZHANG Y. L. and AN Z., *Org. Electron.*, **14** (2013) 2692.