



ELECTRON TRANSFER IN THE MOLECULAR COMPLEX OF DONOR-POLYMER-ACCEPTOR

O.V. Yaltychenko and E.Y. Kanarovskii *

abstract: Electron transfer in the molecular complex donor-polymer-acceptor type was investigated. The carbon chain, which has two possible conformations (homogeneous and dimerized), was taken as polymer. The theoretical model, which described the electron transfer process in such type of the systems, was proposed. The probability of detection of the electron on the each subsequent unit, if originally was located on the first unit, was theoretically investigated. Two types of the electron transfer were revealed.

key words: electron transfer; carbon chain; electron-vibrational interaction; conformational state

received: May 05, 2009

accepted: May 20, 2009

Introduction

The organic compounds are the base materials for the nanoelectronics. Among them are selected polymeric materials, especially π -conjugated polymers, which have strong delocalized properties. These properties are connected with collectivization of the electronic density in all the system. The metal-organic clusters and complexes with charge transfer such as donor-acceptor type complexes are also applied in the sensor's electronics [1÷5]. In the present paper is investigated the kinetics of the electron transfer in the supramolecular complex - donor-polymer-acceptor (D- π -A). The electron transfer from the donor's atom group D through π -conjugated polymer (a carbon chain) to the acceptor's atom group of the complex is studied. The transport properties of this system are essentially depending from nature of the conformational states, in which may be the polymeric chain.

From the analysis of the stability of the homogeneous π -conjugated carbon chain follows, that dimerized conformational state of the carbon chain with alternating both long and short chemical bonds between the carbon atoms is stable. The ground state in the homogeneous chain is degenerate, and deformations of the homogeneous chain remove this degeneration of the energy. The result of such deformation of the double bonds in the carbon chain can become transition of the chain in the new conformational state (dimerized state) with

* Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academic St., MD-2028, Kishinev, Republic of Moldova, *corresponding author e-mail: oialt@mail.ru*

alternating the single (long) and threefold (short) chemical bonds between the atoms of the carbon chain.

Premises of the model

The carbon chain as the basic part of the molecular complex can be considered in the two basic conformations [6]:

$$= [C = C =]_n = \quad (1)$$

and

$$- [C \equiv C -]_n - \quad (2)$$

For the description of the time's dynamics of the supplementary electron, which was brought in the system from the donor's atom group, the model Hamiltonian of the system may be presented as [7÷9]:

$$\begin{aligned} \hat{H} = & \sum_n \left[\varepsilon_0 B_n^+ B_n - t_{n+1,n} B_{n+1}^+ B_n \right] + \\ & + \frac{1}{2} \sum_n \left[\frac{1}{M} p_n^2 + \kappa (u_{n+1} - u_n)^2 \right] + V \sum_n B_n^+ B_n (u_{n+1} - u_{n-1}) \end{aligned} \quad (3)$$

Here B_n^+ , B_n are the operators of the birth and annihilation of the electron on the n -th unit of the carbon chain; u_n , p_n are the canonical connected coordinate and momentum of the vibrational mode for n -th unit of the carbon chain; ε_0 , $t_{n+1,n}$, V are the energy of the electron on n -th unit of the carbon chain, the energy of resonance interaction and the constant of the electron-vibrational interaction on n -th unit of the carbon chain, accordingly. The expression $t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n)$ for the case of the homogeneous π -conjugated carbon chain does not depend from vibrational coordinates and is equal t_0 .

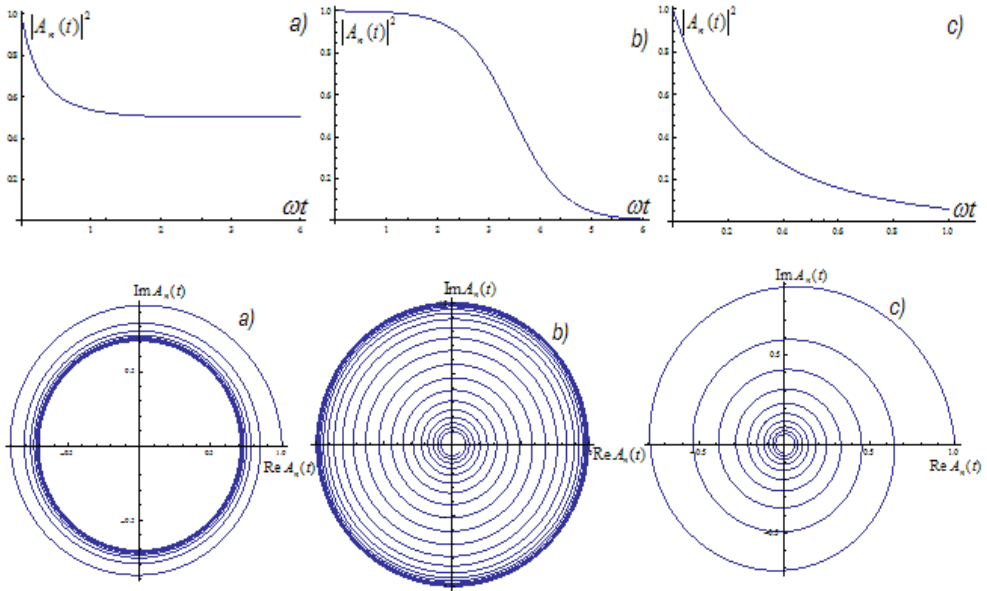
Results and discussions

It is supposed, in this work that the interaction between the degrees of freedom inside the carbon chain in approximation coupling of two nearest units of the carbon chain is such that it results only to the redefinition of the frequency parameter of the system. The system of the kinetic equations concerning amplitudes of the probability of the electron's detection on the n -th unit of the chain was obtained. In this system of the kinetic equations the parameter of the nonlinearity is appearing. Other interactions are taken into account as the dissipation parameter.

$$\begin{aligned} \frac{d}{dt} A_n(t) &= (i\bar{\omega}_n + \bar{\mu}_n) A_n(t) + U_n |A_n(t)|^2 A_n(t); \\ \bar{\omega}_n &= \omega_n + \sum_{n_1 \neq n} \text{Im}(V_{mn_1} |A_{n_1}(t)|^2); \\ \bar{\mu}_n &= \mu_n + \sum_{n_1 \neq n} \text{Re}(V_{mn_1} |A_{n_1}(t)|^2); U_n = \text{Re} V_{nn}; A_n(0) = 1 \end{aligned} \quad (4)$$

The expression $|A_n(t)|^2$ is characterizing the probability of the detection of the electron on the n -th unit of the carbon chain.

It is important to note, that system of the differential equations (4) is essentially a nonlinear system. The numerical resolution (4) for the various values of the parameters, which fall into the n -th unit of the carbon chain, $\bar{\omega}_n, \bar{\mu}_n, U_n$ (the own frequency, the dissipation parameter and the parameter of the nonlinearity, accordingly) is lead. We shall notice, that for the dimerized (nonhomogeneous) chain the parameter ω_n includes the correction to ε_0 which connects with contribution of resonance interaction energy $t_{n+1, n}$. It is aforesaid the local deformation of bonds causes the periodic lattice distortion known as the Peirels instability [10] for the quasi-one-dimensional systems and results to the alternation in the carbon chain.



The probability of the electron's detection on the n -th unit in the D- π -A system and the phase diagrams for the cases – a), b), c), accordingly.

The probability of the electron's detection on the n -th unit of the chain $|A_n(t)|^2$ in the system for the different values of the parameters:

$$\text{a) } -\bar{\mu}_n = 1; U_n = -2,$$

$$\text{b) } -\bar{\mu}_n = -1; U_n = 0.999,$$

$$\text{c) } -\bar{\mu}_n = -1.1; U_n = -1$$

and the phase diagrams for the dependence of the real and the imaginary part of the amplitude $A_n(t)$ are most interesting (Fig. 1).

The analysis of the numerical resolution of system (4) allows to make the next considerations. Thus, three types of the characteristic behavior of the system, which are depending from the system parameters ($\bar{\mu}_n = 1; U_n = -2$, $\bar{\mu}_n = -1; U_n = 0.999$, $\bar{\mu}_n = -1.1; U_n = -1$), can be detected. The case a) corresponds to the type of the electron transfer from the donor's group to acceptor's one at which the supplementary electron leaves of the n -th units of the carbon chain with the probability 0.5. On the phase diagram it corresponds to the limiting cycle. That is typical for the auto-vibrational type of the electron transfer in the system. The case b) corresponds to the positive value of parameter of the nonlinearity (slowly converging focus on the phase diagram). This may be interpreted as the electron transfer from the unit to the unit of the carbon's chain with the delay of the electron (see the horizontal part of time dependence of $|A_n(t)|^2$). Such type of the electron transfer is characterized for the dimerized carbon chain. The parameter of nonlinearity is determined only by value of diagonal part of the electron-vibrational interaction V_{nn} . For the dimerized carbon chain the appearing of nondiagonal part of the electron-vibrational interaction influences on the transfer of electron on the next unit additionally. That is connected with increasing of the potential barrier on the threefold bonds of the carbon chain. The case c) corresponds to the quickly converging focus on the phase diagram and almost exponential decreasing of the probability of the detection of the electron on the n -th unit $|A_n(t)|^2$ in the carbon chain. This is a so-called case of the "quasi-free movement" of the electron from the donor's group of atoms to acceptor one. This case of the electron transfer is typical for homogeneous carbon chain.

Conclusions

In the case when the supplementary electron is completely delocalized on the one-dimensional carbon chain the electron transfer has the soliton's type. Thus, the supramolecular D- π -A complex, when carbon chain is in the conformational state with total π -conjugate ion, has good transport properties.

In the dimerized case, for the same values of the parameters of the considered system takes place only the partial electron's delocalization. That essentially worsens the transport properties of considered donor-polymer-acceptor complex.

REFERENCES

1. Yourre, T.A., Rudaya, L.I., Klimova, N.V. and Shamanin, V.V. (2003) *Semiconductors* **37**(7), 807-15.
2. Carter, F.L., Siatkowski, R.E., Wohltjen, H., eds. (1988) **Molecular Electronic Devices**, Elsevier, Amsterdam.
3. Simon, J. and Andre, J.J. (1985) **Molecular Semiconductors**, Springer-Verlag, Berlin.
4. Choukroun, R. and Lorber, C. (2005) *European Journal of Inorganic Chemistry* **23**, 4683-92.
5. Aleshin, A. N. (2007) *Physics of the Solid State* **49**(11), 2015-33.
6. Yaltychenko, O.V. and Kanarovskii, E.Y. (2008) Abstract of *IIIrd International Conference "Sensor Electronics and Microsystems Technologies"*, Odessa, Ukraine, June 2-6, 180.
7. Yaltychenko, O.V. and Kanarovskii, E.Y. (2008) *Surface Engineering and Applied Electrochemistry* **44**(6), 477-9.
8. Davydov, A.S. (1982) *Uspekhi Fizicheskikh Nauk* **138**(12), 603-43.
9. Rice, M.J. (1979) *Solid State Communications* **31**(2), 93-8.
10. Peierls, R.E. (1995) **Quantum Theory of Solids**, Clarendon, Oxford.