CHARGE CURRENT THROUGH AND INJECTION RADIATION BY CARBON MOLECULES CONNECTING ELECTRODES

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The dependences of the electron affinity levels on the applied electric field for molecular junctions connecting either metal or semiconductor electrodes have been calculated in the framework of the quantum discrete model (QDM). The molecular junctions were assumed to be formed by molecules, whose structure is composed of a chain of atomic rings: bisthiolterthiophene and monolayer graphene. The dependence of the electron current through the molecular junction on the applied electric field has been calculated. The mechanisms of formation of the steplike character of the current-voltage characteristics (CVCs) in the case of metal electrodes, as well as a well-pronounced nonmonotonic behavior of the CVC in the case of semiconductor electrodes, have been analyzed. The spectral intensity of spontaneous radiation emission, which is generated when the electric current runs through the molecular junction, has been calculated.

1. Introduction

Recently, the structures with molecular junctions between macroscopic electrodes have drawn the attention of researchers owing to their interesting electrophysical properties, including CVCs, which have the steplike shape [1—4]. Of special interest is the study of the conditions and requirements, which promote the formation of such a CVC. In this work, we continue to develop the theoretical method intended for the simulation of the electrophysical processes inherent to nanosized junctions. Our calculations are based upon the QDM of a molecular junction [5] which considers the contribution of injected affinity electrons to the charge transfer process as the dominant one. The basic argument in favor of this viewpoint is the fact that the energy states of the intrinsic electrons of the molecular junction lie several eVs below the affinity levels, which, in their turn, are located close to the chemical potentials of a lot of metals and semiconductors. Hence, in order that the intrinsic electrons can participate in the charge transfer, they have to be strongly excited, e.g., by photons; but the steplike features in the CVC are observed even in the absence of auxiliary irradiation. The mechanism of the electron transport consists in that more and more affinity levels fall within the range of effective transfer if the applied electric field grows. Therefore, every new level, which gets into this range in a jumplike manner, increases the probability of the electron transfer from one electrode to another [6, 7].

In work [8], the authors used the QDM of a molecular junction in order to study theoretically a graphene {4,1} molecule in the zigzag configuration (G{4,1}Z) at various values of phenomenological parameters. In the notation above, the first figure in the braces indicates the number of rings in the direction perpendicular to the electrode plane, while the second means the number of rings along the contact planes. In this work, two modifications of graphene – a zigzag (Z) and an armchair (A) — are examined. We determined the phenomenological parameters of the model more precisely by comparing our theoretical results with experimental data and modernized the algorithm of calculations through making the account of the angle between the electric field and interatomic bond directions in a more general manner. As a molecular junction which connects macroscopic electrodes, a bisthiolterthiophene ($T3$) molecule or a graphene {3,1}
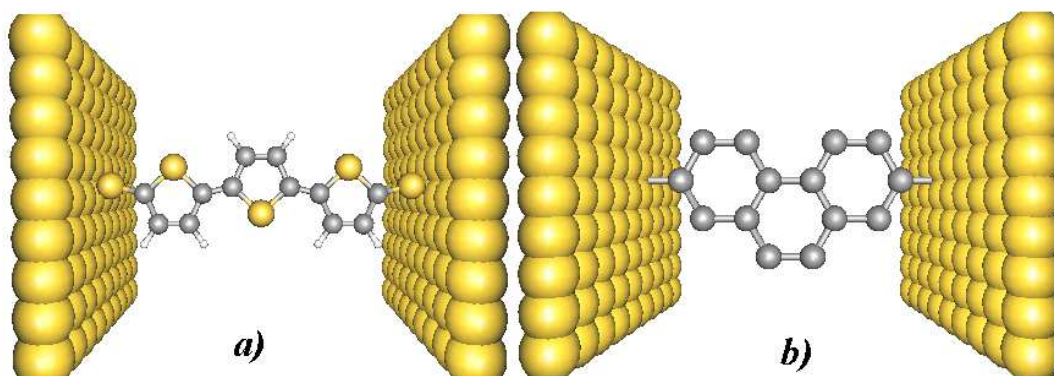
Fig. 1. Adsorbed $T3$ (a) and graphene {3,1} (b) molecules

one in the armchair configuration (G{3,1}A) adsorbed on the metal and semiconductor electrodes was considered (Fig. 1).

2. Molecules as Quantum Junctions

In the representation of secondary quantization, the Hamiltonian of a molecular junction in an electric field looks like

$$\hat{H} = \sum_{i,\sigma} \varepsilon_i \widehat{n}_{i\sigma} + \sum_{i,j,\sigma} V_{ij} \widehat{a}_{i\sigma}^+ \widehat{a}_{j\sigma}. \tag{1}$$

Here, $\varepsilon_i = \varepsilon_0 - Eey_i$, the subscript i enumerates the atoms with coordinates (x_i, y_i), E is the electric field strength, the y-axis is directed along the applied field, V_{ij} are the amplitudes of transfer between lattice sites, and the subscript σ stands for the spin. The electric field is directed along the y-coordinate and normally to the plane of electrodes. The particle number operator, $\hat{n}_{i\sigma} = \hat{a}_{i\sigma}^+ \hat{a}_{i\sigma}$, is expressed through the operators of particle creation and annihilation at lattice sites. The affinity electron occupies the relevant ground affinity level ε_0 in every carbon or sulfur atom in the molecule. The amplitude of the tunnel transition between neighbor atoms in the presence of the field depends on the value of the latter, the orientation of the covalent bond with respect to the field, and the bond length. At low field strengths, the modified tunnel barrier between the atoms with numbers i and j can be described by the quasi-classical formula

$$V_{ij}(U) = V_{ij}(0) e^{U \cdot \cos \varphi / (l \cdot E_0)}, \tag{2}$$

where l is the interelectrode distance, U the absolute value of the external potential difference, E_0 the effective field of the barrier, and φ the angle between the field direction and the direction of the bond between

neighbor atoms. Formula (2) provides a steep growth of the transition probability if the applied potential difference increases, and a reduction of the amplitude down to $V_{ij}(0)$ if the transition occurs across the field. If the applied fields are of the order of 10^6–10^7 V/cm – it is the case, which will be considered below – this formula remains still valid, because the internal crystalline fields are of about 10^8 V/cm, i.e. they are higher by an order of magnitude. In the calculations made for G{3,1}A and $T3$ molecules, we used the collection of phenomenological parameters which gives the CVCs close to experimental ones [1].

The injected particles possess two degrees of freedom in the examined system. The potential model of the problem for the affinity electrons captured by a molecule, which corresponds to the QDM, consists of a system of potential cylindrical wells symmetric with respect to bonds and so deep that the influence of the continuous spectrum states on the states of captured electrons can be neglected. A one-particle eigenvalue problem was considered for affinity electrons in the specified carbon molecules. The energy spectra obtained form a band of about 2.5 eV for the $T3$ or about 2 eV for a graphene molecule; in the case of graphene, the density of states is reduced near its band midpoint $\varepsilon_0(\mathrm{C}) = -3.0$ eV (see Fig. 2).

Among the advantages of the model in use, there is an opportunity to calculate the complete collection of the discrete electron wave functions C_{is}, where s is the state number, and i denotes the lattice site. The affinity states, which arise at that and compose a complete set, are represented by the system of two-dimensional stationary waves corresponding to the distribution of the electron density of states over the lattice sites. In so doing, the two-dimensional oscillation theorem is obeyed: every next state with higher energy is
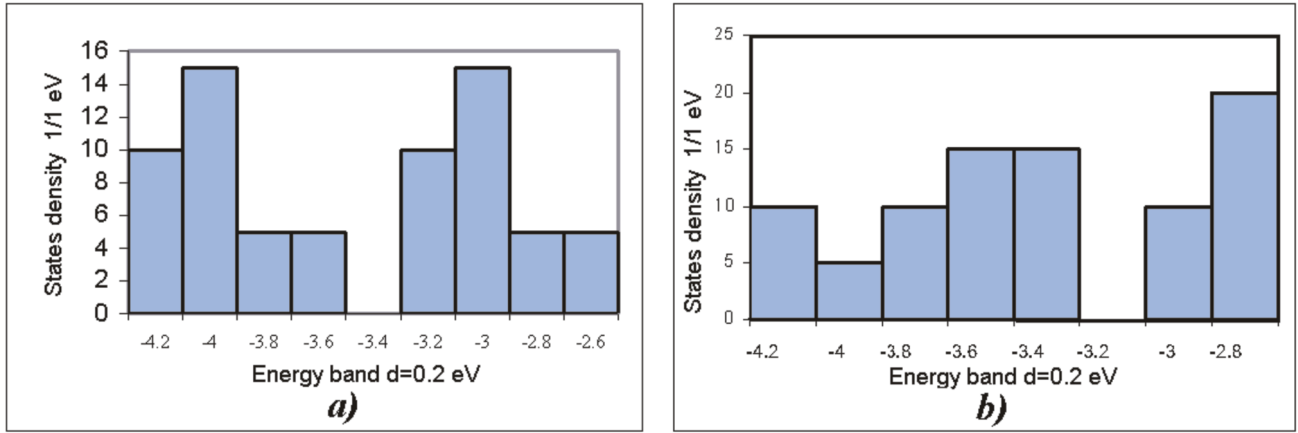
Fig. 2. The density of states (DOS) of the graphene G{3,1} (a) and T3 (b) molecules; d is the energy interval of DOS averaging

characterized by a wave function with an additional node line along the OX or OY direction.

3. Electric Current Through a Molecular Junction

After a molecule having been adsorbed onto the electrode, a thermodynamically equilibrium population of the molecular states of electron affinity is established. The conduction electrons move onto the affinity states from an unlimited source of particles – the electrode. There appears a small additive to Hamiltonian (1)

$$\hat{H}_{ad} = \sum_{i_l,\sigma} G_{i_l}(\widehat{a}^+_{i_l\sigma}\widehat{a}_{i_l\sigma} + \widehat{a}^+_{i_l\sigma}\widehat{a}_{i_l\sigma}) +$$

$$+ \sum_{i_r,\sigma} G_{i_r}(\widehat{a}^+_{i_r\sigma}\widehat{a}_{i_r\sigma} + \widehat{a}^+_{i_r\sigma}\widehat{a}_{i_r\sigma}), \tag{3}$$

where G_l and G_r are the amplitudes of electron hopping between the electrodes and the outermost atoms i_l and i_r, respectively, of the molecule. Hereafter, the subscripts l and r correspond to the left- and right-hand sides or contacts of the molecular junction, respectively. The electron density of states in the electrodes is determined by the following formulas [5]:

$$g(\tilde{\varepsilon}_l) = \frac{4\pi H_l}{h^3}(2m_l)^{3/2}\tilde{\varepsilon}_l^{1/2}.$$

$$g(\tilde{\varepsilon}_r) = \frac{4\pi H_r}{h^3}(2m_r)^{3/2}\tilde{\varepsilon}_r^{1/2}. \tag{4}$$

Here, H_l and H_r are the effective volumes of the left and right electrodes, respectively, which contact with the

molecular junction; m_l and m_r are the effective electron masses in the electrode materials; the quantities

$$\tilde{\varepsilon}_{l,s} = E_{Fl} - \chi_l + E_s + U_l,$$

$$\tilde{\varepsilon}_{r,s} = E_{Fr} - \chi_r + E_s + U_r \tag{5}$$

are equal to the energy of the s-th electron state, reckoned from the beginning of the Fermi steps in the left and right metal electrodes, respectively, taking into account the applied bias voltages U_l and U_r; and E_{Fl} and E_{Fr} designate the corresponding Fermi energies. The chemical potentials of the electrodes, χ_l and χ_r, as well as the energy of the affinity electrons of the molecular junction, E_s, are counted from the vacuum level taken as zero. The equilibrium populations of electron states in the thermostats are described by the Fermi distribution. A bias of the electrode potentials with respect to each other gives rise to the violation of thermodynamic equilibrium in the molecular junction. In the molecule that connects electrodes, a stationary – although nonequilibrium – distribution of the state population is established. This distribution satisfies the condition that electrons are not "accumulated" at the molecule during their transportation. The current through the molecule can be written down as a sum of electron streams through all energy levels s,

$$I = \frac{2\pi e}{\hbar}\sum_{S} |\sum_{i_l} G_{i_l,s}|^2 |\sum_{i_r} G_{i_r,s}|^2 g(\tilde{\varepsilon}_{ls})g(\tilde{\varepsilon}_{rs}) \times$$

$$\times \frac{N_l - N_r}{|\sum_{i_l} G_{i_l,s}|^2 g(\tilde{\varepsilon}_{ls}) + |\sum_{i_r} G_{i_r,s}|^2 g(\tilde{\varepsilon}_{rs})}, \tag{6}$$

where N_l and N_r are the populations in the electrodes. The quantities G_{ls} and G_{rs} are determined as the

products of the amplitude of transfer through the outmost adsorption bonds i_r and i_l, respectively, and the factor C_{is} of the canonical transformation from the initial site representation to the eigenstate one. If the energetic quantities in Eq. (6) are measured in eV units and the effective volume H in $\mathring{A}^3$ ones, the dimensional parts of the total current and the current density are $I_0 = 10.41HG^2$ μA and $10.41H^{1/3}G^2$ μA/$\mathring{A}^2$, respectively.

The CVC of a bisthiolterthiophene molecule junction, calculated in the framework of the proposed QDM, is shown in Fig. 3.

Consider the relation between the CVC and the energy spectrum of a molecular junction connecting gold electrodes. In Fig. 4, the diagrams presented the energy spectrum versus field strength for a graphene G{3,1}A (a) and a $T3$ (b) molecule are depicted. The energy spectrum of the graphene molecule is simpler in comparison with that of the $T3$ one. If an external electric field is applied, four levels in the $T3$ spectrum become split. As the applied voltage U increases, the affinity levels cross, one by one, the range of effective transfer near the Fermi energies E_{Fl} and E_{Fr}.

As a rule, every new level, entering into the active range, is associated with a section in the CVC which grows drastically, while the energy gaps correspond to the CVC plateaus (Fig. 4,c). The step-like character of the CVC is more pronounced at reduced temperatures (Fig. 4,d). However, the contribution of every state to the total current is determined not only by its position with respect to the levels E_{Fl} and E_{Fr}, but also by the orientation of the electron density of the state in relation to the field direction. This phenomenon manifests itself most noticeably when two states enter the active range of transfer simultaneously.

If the electrodes are made up of semiconductor materials, the energies of the s-th states in Eq. (5) should be sought as $\tilde{\varepsilon}_{l,s} = E_s - E_c - U_l$ and $\tilde{\varepsilon}_{r,s} = E_s - E_c - U_r$, where E_c is the bottom of the conduction band in the electrodes. For calculations, we used the following parameters of germanium: the bottom of conduction band $E_c = -4.425$ eV, the chemical potential $\chi = -4.76$ eV, and the energy gap width $E_g = 0.67$ eV. The corresponding field diagrams of the spectra and the CVCs are presented in Fig. 5. Similarly to the case of gold leads, the correlation between the CVC and the band diagram is observed for germanium ones as well. The reduction of the current stems from the lower values of the density of states at the right lead, which corresponds to such a position of the active level of the molecule, when it "approaches" the bottom of the
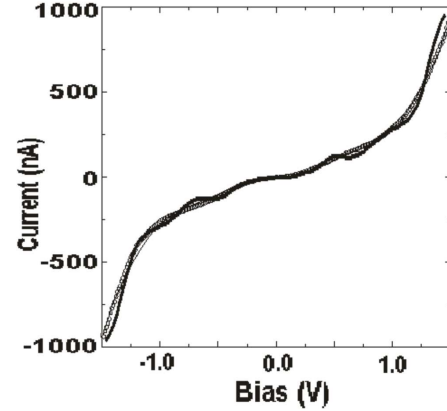

Fig. 3. Experimental (hexagons) and theoretical (solid curve) CVCs of the $T3$ molecular junction connecting gold electrodes. The Fermi energy for gold is $E_F = 5.53$ eV

conduction band. Sharp drops in the CVCs are associated with the fact that, as soon as the level which is responsible for the dominant contribution to the current at a given field strength, falls into the forbidden gap, its contribution to the current becomes zero.

An important difference (by six orders of magnitude) between the current values in the cases of adsorption onto metal and semiconductor electrodes should also be emphasized. It is associated with the fact that the current amplitude is governed by the population of the electron states in the cathode (the right electrode).

4. Spontaneous Radiation Emission

If a current runs through a quantum-mechanical system, a stationary thermodynamically nonequilibrium population of states is established. A substantial inverse population, which arises provided certain voltage values, generates spontaneous radiation emission. The spectral density of radiation, when electrons transit from the top levels of the quantum junction to the bottom ones, looks like [5—7]

$$J(\omega, U) = J_0 \sum_t n_t \sum_{s<t} (1 - n_s) \frac{\omega^4 |d_{st}|^2 \Gamma_{st}^3}{(E_t - E_s - \omega)^4 + \Gamma_{st}^4}. (7)$$

In this expression, Γ_{st} is the width of the line resulted from interactions that were not taken into account, n_s and n_t are the stationary nonequilibrium populations of states that take part in the transition, and d_{st} is the dipole moment of the transition. The current, which flows through the molecule, is accompanied by the polarization of the latter owing to an asymmetric
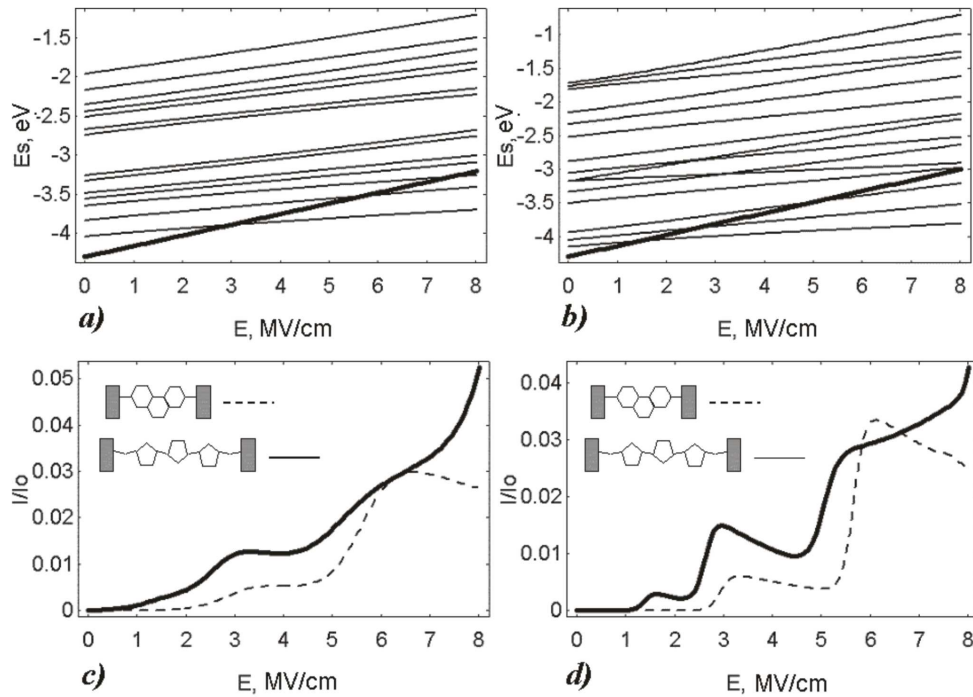
Fig. 4. Comparison of the dependences of the energy spectrum versus the applied field strength for the graphene {3,1} (a) and $T3$ (b) molecular junctions adsorbed on gold electrodes; the thick line shows the field-induced shift of the Fermi level in the electrode. CVCs for the graphene {3,1} and $T3$ molecular junctions at temperatures of 300 (c) and 100 K (d)
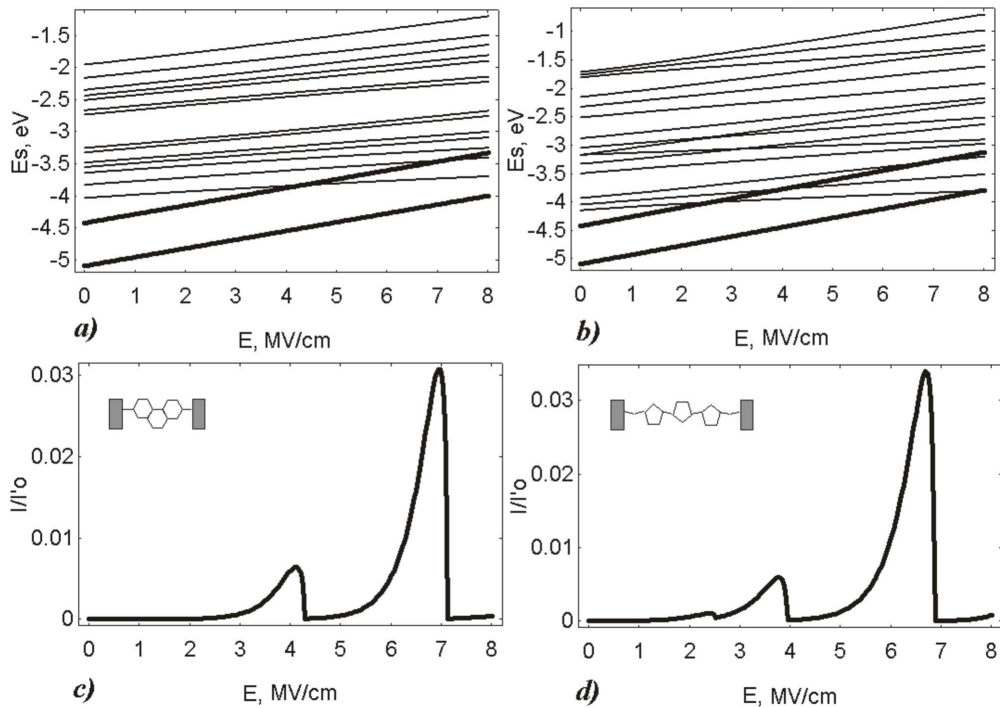

Fig. 5. Comparison of the dependences of the energy spectrum versus the applied field strength for the graphene {3,1} (a) and $T3$ (b) molecular junctions adsorbed on germanium electrodes; two thick lines show the field-induced shift of the forbidden gap edges in the electrode. CVCs for the graphene {3,1} (c) and $T3$ (d) molecular junctions at a temperatures of 300 K. $I_0' = I_0 \times 10^{-6}$
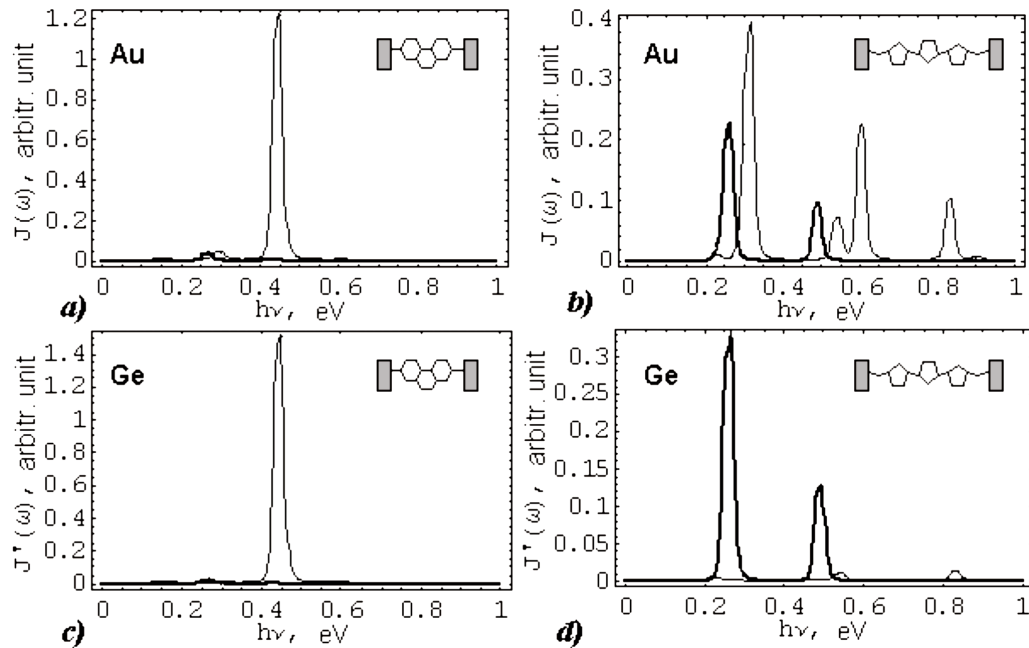
Fig. 6. Comparison of the radiation spectral densities of two molecular – graphene {3,1} (*a* and *c*) and *T*3 (*b* and *d*) – junctions adsorbed on gold (*a* and *b*) and germanium (*c* and *d*) electrodes at various field strengths: $E = 6$ (thick) and 8 MV/cm (thin curve). $J'(\nu) = J(\nu) \times 10^{-6}$

distribution of the injected electron cloud over the molecule in its every state. The maximal value of the dipole moment in every molecular state, calculated without taking the moment sign into account, is attained if the corresponding energy level becomes located near the effective transfer range. The correlation between the field dependences of the dipole moment of every state and the relevant population is observed. The direction of the dipole moment is associated with that of the field-induced outflow of the wave functions. The main contribution to the total dipole moment is given by the states with maximal population. According to the results of our calculations, if the concentration of junctions that connect the plane surfaces of metal electrodes is of the order of 1 nm^{-2}, the integrated intensity of emission of the interelectrode gap should be less than 1 μW/cm^2. The states within the band of width U in the energy spectrum of the molecule participate in the radiation emission processes. The characteristic frequencies lie in the infra-red range of the spectrum.

In Fig. 6, we show the spectral densities of spontaneous radiation emission calculated for the graphene {3,1} and *T*3 molecules and for various strengths of the applied electric field. Here, as was in the CVC case, the difference by six orders of magnitude

is observed for gold and germanium electrodes, which is also caused by the electron population of their levels.

According to the results of our calculations, the main contribution to the spectral density of radiation is made by the electron transition from the 3-rd to 1-st affinity level of the spectrum for the graphene molecule and from the 3-rd to 2-nd one for the *T*3 molecule, irrespective of whether the molecule is adsorbed on the gold or germanium electrode.

5. Discussion and Conclusions

There is no doubt that the mechanism of electron transfer through molecular junctions requires to be studied further, both theoretically and experimentally. In contrast to the junctions consisting of mesoscopic nanowires, which, despite of their small transverse dimensions, nevertheless, do contain statistical amounts of atoms and conduction electrons, the systems considered above are characterized by a small number of atoms. When a current runs through a mesoscopic system, the charging of the latter is relatively weak and practically does not reconstruct the spectrum of the junction. In this case, active is the mechanism of charge transfer by means of either the lowest unoccupied or the

highest occupied states [9, 10]. But this mechanism is often applied for systems, which are similar to molecular junctions, but where the number of atoms and electrons participating in charge transfer is 3 to 4 orders of magnitude lower [1, 4, 11, 12]. The difficulty is that the suitable levels of the excited molecular states are located too low with respect to the chemical potential level in electrodes (from 10 to 12 eV deeper for similar carbon molecules [13]); the same results are given by quantum-chemical calculations in the framework of the MO-LCAO methods and others [11]. This means that a neutral — without charging of the molecule — mechanism of transfer does not work. But charging the molecule moves it up into the class of systems, which have been poorly studied by now — negative molecular ions [14] with a substantially reconstructed spectrum of excited states. The QDM, which was used in this work, does not proceed from a neutral molecule, which, as we believe in accordance with the authors of work [14], reconstructs its highest states too strongly, but proceeds from a separate negative ion C^- with the corresponding level of a captured external electron. In the structure of $T3^-$ molecule, these affinity levels create a band, through which the electron transfer takes place. It should be noted that the total charging of the molecule was supervised in the course of calculations, so that its value did not exceed unity at the potential biases considered. The molecule charge, which exceeds unity at higher voltages, is critical, because it leads to a special state of the molecular junction — a trigger state, in which the molecule spends some part of its time in the charge state $T3^0$ (the current is absent), some part in $T3^-$ and some part in $T3^{2-}$ one (a molecular trigger [6, 15]).

The model allowed us to calculate the CVC of a molecular junction between macroscopic electrodes, which reflects well the features observable in experiment. It was confirmed that the nonmonotonic character of the CVC, the presence of the plateaus and the sections, where the dependences of the current on the external field strength grow up or fall down, are caused, on the one hand, by the passage of the molecular affinity levels near the Fermi surface of the electrodes, and, on the other hand, by a field-induced outflow of the electron cloud from the junction leads. The number of plateaus or peaks in the CVC directly depends on the number of energy levels in the spectrum of the molecular junction, which enter into the range of effective transfer. While comparing the results of computer experiments, it follows that the nonmonotonic behavior of the CVC is more

appreciable if semiconductors are used as electrodes, although the current amplitude strongly diminishes (by approximately 6 to 7 orders of magnitude) in this case.

The model considered above predicts a substantial polarization of the molecule owing to the asymmetry of the affinity electron wave function in an external field. Moreover, in the course of the transfer, there appears the inverse population of affinity levels, which, in its turn, leads to spontaneous radiation emission. The latter effect is an analog of the well-known injection radiation in quantum cascade lasers. The specific feature of the radiation emission spectra of molecular junctions is their infra-red interval and the fact that only one frequency dominates, as a rule. This can be explained by the fact that only a small number of levels belonging to the band of the energy spectrum of the molecule, the width of which is approximately equal to the potential bias U, is engaged in the radiation emission processes.

The predicted effects of polarization and inverse population of the junction, as well as its infra-red injection-induced radiation with dominating frequencies, distinguish the proposed model of charge transfer through the affinity states from the model of charge transfer through the states of a neutral molecule taking the Coulomb barrier into account [1, 4, 11, 12], where similar effects are not considered.

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СТРУМ ТА ІНЖЕКЦІЙНЕ ВИПРОМІНЮВАННЯ
У ВУГЛЕЦЕВИХ МОЛЕКУЛАХ, ЩО
ПЕРЕМИКАЮТЬ ЕЛЕКТРОДИ

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Р е з ю м е

У рамках квантової дискретної моделі виконано розрахунок польових спектральних діаграм рівнів спорідненості до електрона для двох молекулярних перемичок між металевими і напівпровідниковими електродами. Для утворення молекулярної перемички були використані молекули, які мають структуру ланцюжків з атомних кілець: бістіолтертіофен та одношаровий графеновий ланцюжок. Розраховано величину струму електронів у залежності від прикладеного електричного поля. Аналізуються механізми формування східчастого характеру вольт-амперних характеристик (ВАХ) у випадку металевих електродів і різкої немонотонності ВАХ для напівпровідникових електродів. Розраховано спектральну густину спонтанного випромінювання, яке виникає при проходженні електричного струму через молекулярні містки.