Photosensitive Polymeric Composites for Information Technologies

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CHAPTER ONE

SOME CURRENT TRENDS IN THE DEVELOPMENT OF INFORMATION MEDIA

In a broad sense, information technologies include processes, methods of searching, collecting, storing, processing, spread information, as well as methods for implementing such processes and methods. The most important direction in the development of information technologies is the search, development, and improvement of information media, i.e. media for recording, and processing information.

Information technologies are developing rapidly, especially in recent decades. This can be asserted both about the means of recording information and about the means of its processing, transmission, conversion, etc. A lot of new media, devices, and systems are developed for all sorts of applications. As a rule, they are on different physical principles and use a different elemental base. Their creation and improvement often take place in independent ways. In order to become competitive, information technology must have one or more advantageous qualities compared to others. The aspiration for the miniaturization of the elemental base of electronics in general and information systems, in particular, has always been one of the main goals of technology development. The conditional start of this process one can consider the possibility of placing a million solid-state transistors in an integrated circuit with an area of 1 cm^2. The base of the chip was crystalline silicon. The miniaturization of these chips has led to an exponential increase of efficiency and velocity per unit cost (and mass) of computing systems with a doubling period of 2 years. This empirical law was formulated in 1965 by Gordon Moore [1]. New models of microcircuits are developed in 18 - 24 months after the appearance of the previous ones, their capacity increases about twice each time. However, this process cannot continue forever. There are certain fundamental problems limiting such trends. For example, for silicon, this is a problem of strength, oxide thickness, track width, etc. Besides, in accordance with the Moore law, an increase in the functionality of electronic components is accompanied by an approximately exponential increase in the cost of their production.

Currently, as an alternative to traditional semiconductor active elements, tunnel field-effect transistors [2], graphene-based field-effect transistors [3, 4], spin field-effect transistors [5] are considered. Keeping the tendency of miniaturization of active elements of electronics will lead to the fact that they must reach molecular or even atomic sizes. Several molecules or even one molecule placed between the electrodes will have to the basic functions of digital electronics devices. Extrapolation of Moore's law with an exponential decrease in the number of electrons per elementary device yields one electron per device approximately in 2020. In this case, the laws of quantum mechanics become relevant, and distortions of bit-by-bit memory and processor errors due to quantum fluctuations are possible.

Over the past 15 years, a new direction of information technology has been developing intensively - quantum computer science [6, 7]. Using quantum computers, to solve a lot of problems that cannot be solved using traditional computers is supposed, since an entirely new way of information processing can be implemented in them. For example, quantum cryptography and related communication technologies provide a high degree of protection for transmitted information [7, 8].

In general, the idea of recording and processing information at the quantum level was born soon after the discovery of the information properties of the wave function in the Schrödinger equation [9]. A quantum ensemble can simultaneously play the role of both the recording medium and the means of information processing, i.e. some kind of "quantum computer". In it, each element of the algebra of logic can be associated with its own Hamiltonian in the state space of the bistable system, which corresponds to the information units. A very attractive feature of quantum information systems is the supposed possibility of superlight information exchange [10]. This assumption is based on the fact that at the time of the quantum measurement there are non-local correlations. However, all schemes in which correlated quantum systems are spread over very large distances from each other are unsuitable for superlight quantum communications due to the basic probabilistic principle of quantum theory. Most likely, quantum communication is possible at short distances and in complex irreversible systems, for example, in biological ones. Intensive research in this direction and the search for appropriate systems continues. For example, the 2012 Nobel Prize was awarded to S. Haroche and D. Wineland “for ground-breaking experimentalmethods that enable measuring and manipulation of individual quantum systems”.

The search for new media or even new concepts for the development of the element base of information technologies remains relevant. Analyzing the quantity and quality of modern research in the field of physics and chemistry of nanostructures, one can argue that these areas are currently among the priorities in the scientific community. This state of affairs is determined by the wide opening prospects for the practical use of nanoscale objects in electronics, optics, information technology, etc.

The base for determining nanomaterials is the crucial role of having multiple interfaces. With typical particle sizes d = 0.1–100 nm, the fraction of interfaces in the total volume of the material can reach 50% [11]. In this case, there are significant changes in the properties of solids due to the modification of the structure and the electronic structure. It is also possible due to artificial change of these properties by doping or using active matrices in which nanoparticles are placed.

With a decrease in particle size, a macroscopic manifestation of quantum size effects is observed. For example, the electronic excitation of a semiconductor crystal leads to the formation of weakly connected electron-hole pairs. The delocalization area of such a pair can be many times larger than the lattice constant. The decrease of a semiconductor crystal to a size comparable to the size of this area affects its electronic characteristics [12]. Energy bonds are transformed into separate levels, as shown in Fig 1.1 [13]. In fact, nanomaterials are a transitional region between macroscopic and molecular objects. In fact, nanomaterials are a transitional region between macroscopic and molecular objects.

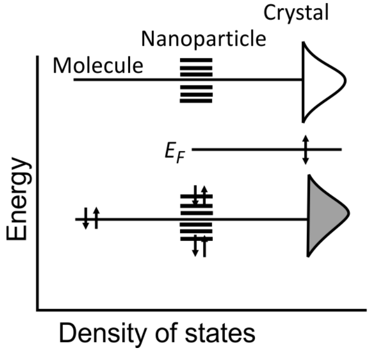

Fig.1.1. Electronic spectra of isolated molecules, nanoparticles, and crystalline semiconductor.

The development of molecular nanostructures can be considered a continuation or one of the directions of modern nanotechnology development. Naturally, organic materials play a crucial role here due to their functionality, wide possibilities for varying parameters, as well as relative cheapness and manufacturability. Their diversity expands every year, and the amount of synthesized compounds increases exponentially. Organic materials in nanotechnology are used both as integral participants in the technological process (for example, in nanolithography) and as independent objects and devices in molecular electronics.

Interesting nanomaterials which have promising practical application are nanocomposites. The most widespread are nanocomposites based on polymer matrices [14 - 16], in which nanosized particles or fibers are placed. Modern interest for them arose from studies of polymers containing particles of exfoliated clay [14 - 17]. In such systems, unique mechanical properties are observed [17]. The reason for adding fillers to polymers was the need to increase their rigidity. Appropriately distributed clay plates in the polymer seemed very effective for this purpose.

Later, studies of nanocomposites with carbon nanotubes, carbon nanofibres, graphene, inorganic particles, and modified fibers appeared. Depending on the properties of the polymer matrix, methods of preparation of mechanical, electrical, electro-optical, etc. properties of nanocomposites can vary widely. This, in turn, determines the variety of possibilities for their applications. For example, the barrier properties of polymer membranes can be significantly modified by introducing inorganic particles of a certain shape and size [18], which results in a change in the diffusion length of penetrating molecules. Another useful property that can be achieved in nanocomposites using nanoplates or fibers is their increased resistance to ignition [19]. The causes of this phenomenon are currently being investigated [14]. A rapidly developing area is the use of polymer nanotechnologies and nanocomposites for biomedical and biotechnological applications [20, 21].

Nanocomposites and nanotechnologies are widely used in the development of modern electronics and optoelectronics devices [22]. The size range of these devices is already close to the nanoscale. Their purpose and properties are very diverse and can be changed by technological methods. For example, the doping with highly luminescent semiconductor particles into an organic semiconductor matrix allows for the optimal combination of the properties of substances to create highly efficient light-emitting diodes and low-cost solar energy converters [23]. Additions of inorganic nanoparticles in polymer matrices can control the conductive, photoconductive, and electrooptical properties of composites and change the spectral ranges for the existence of these effects [24, 25].

The electrical conductivity of carbon nanotubes in thermally insulating polymers is also of considerable interest [24, 26]. The potential of this application includes protection against electromagnetic interference, transparent conductive coatings, electromechanical actuators, etc.

The basic element of information technology is the information medium, i.e. the medium for recording and/or processing information. A huge amount of modern fundamental and applied research is devoted to its creation and improvement. As with electronics, miniaturization is the main trend in this direction. In the case of bitwise recording of information, miniaturization corresponds to a decrease in the amount of compound needed to record of one bit. On the other hand, polymeric materials are used in all spheres of human life and activity. With the development of information technology, they have become almost indispensable when creating material media (media) for recording, storing, displaying and processing information. Polymer composites can be both magnetic [27, 28] and non-magnetic [29 – 31]. Different are and their research methods.

At present, polymer composites are used as photoconductive systems [31, 32], as holographic recording media [33 - 37], as media for polarization-sensitive diffraction gratings [38 - 40], as media for electro-optical modulators [41 - 43], as media for photovoltaic light energy converters [42 – 45], and others.

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CHAPTER TWO

PHOTOCONDUCTIVE POLYMERIC COMPOSITES

Photoactive media are widely used in modern information technologies. Among them, the most important place is occupied by a large class of media based on thin photoconductive film polymer composites (FPC). The most important in the photoconductivity effect is photogeneration, i.e. the formation of free carriers under the light influence. These carriers move in an external electric field and do not interact with each other in the FPC volume. Usually, FPCs consist of a polymeric binder and organic additives. Despite the variety of known and newly synthesized organic compounds, some of which can form thin films and others can absorb visible light, the choice of compounds for photoconductive FPCs seems to be a difficult scientific task because not always intensive absorption of light is accompanied by effective photogeneration. The effective photogeneration is determined by the probability of electronic transitions between the excited photogeneration centers and the molecules through which non-equilibrium carriers are transported. At the present time, a large amount of experimental data has been accumulated and adequate model concepts of photophysical processes in organic materials have been proposed. In this Chapter, only some general patterns of photogeneration and transport of charge carriers in FPC are considered.

2.1. The model of photoconductive film polymeric composite

The absence of translational symmetry in the distribution of molecules is typical for practically used FPC. From the point of view of the disorder model, their structure corresponds to a solid solution [1 - 4]. In general, this is a true solution of three types of compounds in a neutral film-forming binder. The molecules of two compounds in a solid solution form the transport zones for electrons and/or holes, the molecules of the third compounds are the centers of photogeneration and/or recombination of charge carriers. The diagram of the transport zones of electrons and holes as well as electronic levels of photogeneration centers [3] in the sample of practically used FPC is schematically presented in Fig.2.1. In this figure, 1 is the electron transport zone formed by lower unoccupied molecular orbitals (LUMO) of acceptor molecules located at the distance $R_n = N_a^{-1/3}$ from each other (N_a is the concentration of these molecules in FPC), 2 is the hole transport zone formed by higher occupied molecular orbitals (HOMO) of donor molecules located at the distance $R_p = N_d^{-1/3}$ from each other (N_d is the concentration of these molecules in FPC), 3 are the centers of photogeneration and recombination, which are represented by two molecules. Typically, the structures for the investigation of FPC and their applications consist of a solid dielectric substrate with successively deposited layers of electrically conductive contact 1 with the work function of E_{F1}, FPC of thickness L, and an electrically conductive contact 2 with the work function of E_{F2}. Sometimes (for example, in electrography and holography), the contact 2 is absent and external electric field in FPC is formed by the electric charge of ions deposited on the FPC surface by the corona gas discharge.

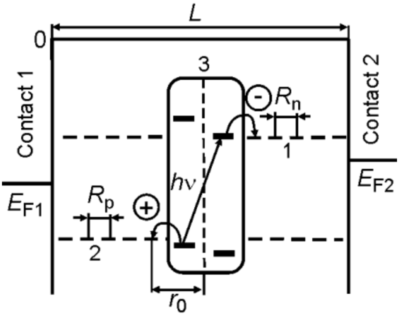

Fig.2.1. Diagram of energy levels in a sample with FPC and electrical contacts.

The electronic levels of the molecules forming the transport zone are not split and remain local but the wave functions of the molecules and their ions overlap. The radii of localization of electron wave functions (α_n) on acceptor molecules and holes (α_p) on donor molecules can differ. Transfer of charge carriers in the transport zone occurs as a result of tunnel transitions between local molecular levels. For the many practically used FPC, the dependence of the mobility (velocity of motion in a single electric field) of electrons (μ_n) and holes (μ_p) in the corresponding transport zones on the intensity of the external electric field (E) and temperature (T) was empirically found [2 - 8]:

$$\mu_n \sim R_n^{2}\cdot\exp(-2R_n/\alpha_n)\cdot\exp(-(W_{0n} - \beta E^{1/2})\cdot(T^{-1} - T^{-1}{}_0)/k_B), \qquad (2.1)$$

$$\mu_p \sim R_p^{2}\cdot\exp(-2R_p/\alpha_p)\cdot\exp(-(W_{0p} - \beta E^{1/2})\cdot(T^{-1} - T^{-1}{}_0)/k_B), \qquad (2.2)$$

where W_{0n} and W_{0p} are the activation energies of mobility of electrons and holes at $E = 0$, β is the coefficient coinciding numerically with the Pool-Frenkel constant [9], k_B is the Boltzmann's constant, T_0 is the temperature at which extrapolated to higher temperatures experimental dependencies of $\lg(\mu_n)$ and $\lg(\mu_p)$ on T^{-1} measured for different field strengths E intersect.

In Fig. 2.1, the photogeneration centers for generality are represented by two-part systems to emphasize that during the excitation of photogeneration, when the light quantum with energy $h\nu$ is absorbed, either complete electron transfer between the molecules or the redistribution of the electronic density and its concentration in one of the parts of the excited dye molecule [10] occur. The first case takes place in intermolecular complexes with charge transfer (CT-complexes) [3, 11] or between donor and acceptor parts of molecules, for example, in compounds with intramolecular charge transfer (CICT) [3, 12, 13].

When the photon is absorbed by the photogeneration center, the electron and hole are separated and can leave the photogeneration center passing to the corresponding transport zone and form a coulomb-bounded (geminal) electron-hole pair (EHP) with an initial distance r_0 between the charges (Fig.2.1). The quantum yield (Φ_0) of the EHP formation is determined by the intramolecular conversion and interconversion of the molecule of the photogeneration center and also by the ratio of the energies of HOMO and LUMO of this center to the energies of the corresponding molecular orbitals of the molecules forming the electron and hole transport zones. The charge carriers in the EHP can then either go away at long distances thereby creating free non-equilibrium carriers of photoconductivity or recombine in the photogeneration center. For many practically used FPC, the quantum yield (η) of photogeneration of free carriers can be described by the following empirical relationship [6]:

$$\eta \sim \Phi_0 R_n R_p \exp(-R_n/\alpha_n - R_p/\alpha_p)\cdot\exp(-(W_{0ph} - \beta E^{1/2})\cdot(T^{-1} - T^{-1}{}_0)/k_B), \qquad (2.3)$$

where $W_{0ph} = e^2/\varepsilon r_0$ is the activation energy of the photogeneration of free charge carriers at $E = 0$ (e is the electron charge, ε is the permittivity, r_0 is the initial distance between the charges in EHP), T_0 is the temperature at which extrapolated to higher temperatures experimental dependencies of $\lg(\eta)$ on T^{-1} measured for different field strengths E intersect. Within the framework of the two-stage process of carrier photogeneration through the formation of EHP and its dissociation, the value W_{0PH} can be identified as the energy of the Coulomb interaction between an electron and a hole in EHP. The non-equilibrium charge carriers can be captured by local energy states (traps) during their movement in the direction of the accumulating contacts in the FPC volume. The traps for holes are formed by the molecules with the ionization potential less than the ionization potential of molecules from the hole transport zone. The traps for electrons are formed by molecules with the electron affinity energy greater than the electron affinity energy of molecules from the electron transport zone. Also, molecules with a large dipole moment or localized electric charge can act as the traps. Besides, non-equilibrium charge carriers photogenerated in different photogeneration centers or injected from electrical contacts can come together near the photogeneration/recombination center and recombine with each other in this center. The described scheme of photogeneration, transport, and recombination of charge carriers in FPCs reflects the actual situation very approximately but it is sufficient to reveal significant differences from crystalline and amorphous glassy semiconductors.

2.2. Electronic transport

Let us briefly consider the main electronic processes determining the photoelectric properties of FPC which are necessary for their practical application in information media: photogeneration, recombination, transport, and capture of charge carriers. The regularities of transport of charge carriers in FPC differ significantly from those in ordered organic solids and in glassy inorganic materials. The values of mobility of electrons and holes in the vast majority of FPCs do not exceed 10^{-4} $m^2/(V \cdot s)$ [5 – 9, 14 – 16]. Such small values restrict the choice of experimental techniques for studying electronic transport. In the investigations, the main attention was paid to the dependencies of μ_n and μ_p on E, T, L, N_a, N_d.

The experimental results of studies of the electronic transport in the most FPCs are satisfactorily described by dependencies (2.1) and (2.2). However, there is no common point of view for explaining these dependencies. This is caused by the presence of general and alternative factors and examples in various model considerations explaining the experimentally observed dependencies (2.1) and (2.2). For example, for explanation of the dependency of the electron mobility on the field strength E and temperature T, one can use the Onsager model [17, 18] whose analytical representation corresponds to the Poole-Frenkel model for a high external electric field strength [19] because the presence of impurity centers can not be excluded in real FPCs. These ones already have an electric charge or it appears as a result of their thermal field ionization from the moment of application of an external electric field during the experiments [6]. Besides, the effect of the dipole moments of the FPC molecules on the motion of free charge carriers [19, 20] should be taken into account. Within the framework of such considerations, the parameter T_0 in (2.1) and (2.2) is related to the peculiarities of the Coulomb centers (for example, to their destruction temperature [21]) controlling the transport of non-equilibrium carriers or to the diffusion and tunnel transport of charge carriers in strong electric fields near Coulomb centers.

However, for the explanation of the dependencies (2.1) and (2.2), only an idea about the amorphous state of FPC is sufficient: the idea of the energy and spatial disordering of local centers from the corresponding transport zones. The transport of charge carriers between individual molecules or fragments of the FPC polymeric chain occurs as a result of tunnel transitions. Therefore, the probability of a charge carrier jump substantially depends on the distance between molecules, steric factors, molecular vibrations, and on the difference between the energies of LUMO (for electrons) and HOMO (for holes) of these molecules [18, 22 - 24]. Thus, the effect of the electric field E and temperature T is in the facilitation of intermolecular electronic transitions. The integral mobility of the packet of charge carriers is described by the dependencies (2.1) and (2.2) due to the dispersion of the distances and energies of the molecules. In polymeric matrixes, the use of conceptions of the long-range order is not fully correct at all. However, from the positions of the cluster model, it is possible to assume the existence of a correlation in the spatial and energy distributions of the molecules through which the transport occurs. In this case, it is possible to speak of the legitimacy of the existence of the discussed model concepts. Besides, partial anisotropy in the distribution of the energy states of molecules in the direction of motion of non-equilibrium charge carriers in the FPC volume can arise when an external electric field is applied due to the polarization of the electron shells of these molecules. This is confirmed, in particular, by the influence of the external electric field on the distribution of the electronic density on the HOMO in organic dyes as it can be seen from the changes of their optical absorption spectra [13, 25 - 28]. Thus, in electronic transport even through nonpolar molecules, the external electric field "makes an order" in the distribution and provides quasi-one-dimensional transport revealing itself in the dependencies (2.1) and (2.2). Taking into account the change of the distribution of the electronic density under the influence of an external electric field can be useful in further improving the theoretical model concepts of electronic transport. The unidirectional displacement of the electronic density in a real organic molecule is accompanied by an increase of the influence of positively charged atomic nuclei from which an outflow of electronic density occurs. Such positive and negative charges induced by the field can interact with non-equilibrium carriers and are analogous to Coulomb centers by the nature of the effect on transport.

Thus, for a significant increase of the velocity of motion of non-equilibrium charge carriers in the FPC, the transport zones should contain molecules (or fragments of the polymeric chain) with minimal and preferably regular distances from each other without additional links increasing steric difficulties for π-electron transitions. Besides, these molecules or fragments of the polymeric chain should have delocalized molecular frontier orbitals but with a small dipole moment. The condition for minimizing the dipole moment of molecules as well as the absence of electric charges of fragments of molecules or ions is determined by the necessity to level out the influence of Coulomb centers on transport. Meeting these conditions in the choice of the FPC components with the achievement of sufficient chemical purity and structural homogeneity is an important factor in the creation of transport and photogeneration FPCs. It should be noted that samples of FPC with high electronic transport parameters do not always possess photoconductive properties. Therefore, a detailed study of the features of photogeneration of charge carriers is an actual problem.

2.3. Photogeneration of charge carriers

Molecular media (both organic crystals and polymeric films with dopants with low molecular weight) are solid state systems formed due to intermolecular interactions. The intramolecular structure of covalently bonded atoms in the molecule and crystal or the CT-complex structure appeared due to the donor-acceptor (D-A) interaction practically do not change when a solid is formed. Depending on the electronic structure of the molecule, the energy of the intermolecular interaction varies within the wide range from 10^{-3} eV (for the Van der Waals interaction) to units of eV (in the case of the D-A bond).

The formation of CT-complexes or polymer doping with different sensitizers (for example, dyes) is determined by a whole set of intermolecular interaction forces: Van der Waals, Coulomb, dipole-dipole, polarization, induction, and others. The complex with charge transfer can be formed at small distances between the donor and acceptor molecules (~

0.35 nm [10, 29]) and their orientation providing the most effective overlapping of their orbitals. In this case, DA complex or CT-complex appear. This process is caused by a redistribution of the electronic density due to electron transfer from the higher occupied orbital of the donor molecule to the lower unoccupied orbital of the acceptor molecule [10]. Partial or complete charge transfer can occur already in the ground or only in the excited state of the complex. Depending on this, the complexes are divided into strong (ion-radical salts), weak, and so-called contact.

According to the quantum chemical theory [30, 31], the intermolecular D-A interaction arises from the quantum-mechanical mixing of two states: the nonpolar (D-A) when only the Van der Waals interaction takes place between the donor and acceptor molecules, and the polar D^+-A^- when the electron is transferred from the donor to the acceptor. The average energy of the D-A interaction W_{DA} is determined by the resonance integral of the polar and nonpolar components, and the dipole $D^{\delta+}$-$A^{\delta-}$ actually describes the mixed state, where $0 \leq \delta \leq 1$ is the degree of charge transfer. In terms of the energy within the range 0.05 - 1.0 eV, the intermolecular D-A interaction (in the complex) is between a covalent bond (unity eV) on the one hand, and a hydrogen (0.05-0.5 eV) and Van der Waals (10^{-4} -10^{-1} eV) bonds on the other hand.

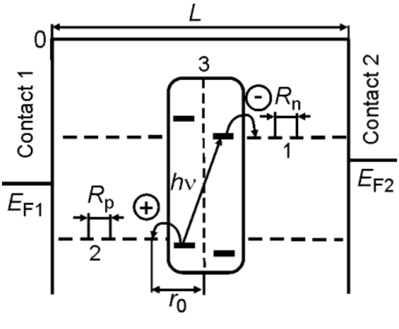

Fig.2.2. The energy scheme of different types of D-A complexes [30].

A generalized energy diagram of D-A systems of different types is shown in Fig. 2.2, where IRS is the ion-radical salt, CT-complex is the complex with charge transfer, CC is the contact complex, E_0 is the ground level, $E_S^{(i)}$ is the singlet excited state, $E_T^{(i)}$ is the triplet level, W_0 is the state of the CT-complex nonpolar component, W_1 is the state of the CT-complex polar component (D^+-A^-), I_d is the ionization potential of the donor molecule, and A_a is the electron affinity of the acceptor molecule.

Based on this, classification of molecular complexes given above was carried out taking into account the difference between the energies of ionization (I_d) and the electron affinity (A_a) of donor and acceptor molecules I_d - A_a. In the weak CT-complexes, the energy W_1 of the state of the polar component D^+-A^- exceeds the energy W_0 of the nonpolar state D-A, i.e. $W_1 >> W_0$ [14]. Polar states can be occupied during photoexcitation as a result of an optical transition with charge transfer.

Since photoconductive information media containing molecular complexes are solid solutions of these molecules in the polymer matrix, the necessity of their plasticization determines another important feature of the investigated media: a low concentration of dopant molecules (less than 5%), which excludes their interaction. Thus, films with D-A complexes as molecular solids are characterized by strong intramolecular interaction (~ ` eV) and weak interaction between the molecules of the complex (10^{-3} - $4 \cdot 10^{-2}$ eV). Therefore, in the D-A complexes, the molecules retain their individuality, the energy structure changes insignificantly (~ 0.2 eV), and the optical and electrical properties of the solid are determined by the properties of molecules and their complexes. The optical absorption is of a molecular type and its spectrum is determined by the energy structure of the complex molecules.

In Fig. 2.3, the energy of the van-der-waals interaction of the ground state (curve I) and excited states curves (II, III) is shown, where E_0 (curve I) is the energy of the ground state S_0; $E_S^{(1)}$ (curve II) and $E_S^{(2)}$ are the energies of the first and second excited states S_1 and S_2; E_{ex} (curve III) is the energy of the exciplex state; r_0^E, r_0, r_{ex} are the charge transport distances in the complex: r_0^E - before the relaxation of the vibration energy, r_0 - after relaxation, r_{ex} - after the formation of the exciplex; W_{DA}^0 and W_{DA}^E are the energies of the D-A interaction in the ground ($\delta = \delta_0 \to 0$) and excited ($\delta \to 1$) states. The energies R_E and R_N characterize the contribution of the Д-A interaction in the excited and ground states, and their difference R_E - R_N is the change of the energy of Д-A interaction upon photoexcitation $\Delta W_{DA} = W_{DA}^E - W_{DA}^0 \approx 1$ eV (Fig.2.3). This change exceeds the energy of the intermolecular interaction more than 2 orders of magnitude providing a weak interaction of the CT-complexes in a solid.

Redistribution of the electronic density upon the formation of the complex involves the appearance of new bands in the absorption spectrum attributed to the charge transfer. Their energies are determined by the following expression:

$$h\nu_{CT} = E_S^{(i)} - E_0 = I_d - A_a + R_E - E_0 - E_C + R_N, \tag{2.4}$$

where E_0 and $E_S^{(i)}$ are the energies of the ground and excited i-th states of the CT-complex; R_E is the energy of destabilization of the excited complex due to exchange-polarization (resonance) interaction; R_N is the energy of charge transfer stabilizing complex; E_C is the Coulomb energy stabilizing the complex in excited states described by curves II and III in Fig.2.3.

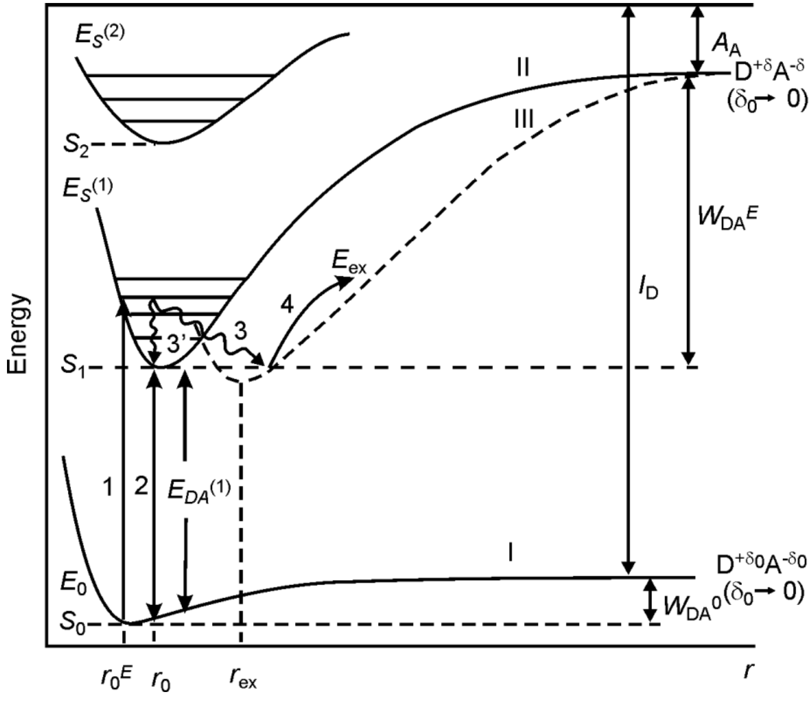

Fig.2.3. The energy diagram of different D-A complexes depending on the distance *r* between molecules.

Weak intermolecular interaction in molecular solids leads to a highly pronounced localization of charge carriers on individual molecules (localization time $\tau_{loc} = 10^{-12} - 10^{-14}$ s). This results in the electronic polarization of the lattice by the charge carrier (the polarization time is $\tau_{pol} = 10^{-16} - 10^{-15}$ s). The time of carrier transfer between neighboring localized states, i.e. time of hopping is $\tau_{hop} = 10^{-12}$ s. As a result, $\tau_{hop} > \tau_{loc} > \tau_{pol}$ and transport of carriers occurs through incoherent jumps between localized states. Within the framework of the phenomenological model of hopping mobility, the rate of transitions Γ_{ij} between two hopping centers with distance r_{ij} and the difference of electron binding energies $\Delta_{ij}E$ can be described by the following relation:

$$\Gamma_{ij} = \Gamma_0 \exp[-2\gamma r_{ij} - (\Delta_{ij}E/k_B T)\Theta(\Delta_{ij}E)], \qquad (2.5)$$

where γ is the decay constant of the wave function of the localized electron which is assumed to be spherically symmetric; $\Theta(x)$ is the Heaviside unit step function. For given spatial distribution of the hopping centers and the type of binding energy distribution, we are dealing with the problem of random wander of the charge carrier on the spatial lattice of non-isoenergetic centers known as the r-E-percolation problem.

The transfer stage, as well as the processes of absorption of photons by complex molecules, are usually described by introducing the concept of a state with charge transfer (CT-states), i.e. excited neutral complex states (Fig.2.4). In Fig.2.4, E_G^{opt} and E_G^{ad} are the optical and adiabatic energy gaps; M_p^+ and M_p^- are the conductivity levels of molecular polarons; S_1 and T_1 are the singlet and triplet states of the molecule; r_{t1} and r_{t2} are the thermalization radii of two possible states of the relaxed connected charge pairs (CPs) with energies E_{CP} and U_{CP}; $E_{CT}^{(1)}$ and $E_{CT}^{(2)}$ are the energies of the CT-states, r_C is the Coulomb radius of the connected pair, and f_d is the dissociation probability.

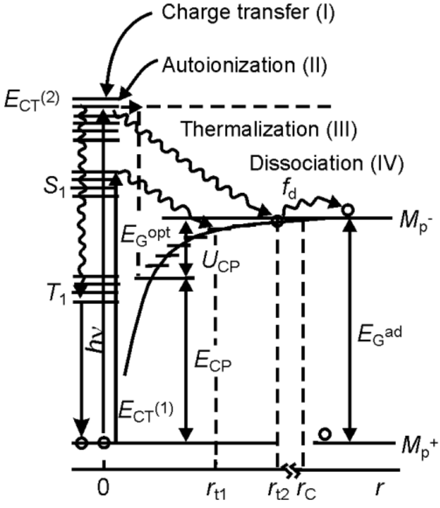

Fig.2.4. Energy diagrams of the main stages of the photogeneration process in molecular crystals of the polyacene type.

In contrast to excitons where the electron and hole are localized on one molecule with a time-independent distance between them, in ST-states, the excited electron passes to the nearest molecule or next behind it but remains Coulomb-connected to its hole. The energies $E_{CT}^{(i)}$ and E_{CP} of these nonconductive ionic states are below the conduction band (Fig.2.4). When a photon is absorbed by a molecule in solid, either autoionization occurs (Frank - Condon transition from the ground state to one of the excited states) or direct excitation of the CT-state happens [31 - 33] with the following formation of a coulomb-connected pair (CP-pair). As a result, free charge carriers can arise (Fig.2.4).

Thus, the features of molecular media are attributed to a weak intermolecular interaction. This results, first, in the molecular character of the light absorption with the further photogeneration of charge carriers through the state of the Coulomb-connected pair with a quantum yield of less than 1. Localization of charge carriers and their low mobility compared to semiconductors is the second result of the weak intermolecular interaction. In semiconductor materials, the carrier mobility μ is not less than 1 $cm^2/(V\cdot s)$. In a molecular solid, the weak intermolecular interaction and strong localization of charge carriers on individual molecules cause the photogeneration of charge carriers through the state of the Coulomb-connected pair formed as a result of molecular absorption of the photon with possible direct excitation of CT-states.

Organic semiconductors are characterized by weak intermolecular interactions of the Van der Waals type and, for example, in a molecular crystal, the photon is absorbed by a separate molecule rather than a crystal. In this case, an electronic transition can occur between the appropriate energy levels of the molecule with the formation of neutral molecular excitations capable to move along the crystal. Such excitations are called the molecular exciton or the Frenkel exciton [30 - 33]. The Frenkel exciton is considered as a strongly coupled system of the excited state of an individual molecule. On the other hand, a weakly connected electron-hole pair with a small Coulomb interaction is known as the Wannier-Mott exciton.

In the neutral Frenkel excitons, the electron and hole are on the same molecule. Besides these ones, excited states can exist in which the electron passes to another next molecule or next behind it but remains connected with the hole by the Coulomb interaction field (Fig.2.5). Such electron-hole pairs are called states or excitons with charge transfer (CT-states). ST-states are not analogs of Wannier-Mott excitons because the electron and hole in the ST-state are localized on certain molecules and can form ionic states. It is assumed that the ST-states are formed at distances between the electron and the hole smaller than the critical distance of the Coulomb capture $r_C = e^2/\varepsilon k_B T$ (Fig.2.5). The electron and hole in the ST-state migrate incoherently through jumps from molecule to molecule changing the distance relative to each other (Onsager model) [2, 17, 18].

The photogeneration of charge carriers in media with weak intermolecular interaction occurs through the state of a Coulomb-connected pair of carriers with opposite signs. The process of separation of such a pair of charges in an external electric field E consists of two stages: the stage of thermalization of the charge carrier connected in a pair and the stage of thermal-field dissociation of the connected pair of charges.

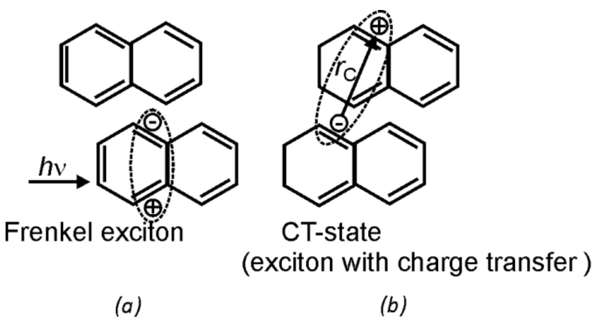

Fig.2.5. Schematic representation of the Frenkel exciton (*a*) and the ST-state (*b*) arising in an organic semiconductor during photoexcitation.

During the first stage, the connected charge carrier (electron) loses the excess of kinetic energy received from the photon and comes into equilibrium with phonons at some distance between the charges called the thermalization radius r_t. This stage is characterized by the quantum yield of formation of connected pairs η_0. The stage of thermal-field dissociation consists in the separation of thermalized connected pairs due to interaction with phonons facilitated by an external electric field. This stage is described by the dissociation probability $f_d(r_t, \theta, E)$. In this case

$$\eta = \eta_0 \cdot f_d(r_t, \theta, E) \cdot g(r, \theta) \cdot dr^3, \qquad (2.6)$$

where $g(r, \theta)$ is the distribution function of pairs in terms of radii r and their orientation respectively to the direction of the field E, θ is the angle between the vectors $\mathbf{r}$ and $\mathbf{E}$. For $r_t < 10$ nm, $g(r, \theta) = \delta(r-r_t)$ and expression (2.6) is transformed into following expression

$$\eta = \eta_0 \cdot f_d(r_t, E). \tag{2.7}$$

Since during the second stage the process of separating the carrier pair in a field E has a diffusion-drift character, in the general case this process can be described by the three-dimensional Smoluchowski equation. It makes it possible to determine the spatially-temporal probability density equal to the probability of mutual thermal-field dissociation of Coulomb-connected charges $f_d(r_t, E)$ with a time-independent constant microscopic mobility.

In the stationary case of an isotropic system of non-interacting pairs of charges in equilibrium state with a medium with a constant dielectric permittivity ε and at a constant temperature T, the probability of dissociation $f_d(r_t, E)$ of a pair of charges located at a distance r_t from each other (r_t does not depend on the field E, the temperature T, and the photon energy) is determined by Onsager's three-dimensional model:

$$f_d = (1 - k_B T/eE_f r_t) \cdot \sum_j (eE_f r_C/k_B T) \cdot \mathrm{I}_j(e^2/\varepsilon r_t k_B T), \tag{2.8}$$

where $I_j(x) = I_{j-1}(x) - x_j/\mathrm{j} \cdot \exp(x), j > 1, \mathrm{I}_0(x) = 1 - \exp(-x)$.

For constant E and T, expression (2.8) can be reduced to the following form:

$$f_d(r_t, E) \sim \exp(1 - \exp(r_t/r_c)). \tag{2.9}$$

To eliminate the limitations of the classical Onsager model, a number of its modifications are proposed: 1) a one-dimensional model [34] for the description of processes in linear systems; 2) the "ballistic" model [24] taking into account the drift of the connected carrier during the thermalization process (at $r_t > 5$ nm), 3) the model of non-stationary photogeneration describing the kinetics of probability $f_d(r_t, E)$ at times $t < 10^{-8}$ s, 4) Mozumder's model [35, 36] describing the dependency of $f_d(r_t, E)$ on the concentration of connected pairs, and 5) Bassler's model of "optical transitions" [18, 29].

For anisotropic media, more generalized Scher-Rakovsky [37] and Ries [38] models are proposed. These models originate from the hopping nature of charge carrier separation in a pair and operate with the Monte Carlo methods. These models allow to determine the areas of applicability of the isotropic Onsager model and demonstrate that this one is valid for $r_t > 1$ nm and $T > 200$ K.

The probability $f_d(E)$ can also be calculated from the Pool-Frenkel model describing the probability of releasing a mobile charge carrier (with a mobility greater than 1 $cm^2/(V\cdot s)$) from the Coulomb center. It was assumed that the external electric field E affects the activation energy of this process and lowers the height of the barrier to overcome by ~ $E^{1/2}$. However, this model and its modifications require the applicability of the band model which is not valid for molecular semiconductors.

From the above-mentioned mathematical models describing the process of photogeneration through the state of a Coulomb-connected pair, the Onsager model gives the most correct representation of the physical process in thermalized pairs. However, since it does not describe the initial stage of the process, it does not allow to take into account the presence of photoexcitation and the influence of the donor-acceptor (D-A) interaction during the thermalization stage and to determine the dependence of η on the photon energy and on the molecular structure of the photogeneration center. Specific physical models of photogeneration are distinguished by processes leading to separation of pairs at the distance r_t. In different hopping models, such a process is a carrier jump from the excited molecule of the complex to the neighboring intermediate state. In the dissociation-hopping model, these are jumps through localized states with dissociation according to the Pool-Frenkel model. The dissociation models of the Onsager photogeneration differ by the stages before dissociation depending on the structure of the medium, i.e. on the nature of the energy relaxation after photoexcitation.

For crystals of polyacenes within the near-threshold absorption range, η increases from 10^{-3} to 0.5 with increasing number of aromatic rings. The photogeneration process in molecular crystals occurs through CT-states formed after a photon absorption (Fig.2.4, transition (I)) due to excess vibrational energy 0.3 - 0.4 eV. This energy is lost (Fig.2.4, transition (III)) for interaction with lattice phonons in 80 - 100 shocks at the distance r_t ~ 6 - 10 nm. This process does not depend on the field strength E. The resulting state of a connected pair with the radius r_t (CP-state) can form free charge carriers (Fig.2.4, transition (IV)) absorbing additional energy from the environment. In the considered model, η and r_t depend on the photon energy [14, 35]. The autoionization process (II) can occur at high energies. However, for the widely known poly-N-vinylcarbazole (PVC), for example, within the range of the singlet absorption bands, the quantum yield of photogeneration η increases stepwise with increasing energy of the radiation $h\nu$ but η and r_t are constant in each band [18].

The mechanism of photogeneration of charge carriers in polymeric semiconductors near the edge of intrinsic absorption can be described by a