Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Studies of Organic Semiconductors for 40 Years—IX

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Studies of Organic Semiconductors for 40 Years—IX

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The first pioneering investigations of organic semiconductors in the USSR were carried out already in 1938–1941 in A. N. Terenin's Laboratory in Leningrad. At this time A. N. Terenin and his coworkers began to study photochemical oxidation processes in organic dyes including electron transfer problems in solid dye-stuffs. The first paper[1] on photoconductivity of organic dyes was published by A. N. Terenin and A. T. Vartanyan in 1941.

However, systematic studies of photoconductivity phenomena in organic solids were renewed at A. N. Terenin's Laboratory only after the Second World War in 1947–1948 coinciding with the formation of organic semiconductor physics and chemistry as a new branch of science in Japan, the United Kingdom and other Western Countries.

As the first milestones in the new field should be mentioned pioneering papers by A. T. Vartanyan on photoconductivity of thin layers of dyes[2] and phthalocyanines[3] in solid state.

Although A. N. Terenin himself was more interested in photochemistry of dyes, a number of his coworkers were active in the field of photophysics of organic semiconductors. In this aspect one should mention the studies of electron and hole conductivity of different dyes and the influence of gases on their electrophysical properties (A. T. Vartanyan), studies of photoemission from organic solids (F. I. Vilesov, A. A. Zagrubskii), spectral sensitization of inorganic semiconductors and polymers by organic dyes (I. A. Akimov, Y. A. Cherkasov), photoconductivity of polymers (Y. A. Cherkasov, B. C. Milnikov) *et al.*

A. N. Terenin introduced in 1967 a new term—photonics[4] in order to describe both photophysical and photochemical aspects of photon interaction with molecules. At present the term photonics is often used as a synonym for a new branch of integral science covering all aspects of light interaction with matter.

Evolution of contemporary organic semiconductor physics has considerably been influenced by the molecular exciton theories developed in the USSR by A. S. Davydov,[5] V. M. Agranovich,[6] E. I. Rashba[7] and other theorists.

The development of Davydov's molecular exciton theory has mainly been based on the experimental work of A. F. Prihot'ko and her Colleagues in Kiev in the

field of low temperature spectroscopy of organic molecular crystals (V. L. Broude, M. S. Brodin, M. V. Kurik *et al.*).[8]

The molecular exciton approach has been fruitful for the description of both intrinsic and extrinsic photogeneration phenomena in which photoexcitation of a neutral Frenkel exciton state is regarded as the first act in multistep charge carrier generation process.

However, we shall limit the scope of this review discussing mainly the works in the field of semiconducting phenomena in organic solids, namely, charge carrier generation, transport and trapping phenomena, and related problems of energy structure of ionized and local trapping states.

In this aspect, first of all, we should mention the photoemission studies by F. I. Vilesov and A. A. Zagrubskii at A. N. Terenin's Laboratory in Leningrad.

These authors in early 60's determined ionization energies I_c for a considerable number of organic solids including different dyes, phthalocyanines, polyacenes etc. (see Reference 4, p. 548). As we know, the parameter I_c is of the utmost importance for the determination of ionized state energy structure in organic solids in the framework of the Lyons model. Later Zagrubskii and coworkers[9] used more sophisticated methods in photoemission studies which, e.g., allowed to obtain sets of energy spectra of photoemitted electrons (see Figure 1). Using this approach authors observed two distinct kinds of electron energy distribution peaks: "moving" (dependent on photon energy) and fixed ones (independent on photon energy).

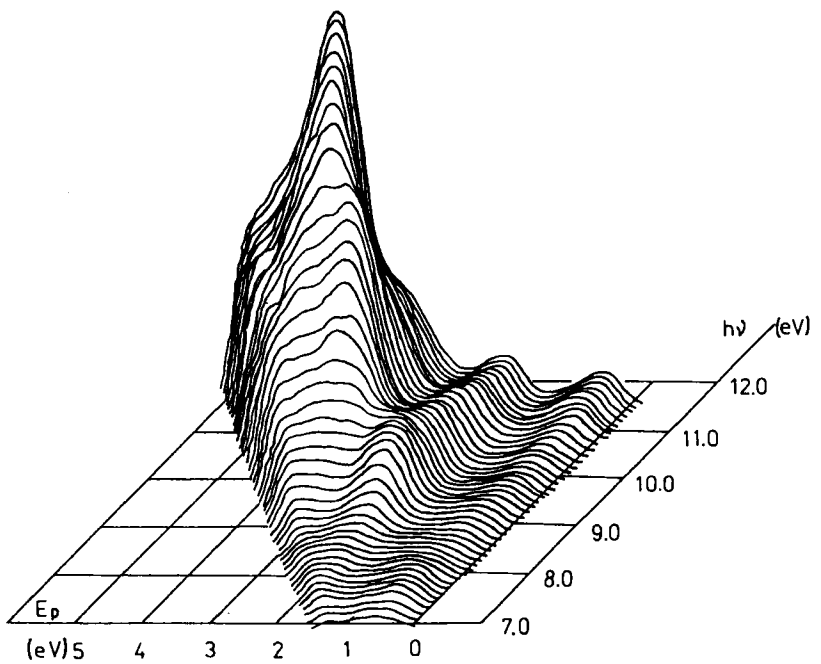

FIGURE 1 A typical set of energy spectra of photoemitted electrons from tetracene crystal as dependent on photon energy.[9]

This demonstrated that there existed two competitive autoionization channels of excited molecules in the crystal—one of direct (prompt) autoionization of excited state, and second—autoionization from a fixed electronic level after intramolecular vibronic relaxation.

In Leningrad, besides the Laboratories of A. N. Terenin at S. I. Vavilov's Optical Institute and Leningrad University, a new Laboratory of organic semiconductor physics was created in the Leningrad branch of Academy of Sciences of the USSR in 60's. The studies of this laboratory were mainly devoted to conductivity, photoconductivity and carrier trapping phenomena in organic molecular and polymer semiconductors (A. V. Airapetyantz, L. D. Rozenstein, R. M. Vlasova *et al.*). Later the interests of the group shifted to optical properties of highly conductive organic metals (R. M. Vlasova).

In 1965 E. L. Frankevich from the Institute of Chemical Physics Ac. of Sciences USSR in Moscow discovered a new physical effect—magnetic field induced change of photoconductivity in organic semiconductors.[10]

This new approach has been so promising that E. L. Frankevich and his coworkers have devoted more than 20 years of penetrating studies to magnetic field effects in organic solids which provided a deeper insight into the intermediate stages of electronic processes. These studies demonstrated that the magnetic field effects emerge via spin dependent interactions between short-living paramagnetic species which may be described in the framework of different interaction models (Δg mechanism, hyperfine interaction mechanism etc.). It was shown that there existed a great variety of interaction types: interaction between paramagnetic species with spin value $S = \frac{1}{2}$ such as free radicals, electrons, holes, ion-radicals etc. as well as interaction with particles having spin value $S = 1$, e.g. triplet interaction with trapped charge carrier, triplet-triplet annihilation, carrier interaction with oxygen molecules etc.[11]

Later Frankevich and coworkers[12] discovered a new magnetic effect—influence of a low magnetic field of the order of 10 to 100 oe on the mobility of charge carriers in polyacetylene and other polymers. This effect is illustrated in Figure 2 and has been interpreted by authors as spin dependent hopping of charge carriers via local states located in the energy gap of the polymer.

In recent years E. L. Frankevich and coworkers have widely applied magnetic resonance methods in order to study spin dependent processes involving pairs of paramagnetic species.[13] This new method, known as Reaction Yield Detected Magnetic Resonance (RYDMR), allowed the authors to study short-lived paramagnetic intermediates in exciton reactions, detected by photoconductivity or luminescence measurements. Figure 3 illustrates the correlation of resonance transitions between Zeeman levels of a triplet pair $^3(D^+ \ldots A^-)$ of ion-radicals D^+ and A^- and magnetic field H_o dependent luminescence L.

It should be emphasized that the RYDMR method yields much higher sensitivity than traditional EPR methods.

In 70's another group from the Institute of Chemical Physics of Ac. of Sciences of the USSR was involved in the studies of photogeneration mechanisms in purified and impurity doped phthalocyanines (V. A. Benderskii, N. N. Usov).

A group at the Dye-stuff Research Institute in Moscow, using electrical field

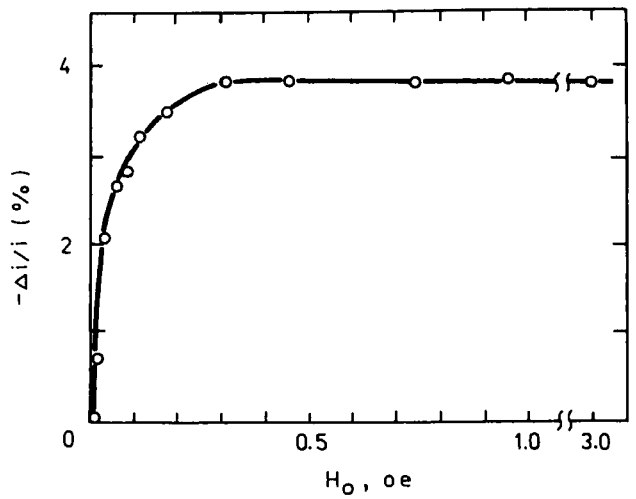

FIGURE 2 A typical dependence of relative change of conductivity of a polyacetylene film in magnetic field at room temperature. (H_0 in kilooersteds).

modulated absorption technique, first detected and characterized optical charge transfer (CT) states in organic semiconductors, viz. in thin layers of phthalocyanine and perylene[14] (L. M. Blinov, N. A. Kirichenko). Later the method of Stark spectroscopy has been successfully used for studying the orientation of polar molecules in LB layers (S. G. Yudin, L. M. Blinov).

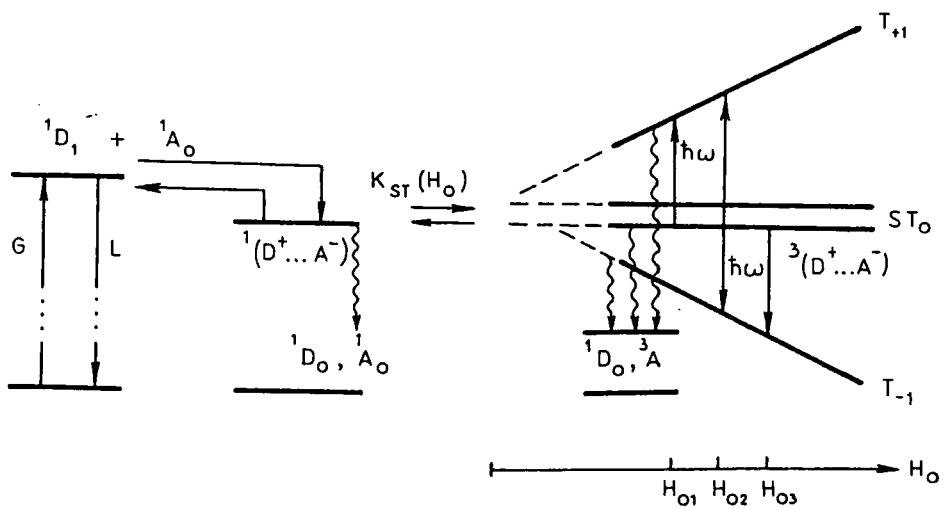

FIGURE 3 Schematic diagram which illustrates the correlation of resonance transitions between Zeeman levels of a triplet pair $^3(D^+ \ldots A^-)$ of ion-radicals D^+ and A^- and magnetic field H_0, dependent luminescence L.

Several groups in a number of institutes of Academy of Sciences of the USSR in Moscow have been engaged since 70's in extensive studies of optical, electrophysical and magnetic properties of pure and doped polyconjugated polymers (A. B. Vannikov, A. D. Grishina, B. E. Davydov *et al.*), and radiation effects on these properties.[15] Systematic studies of photogeneration and carrier transport mechanisms in PVK type undoped and doped photosensitive polymers have been carried out for more than two decades at the Research Institute of Electrophotography in Vilnius (B. I. Gaidalis, Y. B. Sidaravichius *et al.*).

Already in late 60's there emerged at the Institute of Physics of Ukrainian Ac. of Sciences in Kiev a new group, headed by M. V. Kurik, which passed over from exclusively excitonic problems, traditional for Kiev's school of physicists, to problems of charge carrier generation and transport phenomena in molecular crystals. However, this pass-over was gradual and in early 70's M. V. Kurik and his coworkers still continued to study the temperature dependence of the shape and parameters of exciton absorption and emission bands and their low-frequency Urbach tail in polyacene crystals.[16,17] These studies provided a deeper insight into the dynamics of exciton localization due to interaction with lattice environment and transition from coherent (band-like) to diffusive (hopping) mode of motion with increasing temperature. These investigations made a considerable contribution to better understanding of similar processes in the case of charge carriers.[16]

In late 70's Laboratory of M. V. Kurik was engaged in extensive studies of the role of singlet and triplet excitons in charge carrier generation processes. It was shown that this type of extrinsic, so-called excitonic mechanism of photogeneration occurs due to the interaction of excitons with neutral or charged trapping states in the bulk or surface of the crystal. It was also demonstrated that for the description of exciton mechanism of photogeneration, the diffusion model of exciton migration was proved to be valid for higher temperatures.

In the Laboratory photoconductivity action spectra of polyacene crystals have been studied at low temperatures down to 4.2 K. These spectra show some peculiar features, characteristic of low temperature photoconductivity both in excitonic and intrinsic photogeneration regions.[18] For illustration Figure 4 shows photoconductivity spectrum of pentacene layers in spectral region of intrinsic photogeneration at 4.2 K. This spectrum demonstrates a distinct intrinsic photogeneration threshold and a fine structure of peaks (shown by arrows), presumably due to direct optical CT-transitions since these peaks increase with increasing electrical field (M. V. Kurik, Yu. P. Piryatinskii).[18]

Since 1969 the Institute of Physics of Ukrainian Ac. of Sciences in Kiev has become one of the leading centers of the USSR in the field of organic semiconductors. The Institute organizes and sponsors regular coordinative conferences and schools, periodically held in Kiev and other regions of Ukraine.

In 1968 a Laboratory of physics of organic semiconductors was organized at the Institute of Physics and Energetics of Latvian SSR Academy of Sciences in Riga. The major achievements of this laboratory during the 20 years of existence are the following.

A phenomenological model of local trapping states of structural origin in mo-

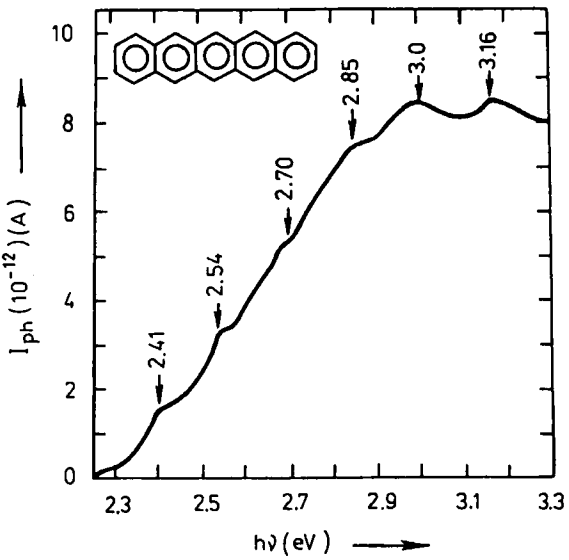

FIGURE 4 Photoconductivity spectrum of pentacene layers in the spectral region of intrinsic photogeneration at 4.2 K.[16,18]

lecular crystals has been developed[19,20] (Silinsh). According to this model local states with Gaussian type of energy spectra are formed in the regions of structural defects (edge dislocations, stacking faults etc.) due to local change of electronic polarization energy of the charge carrier. Figure 5 shows a schematic diagram illustrating the formation of local trapping and anti-trapping states with Gaussian energy spectra due to local displacement of molecules in structural defects. The validity of the model has been proved experimentally using independent space-charge-limited current (SCLC) and thermally stimulated current spectroscopy techniques (E. A. Silinsh, L. F. Taure, I. J. Muzikante).

Combined intrinsic photoconductivity and photoemission methods have been used for determination of energy spectra of ionized states in a number of aromatic and heterocyclic molecular crystals.[16] Based on these and other reported data a modified four level Lyons model of ionized states in organic crystals has been developed[16,20] (Silinsh).

According to this model there are formed, due to many-electron interactions, two energy levels for positive E_p^+ and negative E_p^- electronic polarons, separated by optical energy gap E_G^{opt} and two conductivity levels for negative M_p^- and positive M_p^+ molecular polarons, separated by adiabatic energy gap E_G^{Ad}. This phenomenological four level model, presented in terms of electronic and molecular polaron approach, is illustrated by energy structure diagram for pentacene crystals (Figure 6). The photogenerated charge carrier separation mechanisms have been studied both experimentally and by computer simulation.[16,21] It has been shown that the thermalization stage of hot carrier in charge separation process can be described

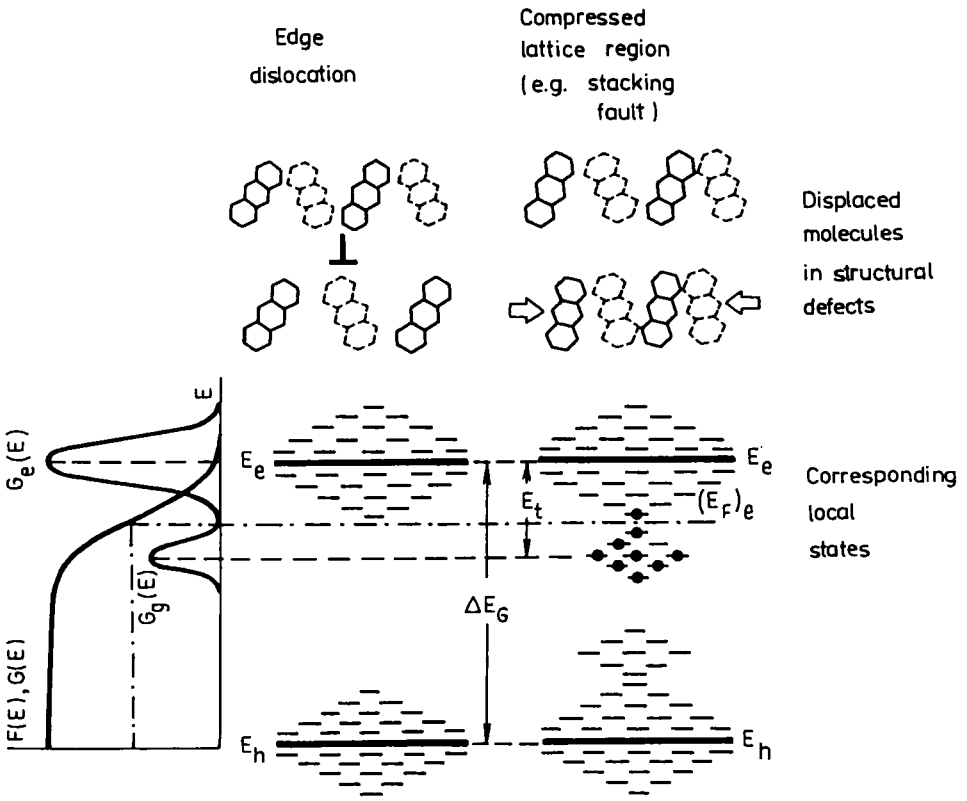

FIGURE 5 Schematic energy diagram for a molecular crystal with Gaussian distribution of local states of structural origin. G_e (E)—Gaussian trap distribution centered at the conductivity level; G_g (E)—Gaussian trap distribution situated in the energy gap.[20]

in terms of a modified Sano-Mozumder's model but the charge pair dissociation—in the framework of an extended Onsager's model. Computer simulated electron thermalization stage as dependent on photon energy is illustrated in Figure 7. It has been shown that the molecular polaron approach may be regarded as valid both for the description of energy structure of ionized states, as well as for the charge carrier photogeneration and transport phenomena in organic molecular crystals.[16]

Although it is outside the limited scope of this review we should like to mention also some recent developments in the USSR in the field of synthetic organic metals and superconductors.

In 1984 a group working in the field of synthetic metals at the Institute of Chemical Physics Ac. of Sciences of the USSR in Moscow synthesized an organic metal $(BEDT\text{-}TTF)_2J_3$, the two modifications of which yield superconductive state with T_c = 1.4–1.5 K and T_c = 2.5 K respectively at normal pressure (I. F. Schegolev,

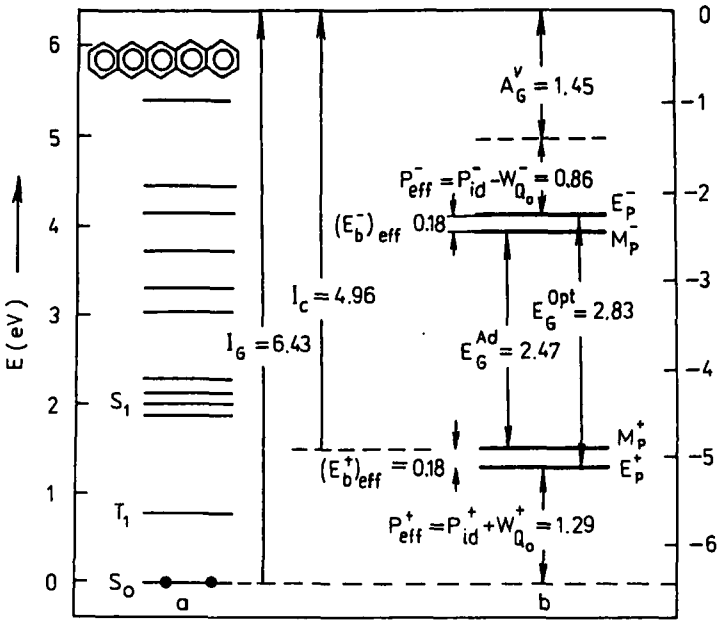

FIGURE 6 Energy diagram of neutral (a) and ionized (b) electronic (E_P^-, E_P^+) and molecular (M_P^-, M_P^+) polaron states in a pentacene crystal.[16]

V. N. Laukhin, E. B. Yagubskii *et al.*). Later this group observed for one modification of similar type of organic metal a superconductive state with T_c = 7–8 K.[22] A number of leading Soviet theorists are also active in the field of organic metals and superconductors (A. S. Davydov, L. N. Bulaevski, S. A. Brazowskii, A. A. Ovchinnikov, V. Y. Krivnov, I. I. Ukrainskii, A. A. Zakhidov *et al.*).

Theoretical aspects of charge carrier transfer problems in molecular biosystems, including soliton theory approaches, have been extensively discussed in recent monographs by A. S. Davydov[23] and E. G. Petrov.[24]

One should also mention considerable contribution of Soviet chemists, synthesizing a great number of new organic mono-molecular and polymer type semiconductors as well as strong electron donors and acceptors for ion-radical salt type organic metals (B. E. Davydov, M. I. Cherkashin, M. L. Khidekel, K. N. Lyubovskaya, R. B. Lyubovskii *et al.* in Moscow, O. Ya. Neiland and J. F. Freimanis in Riga, M. I. Al'yanov in Ivanovsk and many others.

In conclusion it should be emphasized that the evolution of physics and chemistry of organic semiconductors in the USSR did not occur in isolation. Fruitful exchange of ideas, mutual understanding and cooperation with Colleagues from Japan, the USA, East and West European Countries have greatly influenced and stimulated studies in this field in the USSR.

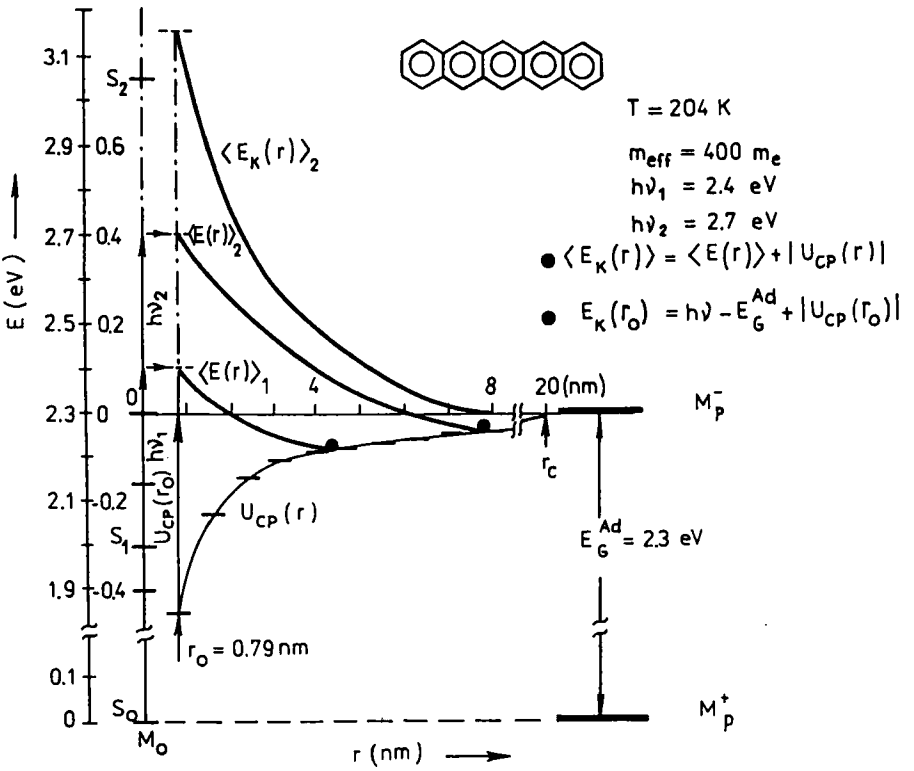

FIGURE 7 Energy diagram representing the thermalization process in the framework of autoionization model in pentacene crystals.[21] Curves obtained by computer simulation of the process shows the variation of the average total energy $\langle E(r)\rangle$, the average kinetic energy $\langle E_k(r)\rangle$ and the potential energy $U_{CP}(r)$ of photogenerated hot electrons as functions of separation distance r from the positive ion during thermalization for two values of photon energy $h\nu_1$ = 2.4 and $h\nu_2$ = 2.7 eV.

REFERENCES

1. A. N. Terenin and A. T. Vartanyan, *Jour. of Physics USSR*, **4**, 173 (1941).
2. A. T. Vartanyan, *Acta Physicochimica USSR*, **22**, 201 (1947).
3. A. T. Vartanyan, *Zhur. Phyz. Chimii*, **22**, 769 (1948).
4. A. N. Terenin, *Photonics of dye molecules* (in Russian) (Nauka, Leningrad, 1967).
5. A. S. Davydov, *Theory of molecular excitons* (in Russian) (Nauka, Moscow, 1968).
6. B. M. Agranovich, *Theory of excitons* (in Russian) (Nauka, Moscow, 1968).
7. E. I. Rashba, Self-trapping of excitons in solids: — In: *Defects in Insulating Crystals* (Zinatne, Riga, 1981) pp. 255–266.
8. *Physics of molecular crystals* (in Russian) (Naukova Dumka, Kiev, 1986).
9. A. A. Zagrubskii, V. V. Petrov and V. A. Lovcjus, *Izv. AN Latv. SSR, ser. phys. i teh.nauk*, **5**, 29 (1981).
10. E. L. Frankevich, *Zh. exp. i theor. phys.*, **50**, 1226 (1966).
11. E. L. Frankevich, *Chimiya visokich energii*, **14**, 195 (1980).
12. E. L. Frankevich, D. I. Kadirov, I. A. Sokolik *et al.*, *Chimicheskaya physica*, **2**, 1642 (1983).
13. E. L. Frankevich, Magnetic resonance in spin dependent processes, In: *Ninth Molecular Crystal Symposium* (Mittelberg, 1980), pp. 93–98.

14. L. M. Blinov and N. A. Kirichenko, *Physica tvyordovo tela*, **14**, 2490 (1972).
15. A. B. Vannikov and A. D. Grishina, *Photochemistry of Polymeric donor-acceptor complexes* (in Russian) (Nauka, Moscow, 1984).
16. E. A. Silinsh, M. V. Kurik and V. Čapek, *Electronic processes in organic molecular crystals*. Localization and polarization phenomena (in Russian) (Zinatne, Riga, 1988).
17. M. V. Kurik, *Phys. Stat. Solidi* (a), **8**, 9 (1971).
18. M. V. Kurik, Yu. P. Piryatinskii, Photogeneration of charge carriers in molecular crystals at low temperatures. In: *11th Molecular Crystals Symposium* (Lugano, 1985), pp. 174–177.
19. E. A. Silinsh, *Phys. Stat. Solidi* (a), **3**, 817 (1970).
20. E. A. Silinsh, *Organic molecular crystals. Their electronic states* (Springer Verlag, Heidelberg, 1980).
21. E. A. Silinsh and A. J. Jurgis, *Chem. Phys.*, **94**, 77 (1985).
22. I. F. Schegolev, V. N. Laukhin, Physical properties of organic superconductor β-$(ET)_2I_3$. In: *Electronics of organic materials. Intern. Conference* (Tashkent, Nov. 1987) p. 6.
23. A. S. Davydov, *Solitons in molecular systems* (in Russian) (Naukova Dumka, Kiev, 1984).
24. E. G. Petrov, *Physics of charge transfer in biosystems* (in Russian) (Naukova Dumka, Kiev, 1984).