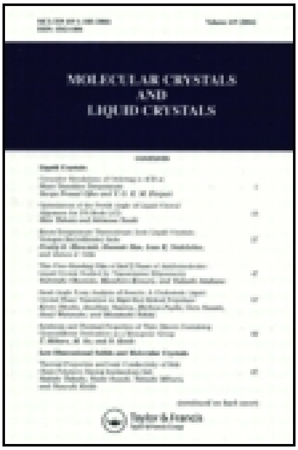

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Transport of Low-Energy Electrons in Thin Organic Films

A. V. Kukhta [a]

[a] Institute of Molecular & Atomic Physics, NAS of Belarus, Belarus

Version of record first published: 31 Aug 2006

To cite this article: A. V. Kukhta (2005): Transport of Low-Energy Electrons in Thin Organic Films, Molecular Crystals and Liquid Crystals, 427:1, 71/[383]-93/[405]

To link to this article: http://dx.doi.org/10.1080/15421400590891948

Mol. Cryst. Liq. Cryst., Vol. 427, pp. 71/[383]–93/[405], 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590891948

Transport of Low-Energy Electrons in Thin Organic Films

A. V. Kukhta
Institute of Molecular & Atomic Physics, NAS of Belarus, Belarus

The different tools for the electron transport studies in ordered and disordered organic systems under the transmission of the electric current and the electron beam are considered. The observed features in both cases (transmission coefficient dependence on the sample thickness, temperature behaviour, elastic and inelastic transport, anisotropy, charging, luminescent properties) are similar confirming a similar nature of the electron transfer processes. The most promising approach to develop the common model describing electron transport in the metal-organics-metal structures has to contain two terms (i) the term concerning injection current including barrier and spectrum of emitting electrons at applied voltage and (ii) the scattering cross section (total or/and differential) as a function of electron energy, scattering angle and temperature. The usage of the electron impact spectroscopy methods possessing to measure much more characteristics than electric current transmission, gives the possibility to study practically all the variety of proceeding phenomena rather clearly, and to help invaluably for the interpretation of electric current transmission data.

Keywords: beam; current; electron; organic film; transmission; transport

INTRODUCTION

Organic compounds are of wide current interest in thin film applications in numerous electronic devices, partly electroluminescent diodes, displays, photovoltaic cells, sensors, transistors, electrically pumped lasers, switching and storage devices, field emitters etc. [1]. Molecular wires and even single molecules are proposed as active molecular devices (diodes, memory cells, etc.) that give the possibility to decrease the dimensions of active elements some orders of magnitude up to about one nm. The process of ultradense circuits manufacturing will represent a routine synthesis. There is a

---

Address correspondence to A. V. Kukhta, Institute of Molecular & Atomic Physics, NAS of Belarus, F. Skaryna Avenue 70, Minsk 220072, Belarus. Tel.: (+375) 172841719, Fax: (+375)172840030, E-mail: kukhta@imaph.bas-net.by

huge amount of organic compounds with a wide spectrum of structures and properties. The low weight molecules and polymers with π-conjugation, i.e., electron delocalization along the molecule, are the most interesting for organic electronics applications. Depending on the structure organic compounds can serve as insulators, semiconductors [2], conductors [3] and even superconductors [4]. Knowledge how electrons flow through molecules is very important in fundamental and applied studies, partly for the development of manifold molecular and optoelectronic devices, for rationalizing electron transfer in biomolecules, for interpretation of processes in STM studies and in electrochemistry of metal-organic interface, etc. In principle, all the electron transfer phenomena are controlled by the similar physical factors.

Complex organic compounds basically differ from inorganic by much stronger intramolecular interactions than intermolecular. As a result, characteristics of energy levels and energy transformation for single molecules and condensed media differ a little, while in inorganics the gas phase and the solid state characteristics strongly differ. Thus, the properties of individual molecules can be used for describing of molecular solids in the first approximation. Due to a large number of atoms in such molecules electronic, vibrational and rotational levels produce continuous energy zones, and transitions between them form wide energy bands. The free charge carriers internal concentration is very low [2] (less than $10^{10}\,\mathrm{cm}^{-3}$), so the most part of organic materials can be considered as insulators rather than semiconductors. Nevertheless, their mobility can be high [2]. The mobility of charge carriers in amorphous and polymeric materials where molecules are located randomly some orders lower than in molecular crystals. The measured carriers mobility values range is very wide (from 10^{-11} to $10^{3}\,\mathrm{cm}^{2}\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$) in organic materials [2]. And the possibility of direct comparison of electron transfer characteristics with microscopic theories of transfer in condensed phase can be strongly limited. Note that intra- and intermolecular electron transfer in donor-bridge-acceptor (D-B-A) organic systems in solutions and even in the gas phase [5] has been studied by spectroscopic methods for a long time. The extensive literature data (see refs. in [6]) indicates that the rate of electron transfer (k) depends exponentially on the distance (L) separating D and A $k = k_0 \exp(-\beta L)$, where k_0 is a preexponential factor, β is a structure-dependent attenuation factor. The theoretical studies [7] have shown that the rate of electron transfer is proportional to electronic coupling between D and A. Transport of electrons can be studied by measuring the current characteristics and by the phenomena they result in.

The aim of this work is to compare the results of electron transport in ordered and disordered organic structures found by transmission of both electric current and electron beam in order to find the common behaviour and to reveal the basic mechanisms.

TRANSPORT IN ORGANIC SYSTEMS UNDER TRANSMISSION OF ELECTRIC CURRENT

In order to study the transfer of electron, i.e., its transport in solid organic materials under transmission of electric current, the structures metal-organic system-metal (MOM) are used, as a rule. Ordered or disordered thin films, molecular wires or single molecules can be considered as molecular systems. It can contain one or several layers of the same or different types of organic molecules. These molecules can be chemically bounded to one or both electrodes. The metallic tip of a scanning tunneling microscope can serve also as one of the electrodes.

The study of electron transport in such structures is based on the measurements of steady-state voltage-current characteristic (VAC) or kinetics of current changes. In time-of-flight method the voltage is applied to metal or semiconductor electrodes of the MOM structure. If we create an excess of electrons at one of the electrodes (for example by pulsed laser) they will move to the second electrode. We can measure the mobility (the main characteristic of charge carrier transport) using transient current decay. Electron transport studies can also be made by kinetic measurements of different processes such as electroluminescence [8,9]. In such measurements different kinds of charge carriers such as electrons and holes are simultaneously observed. Note that there is no unequivocal understanding of the holes nature. Holes are interpreted sometimes as a secondary electron emission from the anode, or cations formed as a result of impact ionization. The electron donating molecules can transfer electrons to the anode and neighboring molecules can be then recharged in the frame of ion-molecule reactions. These consecutive reactions will result in the positive charge movement. Really, a large amount of radical-cations were registered spectrally in electroluminescence cell [10]. The similar reactions can occur also with negative ions.

Disordered Films

The main part of transport studies up to date have been made with disordered organic materials: low weight molecular amorphous and polymeric. The most extensive data are connected mainly with electroluminescence studies.

It is often supposed that the presence of growth and decay periods in electroluminescence kinetics is caused by charge carrier transport. But this interpretation of response gives the mobility some orders of magnitude less than in a time-of-flight experiment [9]. An approach based on accumulation of internal space charge at the interface appeared in the studies with organic films covered by Al or water electrodes [11,12]. Actually, the value of the charge transported during the delay of electroluminescence corresponds to the charge of studied capacity and indicates that this delay is the time for accumulation of internal space charge but not the transit time of the one of the charge carriers. One more argument is appeared from the observation that the delay time changes two orders of magnitude while an external electric field E increases from 0.3 to 1.2 MV/cm. Then the mobility also changes two orders as opposed to all principles of the field dependences. Note that electron injection delay is widely known in the studies of gas discharges using dielectric film coated cathodes [13].

It is known that the energy received by an electron from the electric field in the time between two inelastic collisions is defined by the expression $eE/n\sigma$. This energy can reach the value eU at used applied voltage U and the absence of elastic collisions. The mobility value can also depend on electric field. It was shown [14] that its effect on effective mobility at $E < 5 \cdot 10^5\,\mathrm{V/cm}$ is practically absent in all organic materials including very polar. When $E > 5 \cdot 10^5\,\mathrm{V/cm}$ the essential growth of effective mobility with applied field is observed, with almost universal low $\sqrt{E}$ [14]. Strong temperature dependence of conductivity was observed [8]. The current density exponentially decreases with thickness [8].

In order to describe electron transport in disordered organic films three main models such as hopping, polaron model and model of transport centres, have been proposed. However, in spite of extensive experimental and theoretical studies the situation continues to be unclear [15]. The time-of-flight method of mobility studies for disordered films is connected with a number of complicated experimental factors excluding the possibility of direct comparison of obtained results with available transport theories [14]. VACs are often described by injection function [16].

Ordered Films

Examples of organic films with ordered location of molecules are molecular crystals, Langmuir-Blodgett (LB) and self-assembled

(SAM) films, etc. The charge carriers mobility is much higher in ordered films than in disordered. It decreases with temperature and molecule branching [2]. A number of different methods for creation of ordered films such as different kinds of self-assembly using surface and volume templates, poling methods, etc. are developed. The current transmission through reliable MOM structures (single and two layered SAM) [6] indicates that for description of electron transfer in the solid MOM structures the same formula as for solutions can be used. For alkanethiols the measured β was found to be $\sim$0.8–0.9, and for oligophenylene thiols $\beta \sim 0.5 - 0.7\,1/\text{Å}$, that is in a good agreement with corresponding values obtained by photoinduced electron transfer in molecular D-B-A systems. The values of β for aromatic and aliphatic SAMs did not change significantly over the range of 0 to 1 V; they are essentially determined by the injection barrier. The studied compounds do not show strong electronic interaction among the chains organized into SAMs. The current density decreases exponentially with the distance separating the electrodes and it depends exponentially on the square root of the applied potential. It is concluded from these data that the mechanism of transport is superexchange tunneling. The van der Waals interface between the SAM on Hg and the SAM on Ag does not represent insurmountable barrier to tunneling and its relative location between electrodes does not have a significant effect on the magnitude of the current density. Note that the breakdown electric field for studied compounds is about 4–5 MV/cm, except benzenethiol (2 MV/cm), i.e. as in inorganic materials. The most fruitful approach to study the mechanisms of electron transfer was shown to be the search of correlation between molecular structure and rates of electron transport. MOM structures with parallel molecules revealed Coulomb charging [17]. The enormous amount of molecules complicates the analysis of transport in single molecules. The luminescence of ordered organic films is polarized [18]. The ordered organic materials show a current rectification even in symmetric MOM structures [19].

Nanowires and Single Molecules

Single molecules give a unique possibility to study the mechanisms of electron transport [20–26]. The first experiments with single molecules were performed in [23]. Two rod-like aromatic molecules, which differed by their spacial symmetry, showed discrete stable conductance properties. While the asymmetric molecule always generated asymmetric VAC, the symmetric molecules often showed asymmetric VAC. This allows clearly to identify the observed VACs as transport through sample molecules. The effects of rectifying [17], negative differential resistance and memory effect [20] were observed. VAC is very sensitive to temperature [20] and to realization of microcontacts. The similar results are also obtained with nanowires [25]. The molecular properties determine the way of charge movement through the molecule or the molecular wire.

The elastic and inelastic electron transfer is considered to explain the electron transport mechanisms in organic systems [17,21,25,26]. The most common situation for long range electron transfer occurs when the Fermi levels of the contacts are arranged in the middle of the HOMO/LUMO gap and if the characteristic time of hopping process through the wire, τ_{hop}, strongly exceeds the characteristic time of the direct tunneling, τ_{tun}, the interelectrode current takes place as an elastic tunnel process, and the conductivity decreases exponentially with an increase of interelectrode distance L. If the Fermi level is in the resonance with the LUMO levels the conductance oscillates with the L increase. These oscillations are caused by the dimensionality of the contacts and of the electrode, and by the geometry of the interface between the wire and the contact. If $\tau_{hop} \ll \tau_{tun}$, the current is determined by inelastic hopping transitions, and the electron tunneling is accompanied by energy dephasing at the terminal sites and the internal units [25]. Inelastic (called sequential) electron transport becomes more efficient than elastic (called superexchange) if the number of bridging units is increased.

It can be noted that in all considered MOM structures a number of common regularities is observed. However, in spite of enormous amount of experimental and theoretical studies on electron transport in organic molecules and organics based structures made during the last years, the universally recognized theoretical model describing all the observed results is absent up to date. As can be seen from the considered above approaches, the mechanisms of electron transport is determined essentially by electrodes. The main properties of current transmission through the sandwich structures are: (i) the dependence of the process on the electron energy and its changes with applied voltage cannot be monitored, (ii) this process involves electrons, holes and other charge carriers, (iii) a little amount of the measurable characteristics. The transport properties of even extremely pure organic compounds in surrounding air are affected by oxygen adsorbed by organic molecules [27]. Moreover, oxygen molecules can be not only physisorbed, but also they can form chemical bonds especially with π-conjugated rings [28]. In experiments with single molecules dimensional contact phenomena and interaction with metal contacts are clearly observed. In the whole, two different processes such as electron injection and properly transport should be separated in the studies of the electron transport in the MOM structures.

Injection

The surface and volume charge carrier injection can be separately considered. At present there is no conclusive understanding of the mechanism of charge injection into organic materials. Mainly two mechanisms of surface injection relating to the physics of solid-state inorganic semiconductors are considered [1]: the Fowler-Nordheim tunneling and the Richardson-Schottky thermionic emission. The main characteristics determining injection current are the electric field and the work function Ψ, or injection barrier. The termionic emission grows with temperature. The barrier of tunneling into many materials is essentially lower than in vacuum at the same geometry (see, for example [29,30]). There is no fundamental difference between the injection into a vacuum or solids [30,31], confirming the same nature of electron injection in the MOM structures and in the vacuum devices. Organic molecules placed on the metal cathode result in the emission threshold decrease [30,32]. Some organic molecules were found to be good electron emitters with the lowest emission threshold (about 2 kV/cm for a current density of 1 μA/cm^2) [33]. Organic molecules in such devices serve as conducting channels for electrons [32]. The electron emission ability is apparently determined by the electron transporting properties of organic molecules. It is connected with the metal-organic interface nature.

For solids, the vacuum level is on the surface. On the metal-organic interface, an alignment of the energy levels can take place, although for most organic compounds it is absent [34]. If the carrier concentration is high enough in organic material, some of the electrons will go from the organic material to the metal, and the layers will be charged. This process proceeds until the metal and organic material levels became aligned. However, in the majority of organic materials the carrier concentration is very low. On the metal-organic interface, a sharp shift of the vacuum level occurs due to the electric dipole layer formation [34]. The dipole-layer thickness is limited by the interface and measures a few nanometers [34]. It was established [35] that thin organic films (up to about 2.5 nm) which are covalently bound to the metal substrate do not tend to be charged, while physisorbed films of similar thickness are charged.

The effect of organic and inorganic adsorbates on work function of photoelectrons emitted by the metal surfaces has been studied for a long time [36,37]. Physical and chemical adsorbates on the metal surface create electric fields and shift the surface potential and the photoemission threshold, as a consequence. For example, charge transfer from Cs to a surface generates a dipole layer that is responsible for the large threshold reduction that accompanies cesiation [38]. The study of organic adsorbates revealed [38] that a nitrogen lone pair electronic orbital in molecules located perpendicularly to the surface (such as piridine, methylamine etc.) is essential for a large threshold shift ($\sim 1.5\,\mathrm{eV}$) due to a charge transfer to the metal surface. These molecules act as a weak form of Cs. Other molecular properties, such as dipole moment, dissociation constants, polarizability etc. have a rather small effect. The shift of emission current appearance during the first layer deposition was observed [34,38]. At higher adsorbate thicknesses Ψ changes weakly.

The electron injection from a metal into organic material is essentially improved if an additional layer of a compound with a large value of electron affinity [31] is placed between them. The value of Ψ strongly depends on the electrostatic conditions on the surface; therefore, it can be changed by bipolar adsorbates [39]. For this purpose thin layers of ionic insulators as LiF, Al_2O_3 etc. [40,41], self assembled polar molecules [30,42] or electrostatic nanoparticles [43]; grafted molecules [44]; special treatment of electrodes in base or acid [45]; ordering of the molecules on the electrode surface [29]; additional injection layers [46]; complex electrodes consisting of two metal layers, e.g., of Sn and Al [47] are used. Doping can also lead to an increase of injection [48]. But, filling the part of the interelectrode space by oxygen atoms or molecules which are essentially impenetrable for tunnel electrons results in injection barrier growth [29].

The injection rate depends on the surface structure. A rough surface creates a nonuniform electric field and, accordingly, a nonuniform distribution of the injection rate [49]. Metal atoms diffuse into organic layer when deposited on it; the organic layer upon the deposition is rough. The tunneling becomes stronger by formation of the transient resonances caused by cavities in the adsorbate structure [29,50]. The porous emitters with very low Ψ are known [36]. The photoemission threshold decreases after deposition of super thin organic films with an island structure [51].

Note, that the ejected electrons energy spectrum represents a narrow band with a maximum near the Fermi energy E_f [52] shifting with electric field [30]. The tunneling time determined as d/v, where v is the electron velocity, to average some femtoseconds [53].

The volume injection can be observed in photoconduction experiments under the light irradiation of the organic materials. At rather high applied electric fields both surface and volume injection occurs. It was found that charge carriers photogeneration is caused by the light absorption confirming by the correlation between absorption spectrum and carrier photogeneration yield [2] and by the luminescence quenching during charge transfer [54]. The process of charge photogeneration in electric field starts with the electron-hole pair formation and their following dissociation into free charge carriers due to redistribution of electronic density in molecules [55]. In the case of irradiating by the high energy photons the charge carriers are appeared directly [14]. The efficiency of photogeneration strongly depends on the molecular structure and its surroundings as well as temperature. Note that the processes of photogeneration, transport and recombination are not separated complicating the data analysis. It was found [55] that the photogeneration current depends exponentially on the square root of the applied potential, and independent on electrodes. In the ordered organic structures the photoconductivity is higher than in disordered [56].

TRANSPORT IN ORGANIC SYSTEMS UNDER TRANSMISSION OF LOW-ENERGY ELECTRONS

The most valuable tool of "clean" electron transport studies is the spectroscopy of low-energy electron transmission [57–61]. A well-collimated monokinetic electron beam is incident normally from vacuum on a thin solid organic film. The transmission of electron beam through molecular medium results in its attenuation depending on electron energy and organics properties. This attenuation is caused by elastic and inelastic electrons scattering at different angles producing excited molecules, positive and negative ions, etc. The transmitted current value measured as a function of the incident electron energy from 0 to 20–50 eV gives the transmission spectrum (LEET). In the similar manner we can obtain the spectrum of reflected [62] and/or emitted [63]) electrons (see Fig. 1). If we analyse the transmitted or emitted electrons on energy, we obtain an electron energy loss spectrum (EELS) determined by subtraction of transmitted/reflected electron energy from initial. One of this method modification is the transmission of photoemitted electrons with a wide spectrum [64] or energy tunable [35]. Transmission and loss spectra can be registered at different incidence and registration angles, sample types and thickness, substrates and temperatures. The main advantages of this method are the possibility of the incident electron energy change and the electrodes absence. But, very thin films are required for such studies. Unfortunately, it is not practically possible to construct very

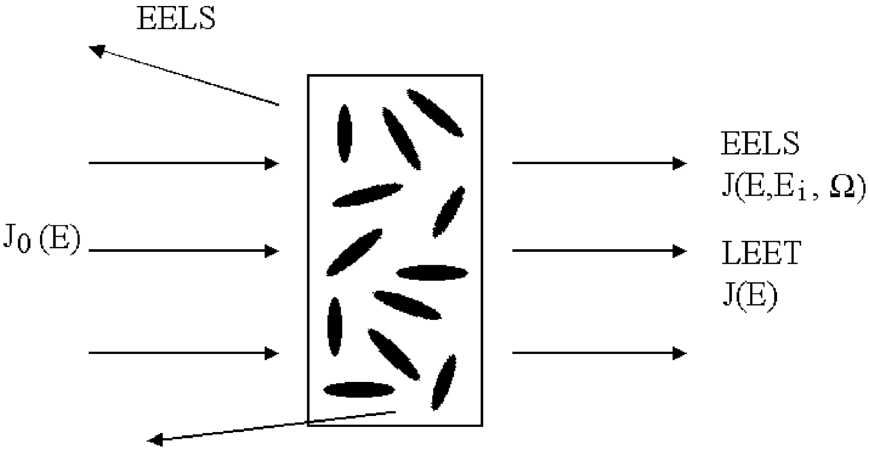

FIGURE 1 Schematic diagram of low-energy electrons transmission through thin organic films.

thin (less than 5 nm) free-standing solid film (even polymeric). Instead, molecules are condensed on a metal substrate being an electrode for transmission measurements. Due to weak intermolecular interactions in organic materials, good results can be obtained in the gas phase, without metal substrate. In the case of the reflected and emitted electrons studies the measurements can be made with thick enough films.

The electron impact spectroscopy gives the possibility to study transport of electrons and their behaviour at the interfaces in thin organic films, effect of molecule geometry location, Coulomb electron-electron interactions, hot electron relaxation, to determine ranges and the charge carrier generation thresholds. It is good for the molecular electronic structure and secondary electron emission studies. It represents enormous interest for registration of singlet-triplet transitions and vibrational excitation [65], determination of cross sections of excitation, trapping and fragment production from molecule dissociation.

Many phenomena connected with low-energy electron transport in the solid organic media, and multiple scattering result in complication of theoretical studies (though some progress is available: see, for example, [66]) and interpretation of obtained data. Note, that theoretical approaches for calculation of interaction cross sections and electron transfer through single organic molecules are similar. At high electron energies (more than 50–100 eV) inelastic scattering by molecules can be described in terms of optical transitions. In Born approximation the incident electron may be regarded as a sudden and small external perturbation arising from the long-range dipole interaction between the incident electron and the molecular target. The electron wavelength at such energies is short as compared to molecule dimensions and electron can be considered interacting independently with every molecule. Then the scattering amplitude equals to the sum of individually scattered waves. At low impact energies, and especially near the excitation threshold, the target orbitals are strongly perturbed by the presence of a nearby electron and the electron-target potential is severely distorted. This perturbation, connected with the possibility of spin exchange through a short-range interaction is responsible for the optically forbidden transitions excitation. In molecular solids it is not known exactly how electron-molecule potential is perturbed by the presence of other similar molecules. If electron wavelength is of the order of intermolecular distance, electron can interact collectively with many molecules [59].

LEET Spectra

The typical LEET spectra and the difference between spectra with and without organic film are presented in Figure 2. Such spectra reflex

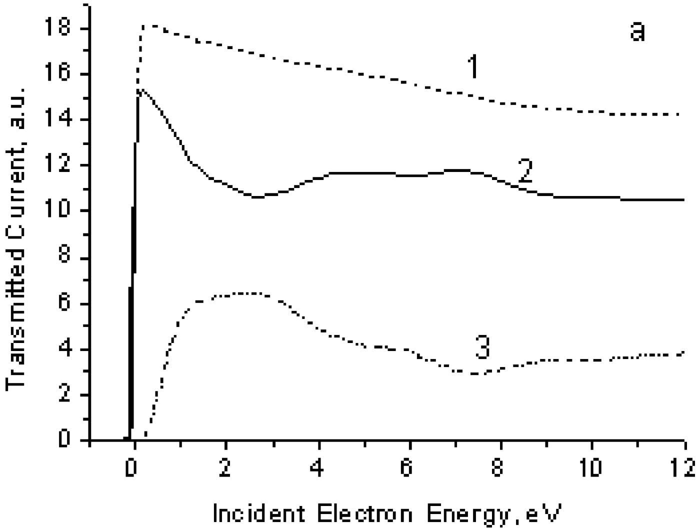

FIGURE 2 LEET spectra with (2) and without (1) organic film, and interaction total cross sections (3) derived from curves (1) and (2) for (a) benzene [65] (with permission) and (b) Alq_3 (our data).

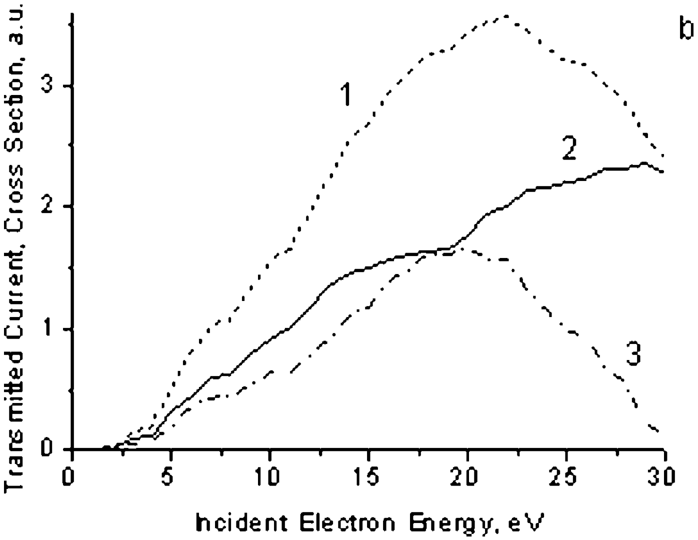

FIGURE 2 Continued.

elastic and inelastic scattering of the electrons inside the film and at the interfaces; they depend on the molecule nature, molecules ordering degree and substrate. A correlation between band structure and LEET spectrum was first pointed out in [62]. At electron energies under the molecule ionization energy the transmitted current consists of unscattered part of the beam, elastic scattered current and inelastic scattered current. In the case of higher electron energies the secondary electrons with a kinetic energy of several electron-volts also contribute in the back scattered current exceeding initial [60,67]. The secondary electron emission from some polymers, anthracene, tetracene and pentacene [68] was observed. As follows from LEET spectra registered at different film thicknesses, the current of transmitted electrons decreases exponentially with thickness L in amorphous tetracene [51] and other compounds [69–71], in accordance with a scattering formula $I = I_0 \exp(-\sigma n L)$. It has been established that the conduction band in many alkanes is at about 0.2–0.8 eV above the vacuum level [72].

It is supposed [57] that in the electron energy range from zero to band gap energy only elastic scattering occurs. The interference of the electronic wave in potential well formed by vacuum-film and film-substrate interfaces is observed in crystalline structures [72,73]. The width and depth of the potential well can be obtained from LEET spectra of these films. It was found for some phthalocyanines, coronene etc. that the effective potential strongly depends on interaction between molecule and substrate, and the width of this potential is much higher than the molecular thickness [73]. In amorphous films the interference is absent.

The experiments [64] on transmission of low-energy electrons (~1 eV) through organized organic thin films shows the importance of the molecules ordering. Before the film is heated, electrons with an energy above 1 eV pass through it almost balistically. Heating of the film causes their considerable scattering. The transmission of electrons through such films is very sensitive to composition, film structure and substrate. The general lows of electron transport in these films are the three-dimensional character of the transmission process and the dependence of on the structure of the electronic band of the underlying organic material. As the film thickness is increased, the electron spectrum spreads and the kinetic energy of higher-energy electrons decreases. The electron transmission strongly depends on their packing. Elastic processes are very sensitive to crystalline order and film thickness due to quantum dimensional effects. LEET spectra are strongly changed under transformation of the film crystalline structure and its phase transition to amorphous state [74], and temperature [57]. Thin structure in LEET spectrum is disappeared during melting and again appears after recrystallization [74]. The observed oscillations in the transmission probability for porphyrin-based films as a function of the kinetic energy is argued to be due to effects of band structure above the vacuum level in the well ordered molecular adsorbate [35]. If molecules in the film are disordered, electrons strongly scattered near the surface in all directions, and momentum of incident electrons is essentially not determined [75]. The probability of tunneling increases with increasing of electron energy.

Electron trapping or space charge causes a transient potential due to Coulomb electron repulsion [76]. Electronic charge appearing on the film surface after irradiation by electrons of a known energy or as a result of termalization of electrons with higher energies, produces a retarding potential, which is apparent as a displacement of any subsequent LEET spectrum to higher incident energies, especially for electronegative molecules (partly oxygen) [57]. Note that the similar phenomena determining space charge limited current are also observed in MOM structures [8]. The observed rate of charging k is connected with a charge trapping cross section σ_t as $k = LJ_0\sigma_t n_0/\varepsilon e$, where ε and L is the dielectric constant of the film and its thickness, J_0 is the incident current density, n_0 is the initial trap density, e is the unit charge [58], i.e., k depends on the primary beam current. This charge is caused by electron attachment with negative ions formation and determined by electron energy. These ions are revealed in LEET spectra [77]; they strongly effect on electron transport in the film.

EELS

The typical EELS contains the elastic and inelastic scattering bands. Inelastic electron scattering is determined by the molecule electronic structure. An exact accordance to this structure can be found not with LEET spectra, but using the transmitted or reflected electrons energy distribution, i.e., EELS. Typical EELS of tris(8-hydroxyquinolinato) aluminum (Alq_3) is presented in Figure 3. Note that EELS of organic compounds in the gas phase and solid film are very similar [78] (solid state EELS is shifted 0.2–0.3 eV relative to the gas phase) pointing out the same transport nature. A good coincidence of EELS was observed also for other molecules [79,80]. Electrons, interacting with a molecular ensemble, cause transitions into different electronic states. The typical EELS contains bands of the singlet-singlet and singlet-triplet

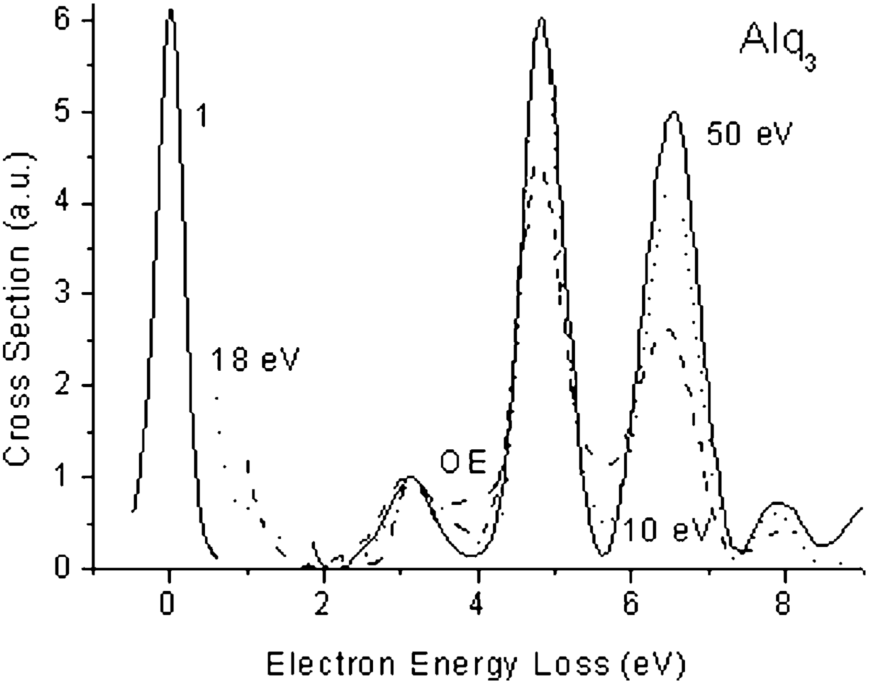

FIGURE 3 Electron energy loss spectra of Alq_3 at different electron energies. Curve 1-elastic scattering (reduced), OE-photoabsorption spectrum.

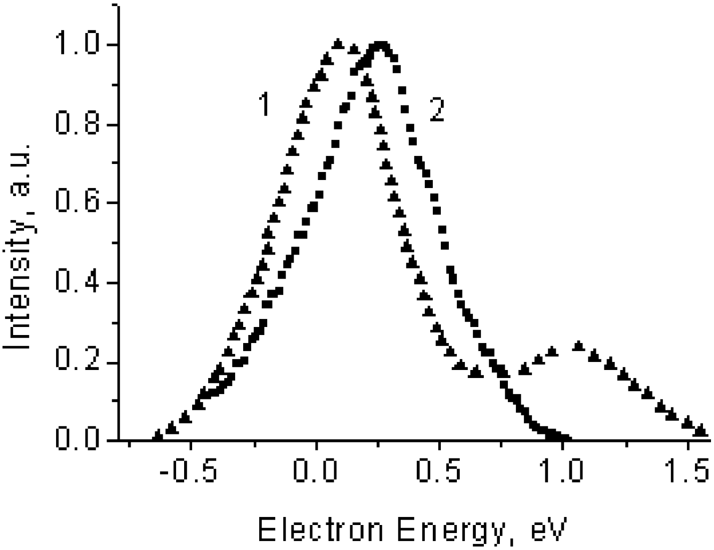

FIGURE 4 Effective yields of phenantrenquinone$^-$/phenantrenquinone (1) and Alq_3^-/Alq_3 (2).

transitions, vibrational excitation, positive and negative ions formation. In EELS in Figure 3 the losses less than 2 eV are caused by vibrational excitation, that is responsible for the elastic peak on the EELS side broadening. The vibrational spectra can be fully resolved with complicated spectrometers [81] showing strong dependence of band intensities on packing and sample thickness. At low incident electron energies the transient negative ions formation peak (Fig. 4) can be observed [82]. They decay by stabilization, formation of vibrationally and electronically excited molecules or dissociation into stable anion and neutral radical [78]. The electron attachment in the solid state occurs at electron energies which are close, but less than in the gas phase. Losses (Fig. 4) in the more than 4 eV region are caused by electronic transitions. The position of these bands does not depend on initial electron energy, but the intensity changes strongly. The shape of these bands can slightly change under the transition from amorphous structure to ordered. It was shown for a wide number of organic compounds [83–86] that EELS are close to the spectra of optical absorption, and at rather high electron energies they are fully coincide. The difference is connected mainly with the presence of bands caused by direct excitation of triplet states. As opposite to optical excitation (molecular coefficients of the photoabsorption from the basic state into singlet and triplet states differ three-five orders of magnitude), in the case of inelastic excitation by electrons these cross sections can be comparable. Excitation of molecule into triplet state occurs by exchange of the incident and molecular electrons with opposite spin projections. In such interaction, the molecular spin changes by unit, but the total spin of electron-molecule system before and after collision remains the same. In the case of excitation by proton impact such transitions were not found in EELS [87]. These transitions have resonance character, so their cross section quickly decreases with electron energy. Changes in EELS are also confirmed by triplet transitions calculated spectrum. But, the differences observed in EELS are essentially lower that the bands intensities in calculated triplet spectra. This indicates only partial elimination of intercombination transitions forbidenness [88]. Note that a quarter of inelastic exchange scattering populates singlet states in accordance with their statistical weights (1:3). The introducing of heavy atoms into molecule was shown to increase the probability of triplet transitions [86,88]. It should be noted that the stability of molecules have to be accounted interpreting both transmission and loss spectra because the destruction products can contribute to the obtained data.

It is very interesting how electron flow through the molecular orbitals. The scattered energy value was found to depend essentially on the electron movement direction, according to transition dipole momentum. Even at high energy electron excitation the anisotropy of the electron scattering in EELS of anthracene monocrystals was observed [89]. As it was mentioned above, LEET spectra are strongly changed under transformation of the film crystalline structure and its phase transition to amorphous state [74]. Note that the different transitions cross sections essentially depend on scattering angle [90]. Such studies are also very useful for interpretation of electron transport in MOM structures. The observed behaviour is in accordance with conductivity data. A strong conductivity anisotropy occurs in ordered organic films [91]. The mobility of electrons along a molecule of the polydiacetylene reaches $6000\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{sec}^{-1}$ that is much higher than across molecules [2]. The electrons are better conducted through all-trans amphiphilic chains (where the electronic wave functions in the band are delocalized) than through chains containing some gauche bonds (introducing disorder which increases scattering and localizes the electronic wave function) [64].

The intensity (and cross section) of elastic and two inelastic bands energy dependence, characterizing the probability of energy transfer from electron to molecule, is presented in Figure 5. It can be seen that the elastic band is much (10–15 times) more intense than inelastic. It is known that the elastic scattering probability increases with the

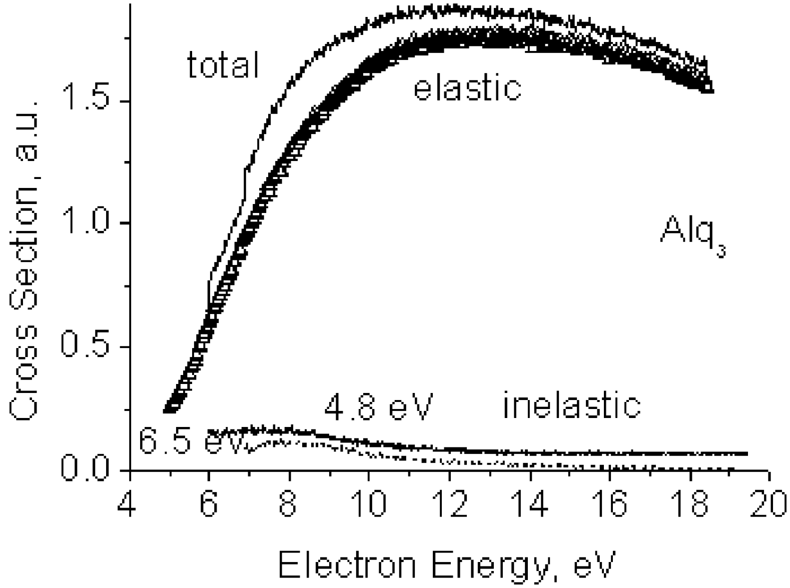

FIGURE 5 Dependence of total, elastic and inelastic (bands 4.8 and 6.5 eV) scattering on the projectile electron energy.

number of atoms in the molecule. It is caused by three type of electron-molecule interaction (i) Coulomb (it is essential at the ranges of molecular dimensions), (ii) polarization (at long ranges), and (iii) exchange (at low electron velocities). The elastic cross section is close to its geometrical dimensions [84]. The depositions of exchange and polarization interactions at rather high electron energies is not essential, it grows at low energies. The shielding effect at rather low electron energies results in cross section decreasing [92]. The maximal value of the inelastic transition cross section is reached at approximately 2–3 E_{th}, where E_{th} is the energy of considered electronic molecular transition. Therefore, the most effective for molecule excitation electrons with the energy not equal to E_{th}, but 2–3 times exceeding it. If electron energy equals to E_{th}, the cross section of this process is near zero. Therefore, it is unlikely that resonance transition will occur in the case of coincidence of Fermi and LUMO levels for metal electrode and molecule, accordingly. The energy behaviour of the elastic band is similar. The positions of maximums for elastic and inelastic scattering are different, so the most preferable energy for inelastic excitation of Alq$_3$ is about 8 eV. The summation of mentioned dependences for all bands of elastic and inelastic scattering gives the total scattering cross section curve (Fig. 5). It is easy to show that this curve is connected with the difference of LEET spectrum with and without organic film. For very thin films this difference gives also the total scattering cross section (Fig. 2). So, the main deposition to the LEET spectrum gives elastic scattering, and inelastic losses are appeared as an additional structure in LEET spectrum.

Range

Passing through the molecular medium, electron undergoes multiple scattering and its velocity decreases. A range is determined as a distance passing by electron until stop. In radiation physics the real (determined from full energy losses) and the extrapolated (projection to the initial movement direction; it is experimentally determined) range is distinguished. The real range is some times higher than extrapolated. A mean free path (MFP) $d = 1/n\sigma$ (where n is the concentration of scatterers, σ is the cross section of a process) describes the average distance between collisions. This indirect characteristic is determined also by the scattering cross section of the corresponding elastic and inelastic process. The estimated value d of the inelastic process is about 100 nm, and 6 nm for elastic [1] that is in satisfactory agreement with experimental data presented below. Both cross section (see above) and mean free path depends on electron energy. In polysulfone film with tris(stylben)amine at $E = 2\,\text{MV/cm}$ the electron range was found to be 55 nm [16]; the inelastic MFP in tryptophan was measured to be from 9 to 28 nm, and elastic was from 0.43 to 0.85 nm [93], the inelastic MFP was found to be about ten nm in pentacene and naphthacene, and some tens nm in perylene and coronene [69]. Mean free path in thin (1–8 nm) Cu-phthalocyanine films reaches 6.4, 3.9, 2.6 and 2.3 nm at electron energies above Fermi level 5, 7.2, 14.4 and 18 eV, correspondingly [71]. MFP is essentially lower in the big losses region. The presence of inhomogeneities in the organic film increases the electric field and, as a consequence, mean free path [51].

Excitation

Many π-conjugated organic molecules can fluoresce, i.e., emit light upon excitation. As follows from EELS, at rather high electron energies the molecules in the film become excited into different electronic states. The feature of the organic compounds is that luminescence emits under transition from lower singlet excited level with the energy of 2–4 eV, independently on excited level. Note that in the gas phase this luminescence spectrum is very sensitive to the excitation energy.

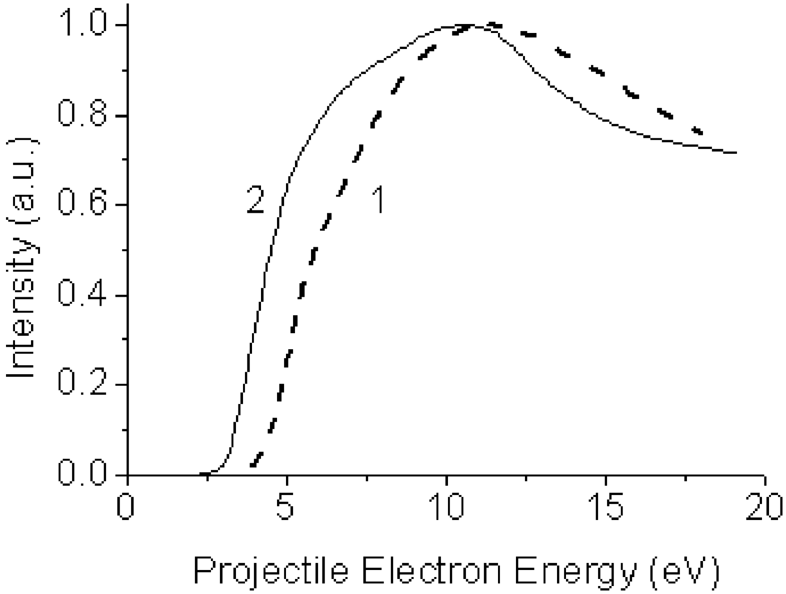

FIGURE 6 Excitation functions of (1) TPD and (2) Alq_3.

The resulting fluorescence spectrum was found to be formed by the deposition of molecules excited into all electronic levels regarding the excitation cross sections of these levels as a function of the electron energy and the fluorescence quantum yields corresponding to these levels [60,94]. The qualitative description of the efficiency of electron energy transformation into light gives a fluorescence excitation function (FEF) representing the fluorescence intensity dependence on electron energy. This function reaches its maximal value at an exciting electrons energy three or four times higher than the threshold energy (approximately equal to the excitation energy of the first excited singlet state) [95]. A further increase in the electrons energy leads to a slow decrease in the fluorescence intensity. The FEF value is proportional to the sum of the excitation cross sections of all electronic states for a given energy of electrons regarding the fluorescence quantum yield, i.e., the FEF behaviour reflects essentially both the intramolecular processes and the efficiency of the electron-molecule interaction [94]. The typical excitation function of N,N′-diphenyl-N, N′-bis(3-methyl-phenyl)-1,1′-biphenyl-4,4′-diamine (TPD) and Alq_3 is given in Figure 6. Note, that taking into account the inelastic interactions gives the possibility the relatively simple description of the electroluminescence processes [96].

For many organic compounds the fluorescence radiation under electron beam excitation is polarized even in the gas phase [97], it essentially depends on electron energy. This polarization reaches rather high values in anthracene monocrystals under irradiation by high energy electrons [98] and in the ordered organic films electroluminescence [18]. The fluorescence polarization is essentially connected with the molecular electronic shell, so it gives an additional information about shell properties and electron-molecule interactions determining electron transport.

It can be note also a number of another methods of electron impact spectroscopy suitable for transport and electron-molecule interaction studies such as mass spectroscopy, electron stimulated desorption, molecular dissociation, electron and ion induced reactions [57]. The latter method possesses electron induced chemical nanolithography [99].

CONCLUSION

Thus, the consideration of different tools for the electron transport studies in organic systems reveals that the observed features of the transmission of the electric current and the electron beam (the transmission coefficient dependence on the sample thickness, temperature behaviour, elastic and inelastic transport, anisotropy, charging, luminescent properties) are similar. It confirms a similar nature of the electron transfer processes. It can be claimed that there is no fundamental difference in conductivity properties of ordered and disordered organic materials. Position, structure and temperature disordering result in the increase of electron scattering processes and, as a consequence, the organics conductivity. At very low electron energies (less than 1 eV) a strong electron attachment occurs especially for electronegative molecules. The most promising approach to develop the common model describing electron transport in the MOM structures has to contain two terms (i) the term concerning injection current including barrier and spectrum of emitting electrons at used applied voltage and (ii) the scattering cross section (total or/and differential) as a function of electron energy, scattering angle and temperature. Then it will be possible to compare the numerical data on electron transport obtained by both methods. The usage of the electron impact spectroscopy methods possessing to measure essentially more characteristics than under electric current transmission, gives the possibility to study practically all the variety of proceeding phenomena rather clearly, and to help invaluably for the interpretation of electric current transmission data.

REFERENCES

[1] Kukhta, A. (2003). *J. Appl. Spectrosc.*, *70*, 165.

[2] Symon, J. & Andre, J. -J. (1988). *Molecular Semiconductors* (Russian Edition), Mir: Moscow.

[3] Heeger, A. J. (2002). *Synth. Met.*, *125*, 23.

[4] Jerome, D. & Bechgaard, K. (2001). *Nature*, *410*, 162.

[5] Zalesskaya, G. A., Sambor, E. G., & Bely, N. N. (2004). *J. Fluorescence*, *14*, 173.

[6] Holmlin, R. E., Haag, R., Chabinyc, M. L., Ismagilov, R. F., Cohen, A. E., Terfort, A., Rampi, M. A., & Whitesides, G. M. (2001). *J. Am. Chem. Soc.*, *123*, 5075.

[7] Markus, R. A. & Sutin, N. (1985). *Biochem. Biophys. Acta*, *811*, 265.

[8] Brütting, W., Berleb, S., & Mückl, A. G. (2001). *Org. Electronics*, *2*, 1.

[9] Brown, A. R., Bradley, D. D. C., Burroughes, J. H., Friend, R. H., Greenham, N. C., Burn, P. L., Holmes, A. B., & Kraft, A. (1992). *Appl. Phys. Lett.*, *61*, 2793.

[10] Book, K., Nikitenko, V. R., Bässler, H., & Elschner, A. (2001). *Synth. Met.*, *122*, 135.

[11] Pommerehne, J., Vestweber, H., Tak, Y. K., & Bässler, H. (1996). *Synth. Met.*, *76*, 67.

[12] Österbacka, R., Juška, G., Arlauskas, K., Pal, A. J., Källman, K. -M., & Stubb, H. (1998). *J. Appl. Phys.*, *84*, 3359.

[13] Korolev, Yu. D. & Mesyats, G. A. (1982). *Autoemission and explosive processes in gas discharge* (in Russian), Nauka: Novosibirsk.

[14] Tyutnev, A. P. & Sadovnichii, D. N. (1998). *Chem. Phys.* (Russian), *17*, 121.

[15] Vannikov, A. V., Grishina, A. D., & Novikov, S. V. (1994). *Chem. Usp.*, *63*, 107.

[16] Vestweber, H., Bässler, H., Grüner, J., & Friend, R. H. (1996). *Chem. Phys. Lett.*, *256*, 37.

[17] Reed, M. A. (1999). *Proc. IEEE*, *87*, 652.

[18] Godbert, N., Burn, P. L., Gilmour, S., Markham, J. P. J., & Samuel, I. D. W. (2003). *Appl. Phys. Lett.*, *83*, 5347.

[19] Sentein, C., Fiorini, C., Lorin, A., Socot, L., & Nunzi, J.-M. (1998). *Opt. Mater.*, *9*, 316.

[20] Chen, J. & Reed, M. A. (2002). *Chem. Phys.*, *281*, 127.

[21] Weber, H. B., Reichert, J., Weigend, F., Ochs, R., Beckman, D., Mayor, M., Ahlrichs, R., & Löhneysen, H. V. (2002). *Chem. Phys.*, *281*, 113.

[22] Di Ventra, M., Lang, N. D., & Pantelides, S. T. (2002). *Chem. Phys.*, *281*, 189.

[23] Reed, V. A., Zhou, C., Muller, C. J., Burgin, T. P., & Tour, J. M. (1997). *Science*, *278*, 252.

[24] Lehman, J., Ingold, G. L., & Hänggi, P. (2002). *Chem. Phys.*, *281*, 199.

[25] Petrov, E. G., May, V., & Hänggi, P. (2002). *Chem. Phys.*, *281*, 211.

[26] Samanta, M. P., Tian, W., Datta, S., Henderson, J. I., & Kubyak, C. P. (1996). *Phys. Rev.*, *53*, R7626.

[27] Kukhta, A. V., Kolesnik, E. E., Lappo, A. N., Pochtennyi, A. E., & Grabchev, I. K. *Solid State Physics* (in press).

[28] Seip, M. & Brauer, H.-D. (1992). *J. Am. Chem. Soc.*, *114*, 4486.

[29] Galperin, M., Nitzan, A., & Benjamin, I. (2002). *J. Phys. Chem.*, *A106*, 10790.

[30] Cade, N. A., Cross, G. H., Lee, R. A., Bajic, S., & Latham, R. V. (1988). *J. Phys.*, *21*, 148.

[31] Elinson, M. I. & Vasiliev, G. F. (1958). *Autoelectron emission* (in Russian). Nauka: Moscow.

[32] Komar, A. P. & Savchenko, V. P. (1965). *Solid State Physics*, *7*, 758.

[33] Musa, I., Munindrasdasa, D. A. I., Amaratunga, G. A. J., & Eccleston, W. (1998). *Nature*, *395*, 362.

[34] Ishii, H., Sugiyama, K., Ito, E., & Seki, K. (1999). *Adv. Mater.*, *11*, 605.
[35] Haran, A., Naaman, R., Ashkenasy, G., Shanzer, A., Quast, T., Winter, B., & Hertel, I. V. (1999). *Eur. Phys. J.*, *B8*, 445.
[36] Fomenko, V. S. (1981). *Emissive properties of materials* (in Russian). Naukova dumka: Kiev.
[37] Ueba, H. (1991). *Surf. Sci.*, *242*, 266.
[38] Kim, C. -W., Villagran, J. C., Even, U., & Thompson, J. C. (1991). *J. Chem. Phys.*, *94*, 3974.
[39] Lang, N. D. & Kohn, W. (1970). *Phys. Rev.*, *B1*, 4555.
[40] Li, F., Tang, H., Anderegg, J., & Shinar, J. (1997). *Appl. Phys. Lett.*, *70*, 1233.
[41] Jabbour, G. E., Kippelen, B., Armstrong, N. R., & Peyghambarian, N. (1998). *Appl. Phys. Lett.*, *73*, 1185.
[42] Hatton, R. A., Day, S. R., Chesters, M. A., & Willis, M. R. (2001). *Thin Solid Films*, *394*, 292.
[43] Bliznyuk, V., Ruhstaller, B., Brock, P. J., Scherf, U., & Carter, S. A. (1999). *Adv. Mater.*, *11*, 1257.
[44] Nüesch, F., Rotzinger, F., Si-Ahmed, L., & Zuppiroli, L. (1998). *Chem. Phys. Lett.*, *288*, 861.
[45] Le, Q.-T., Forsythe, E. W., Nüesch, F., Rothberg, L. J., Yan, L., & Gao, Y. (2000). *Thin Solid Films*, *363*, 42.
[46] Carter, S. A., Angelopoulos, M., Karg, S., Brock, P. J., & Scott, J. C. (1997). *Appl. Phys. Lett.*, *70*, 2067.
[47] Li, F., Feng, J., Cheng, G., & Liu, S. (2002). *Synth. Met.*, *126*, 347.
[48] Sakuratani, Y., Asai, M., Tokita, M., & Miyata, S. (2001). *Synth. Met.*, *123*, 207.
[49] Novikov, S. V. (2004). *Macromol. Symp.*, *212*, 191.
[50] Polymeropoulos, E. E. & Sagiv, J. (1978). *J. Chem. Phys.*, *69*, 1836.
[51] Grechov, V. V. (1983). *Chem. Phys. Lett.*, *96*, 237.
[52] Wert, C. A. & Thomson, R. M. (1964). *Physics of solids*. McGraw-Hill Book Company: New York.
[53] Galperin, M., Nitzan, A., & Peskin, U. (2001). *J. Appl. Phys.*, *114*, 9205.
[54] Ohta, N., Kanada, T., Yamazaki, I., & Itoh, M. (1998). *Chem. Phys. Lett.*, *292*, 535.
[55] Davidenko, N. A., Zabolotny, M. A., Ishchenko, A. A., Kuvshinsky, N. G., & Borolina, N. P. (2004). *High Energy Chemistry* (Russian), *38*, 1.
[56] Chen, H. -Z., Wang, M., & Yang, S.-L. (1999). *Thin Solid Films*, *357*, 208.
[57] Sanche, L. (1995). *Scan. Microsc.*, *9*, 619.
[58] Bass, A. D. & Sanche, L. (1998). *Radiat. Environ. Biophys.*, *37*, 243.
[59] Sanche, L. (1979). *J. Chem. Phys.*, *71*, 4860.
[60] Kukhta, A. V. (1998). *J. Appl. Spectrosc.*, *65*, 722.
[61] Allan, M. (1989). *J. Electron Spectr. Rel. Phenomena*, *48*, 219.
[62] Hiraoka, K. & Hamill, W. H. (1972). *J. Chem. Phys.*, *57*, 3870.
[63] Botelho Do Rego, A. M., Rei Vilar, M., Lopes Da Silva, J., Heyman, M., & Schott, M. (1986). *Surf. Sci.*, *178*, 367.
[64] Naaman, R., Haran, A., Nitzan, A., Evans, D., & Galperin, M. (1998). *J. Phys. Chem.*, *102*, 3658.
[65] Apai, G. & McKenna, W. P. (1994). *J. Phys. Chem.*, *98*, 9735.
[66] Dwyer, V. M. (1993). *Phys. Rev.*, *A47*, 3044.
[67] Ueno, N., Sugita, K., Seki, K., & Inokuchi, H. (1986). *Phys. Rev.*, *B34*, 6386.
[68] Rei Vilar, M., Heyman, M., & Schott, M. (1983). *Chem. Phys. Lett.*, *94*, 522.
[69] Hino, S., Sato, N., & Inokuchi, H. (1977). *J. Chem. Phys.*, *67*, 4139.
[70] Chang, Y. C. & Berry, W. B. (1974). *J. Chem. Phys.*, *61*, 2727.
[71] Komolov, S. A., Lazneva, E. F., & Komolov, A. S. (2003). *JETP Lett.*, *29*, 13.

[72] Perluzzo, G., Bader, G., Caron, L. G., & Sanche, L. (1985). *Phys. Rev. Lett.*, *55*, 545.

[73] Yamane, H., Ito, K., Kera, S., Okudaira, K. K., & Ueno, N. (2002). *J. Appl. Phys.*, *92*, 5203.

[74] Ueno, N., Sugita, K., & Shinmura, T. (1991). *Phys. Rev.*, *B44*, 6472.

[75] Bader, G., Perluzzo, G., Caron, L. G., & Sanche, L. (1984). *Phys. Rev.*, *B30*, 78.

[76] Sanche, L., Bader, G., & Caron, L. (1982). *J. Chem. Phys.*, *76*, 4016.

[77] Burrow, P. D., Michejda, J. A., & Jordan, K. D. (1987). *J. Chem. Phys.*, *86*, 9.

[78] Kukhta, A. V., Kazakov, S. M., Murtazaliev, D. V., & Ritchik, D. V. (2003). *Chem. Phys. Lett.*, *373*, 492.

[79] Asmis, K. R., Allan, M., Schafer, O., & Fulscher, M. J. (1997). *Phys. Chem.*, *A101*, 2089.

[80] Swiderek, P., Michaud, M., & Sanche, L. (1995). *J. Chem. Phys.*, *103*, 8424.

[81] Swiderek, P., Winterling, H., & Ibach, H. (1997). *Chem. Phys. Lett.*, *280*, 556.

[82] Kukhta, A. V., Ritchik, D. V., Asfandiarov, N. L., Falko, V. S., Lukin, V. G., & Pshenichnyuk, S. A. (2003). *Int. J. Mass Spectrometry*, *230*, 41.

[83] Borisevich, N. A., Kazakov, S. M., Kolesnik, E. E., Kukhta, A. V., Mitkovets, A. I., Murtazaliev, D. V., & Khristophorov, O. V. (2001). *J. Appl. Spectrosc.*, *68*, 447.

[84] Borisevich, N. A., Kazakov, S. M., Kukhta, A. V., Mitkovets, A. I., Murtazaliev, D. V Raichenok, T. F., & Khristophorov, O. V. (2001). *J. Appl. Spectrosc.*, *68*, 871.

[85] Borisevich, N. A., Kazakov, S. M., Kukhta, A. V., Murtazaliev, D. V, & Khristophorov, O. V. (2002). *J. Appl. Spectrosc.*, *69*, 190.

[86] Borisevich, N. A., Kazakov, S. M., Kukhta, A. V., Murtazaliev, D. V, Pavich, T. A., & Khristophorov, O. V. (2002). *J. Appl. Spectrosc.*, *69*, 487.

[87] Doering, J. P., & Moore, J. H. Jr. (1972). *J. Chem. Phys.*, *56*, 2176.

[88] Borisevich, N. A., Kazakov, S. M., Kukhta, A. V., Murtazaliev, D. V, Khristophorov, O. V., Ivanov, A. L., & Artukhov, V. Ya. (2004). *J. Appl. Spectrosc.*, *71*, 628.

[89] Venghaus, H. (1970). *Z. Phys.*, *239*, 289.

[90] Gianturco, F. A. & Lucchese, R. R. (2000). *J. Chem. Phys.*, *113*, 10044.

[91] Collet, J., Lenfant, S., Vuillaume, D., Bouloussa, O., Rondelez, F., Gay, J. M., Kham, K., & Chevrot, C. (2000). *Appl. Phys. Lett.*, *76*, 1339.

[92] Kukhta, A. V., Kolesnik, E. E., & Ritchik, D. V. (2003). *Doclady NAN Belarusi* (in Russian), *47*, 69.

[93] Leclerc, G., Goulet, T., Cloutier, P., Jay-Gerin, J.-P., & Sanche, L. (1987). *J. Phys. Chem.*, *91*, 4999.

[94] Kukhta, A. V., Kazakov, S. M., Kolesnik, E. E., Mit'kovets, A. I., Murtazaliev, D. V., & Sorokin, G. (2002). *Proc. SPIE*, *4747*, 224.

[95] Kazakov, S., Kukhta, A., & Suchkov, V. (2000). *J. Fluorescence*, *10*, 409.

[96] Kukhta, A., Kolesnik, E., Taoubi, M., & Galkin, V. (2002). *J. Optoel. Adv. Mat.*, *4*, 575.

[97] Kukhta, A. V., Mitkovets, A. I., & Ritchik, D. V. (2004). *J. Appl. Spectrosc.*, *71*, 472.

[98] Zhevandrov, N. D. (1987). *Optical anisotropy and energy migration in molecular crystals* (in Russian), Nauka: Moscow.

[99] Gölzhäuser, A., Eck, W., Geyer, W., Stadler, V., Weimann, T., Hinze, P., & Grunze, M. (2001). *Adv. Mater.*, *13*, 806.