PHYSICAL REVIEW B **76**, 045210 (2007)

Analytic model of hopping mobility at large charge carrier concentrations in disordered organic semiconductors: Polarons versus bare charge carriers

I. I. Fishchuk,[1,*] V. I. Arkhipov,[2,†] A. Kadashchuk,[2,3] P. Heremans,[2] and H. Bässler[4]
[1]*Institute for Nuclear Research, National Academy of Sciences of Ukraine, Prospekt Nauky 47, 03680 Kyiv, Ukraine*
[2]*IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium*
[3]*Institute of Physics, National Academy of Sciences of Ukraine, Prospekt Nauky 46, 03028, Kyiv, Ukraine*
[4]*Institute of Physical, Nuclear and Macromolecular Chemistry and Material Science Center, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany*

(Received 14 March 2007; revised manuscript received 2 June 2007; published 16 July 2007)

An analytical theory based on the effective medium approach (EMA) is formulated to describe the charge carrier mobility as a function of the charge carrier concentration in a disordered organic material with a Gaussian density-of-state distribution using jump rate expressions based on either the Miller-Abrahams or polaron model. In this study, we address the problem of how the carrier density dependence of charge mobility is affected by the type of jump rate and, consequently, by polaron effects. Our theoretical consideration employs the concept of the effective transport energy. Results of the EMA calculations in the framework of the Miller-Abrahams jump rate model show a considerable increase of the drift charge carrier mobility with increasing carrier concentration, in good agreement with previous theoretical studies, numerical simulation data, and experiment. At very large carrier densities, however, the theory predicts an abrupt decrease of the charge mobility. A key result of the present study is that a considerably weaker dependence of the mobility on the carrier concentration is found for the polaron jump rate model. Also, with this model, the polaron mobility dramatically decreases at very high carrier densities. An important implication of this study is that the common observation of a field-effect mobility that is orders of magnitude larger than time-of-flight (ToF) or space-charge-limited-current mobilities is incompatible with a polaron binding energy large compared to the width of the distribution of states. On the other hand, the existence of a significant polaron binding energy offers a plausible explanation why, in certain organic disordered materials, field-effect transistor and ToF mobilities are similar.

DOI: 10.1103/PhysRevB.76.045210 PACS number(s): 72.20.Jv, 72.20.Ee, 71.38.−k, 66.30.−h

I. INTRODUCTION

Charge carrier hopping within a positionally and energetically disordered system is a commonly accepted model describing charge carrier transport in disordered organic semiconductors (see for review Refs. 1–4). In an energetically disordered hopping system, charge carriers present in the semiconductor after photogeneration or injection from electrodes tend to relax toward the tail states of the density-of-states (DOS) distribution. For organic semiconductor, the DOS is usually assumed to be of Gaussian shape, characterized by a width σ.[5,6] Depending on the magnitude of energetic disorder, quasiequilibrium is established sooner or later, as described by the Gaussian disorder model of Bässler.[1] A notorious feature of the Gaussian DOS is that at small carrier concentrations, when charge carriers are noninteracting, the majority of equilibrated carriers mostly occupy weakly filled states well above the Fermi level. In this case, the equilibrium occupational DOS (ODOS) is also a Gaussian with width σ but offset from the center of the intrinsic DOS by an energy $\varepsilon_0 = -\sigma^2/k_BT$. The charge transport is controlled by carrier jumps from states around the energy level ε_0 to the so-called effective transport energy level (see below). Therefore, at low carrier concentration, the position of the Fermi level in case of an empty DOS is irrelevant for the charge carrier mobility. This case is typically realized in time-of-flight (ToF) experiments of study of charge carrier mobility.

Recently, however, it was recognized that this is no longer true at high carrier concentrations when the deep tail states of the DOS are completely filled by carriers and the Fermi level raises above the mean quasiequilibrium energy level.[7–9] At sufficiently high carrier densities, charge transport is then controlled by carrier jumps from states around the Fermi level to the transport energy level. In this case, the equilibrium energy distribution of carriers is described by the Fermi-Dirac distribution.[7–9] Such a situation is realized in an organic thin-film transistor (OTFT) and in chemically doped organic semiconductors. Experimentally, it was found that charge mobility in the same material can differ up to 3 orders of magnitude depending on whether the mobility is measured in a diode or a field-effect transistor (FET) device geometry.[7,8,10] This demonstrates that the concentration dependence of the mobility must be taken into account in an adequate description of charge transport properties in organic electronic devices such as organic FETs (OFETs).

There were already several attempts to describe charge transport at high carrier densities.[10–17] Arkhipov *et al.*[7] pointed out that in chemically doped materials and in the conductive channel of a FET, the number of charge carriers occupying deep tail states of the Gaussian DOS distribution can be comparable to the total density of the localized states. They suggested a stochastic hopping theory incorporating the Fermi-Dirac distribution to describe the temperature dependence of the charge mobility at high concentration and proved that the activation energy of the mobility decreases with increasing carrier concentration.[7] This can explain the much higher mobility in FET devices compared to that in organic light emitting diodes. It should be mentioned that there exist, however, organic disordered materials with a rather small difference in FET and ToF mobilities. A representative example is the polyfluorene derivative where these mobilities are all within the same order[18] and this observation has no plausible explanation.

The problem of carrier density effect on charge transport was further considered by several groups (Tanase *et al.*[8] Rubel and co-workers,[11–13] Arkhipov *et al.*,[16] Roichman and co-workers,[9,15,17] and Pasveer and co-workers.[10,14]). A mean medium approximation (MMA) analytical theory[9,15] was used to calculate the carrier concentration dependence of the charge mobility assuming the Miller-Abrahams jump rate and a Gaussian DOS distribution. In this treatment, however, local fluctuations of the electrochemical potential were neglected, which, as mentioned in Ref. 10, has resulted in considerable overestimation of the mobilities by several orders of magnitude at low temperatures, thus making this model unrealistic. Besides, MMA calculations of the carrier density effect have not been performed for the polaron jump rate model.

To our knowledge, an influence of possible polaron formation on the charge mobility at high carrier densities has not been considered, although for some organic systems, it is believed that the deformation energy due to polaron effects might be comparable to the disorder energy and polaron formation has to be taken into account to describe the observed temperature dependence of mobility.[19] The polaron transport under the influence of energetic disorder was considered for the small-concentration limit by an analytical theory of Kenkre and co-worker[19,20] using the variable range hopping technique[20] assuming that disorder plays the key role and polarons are always in the diabatic limit. Later on, computer simulations by Parris *et al.*[21] suggested a polaronic correlated disorder model incorporating a small polaron transfer rate to explain the Poole-Frenkel-type dependences of polaron mobility with electric field. With this model, the polaron transport with realistic values for the transfer integral and the polaron binding energies can be in good agreement with experimental observations for low carrier concentrations. These results have been recently supported also by analytical theory of Fishchuk *et al.*[22] using an effective medium approach.

In the present work, an analytical theory based on the effective medium approximation (EMA) is formulated to describe the charge carrier mobility as a function of the carrier concentration in a disordered organic material with a Gaussian density-of-state distribution using jump rate expressions based on either the Miller-Abrahams or polaron model (for application of the EMA method for low carrier concentrations, see Refs. 22 and 23). It will be shown that EMA calculations in the framework of the Miller-Abrahams model predict a considerable increase of the drift charge carrier mobility with increasing carrier concentration, in agreement with earlier calculations and experiments. The key result of the present study is that a much weaker carrier concentration dependence of the charge mobility is found for the polaron jump rate. Also, the theory demonstrates that the observation of a FET mobility that is orders of magnitude larger than a ToF or space-charge-limited-current (SCLC) mobility is incompatible with the notion of a large polaron binding energy ($E_a/\sigma \geqslant 3$). On the other hand, the present theory offers a possible explanation why certain organic disordered materials show a rather small difference between these mobilities. This agrees with predicted charge transport properties in organic semiconductors with large polaron binding energies. The effect was observed in polyfluorene copolymers where, indeed, a quite considerable polaron binding energy has been recently found from analysis of the charge transport data.[24]

This paper is organized as follows. First, we formulate basic equations of our EMA approach (Sec. II). Section III considers the carrier density effect on charge mobility within the EMA formalism. In Sec. IV, we discuss the configurational averaging procedures which have been used in charge transport theories for disordered organic solids. Section V considers the effective transport energy concept in the framework of the Miller-Abrahams and polaron jump rate models. Finally, in Sec. VI, we present the EMA calculation results for the Miller-Abrahams and polaron jump rate models and compare the prediction of the theory with available calculations and experimental results.

II. GENERAL EFFECTIVE MEDIUM APPROXIMATION FORMULATION

In the present paper, the EMA formalism is applied to consider the dependence of the drift charge carrier mobility on *carrier concentration* and *temperature* employing both the Miller-Abrahams- and the polaron-type of the jump rates. Hence, we investigate how a specific jump rate, i.e., presence or absence of the polaron effects, affects the charge transport properties at high carrier densities. We note that, in principle, two approaches could be used to calculate the charge carrier mobility at higher carrier concentrations. In the first approach, the many-particle problem of the kinetic equation is reduced by calculations to the effective single-particle transport by already applying the so-called mean-field approximation at the beginning.[25] The second approach implies the theoretical treatment of the single-particle charge carrier mobility, while the many-particle nature of the problem is accounted for at the stage of configuration averaging, as shown recently by Arkhipov *et al.*[16] We consider the second approach to be more appropriate and use it further in the present work. Within our single-particle EMA approach, we replace the disordered organic system by an effective three-dimensional (3D) manifold of localized sites with average intersite distance $a=N^{-1/3}$, where N is the concentration of the localized states.

To consider the charge transport issue for an *arbitrary type of jump rate* W_{ij} between localized states, we proceed from the general expression for the effective jump rate W_e and which has been obtained by the EMA formalism for three-dimensional disordered systems based on a two-site cluster approximation,[26]

$$\left\langle \frac{W_{12}-W_e}{\dfrac{W_{12}+W_{21}}{2}+2W_e} \right\rangle = 0. \tag{1}$$

Here, the angular brackets denote in the general case the configuration averaging over the distribution of site energies and distance between two sites in jump rates W_{12} and W_{21}. If the energy disorder is absent, one has $W_{12}=W_{21}=W$. Then, from Eq. (1), the well-known expression $\langle (W-W_e)/(W+2W_e)\rangle=0$ can be derived. The energetic averaging must be performed over the equilibrium energy distribution of charge carriers in their starting states $P(\varepsilon_1)$ and over the distribution of target unoccupied localized states $Q(\varepsilon_2)$.

In our treatment, we hereafter consider two conventional jump rate models of the hopping transport and corresponding expressions for the intersite jump rates W_{ij} which have been extensively used before in analytical calculations and computer simulations of the charge transport phenomena, namely:

(1) The *Miller-Abrahams model* assuming the jump rate

$$W_{ij} = \nu_0 \exp\left[-2\frac{r_{ij}}{b} - \frac{|\varepsilon_j-\varepsilon_i| + (\varepsilon_j-\varepsilon_i)}{2k_BT}\right], \qquad (2)$$

where ε_i is the energy of site i, r_{ij} the distance between sites, b the localization radius of a charge carrier, and ν_0 the attempt-to-escape frequency.

(2) The *polaron model* where W_{ij} is described by the Marcus jump rate expression

$$W_{ij} = W_0 \exp\left(-2\frac{r_{ij}}{b} - \frac{\varepsilon_j-\varepsilon_i}{2k_BT}\right), \qquad (3)$$

where

$$W_0 = W_1 \exp\left(-\frac{E_a}{k_BT}\right), \quad W_1 = \frac{J_0^2}{\hbar}\sqrt{\frac{\pi}{4E_ak_BT}}. \qquad (4)$$

Here, E_a is the *polaron activation energy*. It should be noted that Eq. (3) is a somewhat simplified version of the exact Marcus rate expression, in which only linear terms in the exponent with respect to the energy of localized states have been retained. Such approximation is valid when $\sigma \ll E_a$, which is justifiable for disordered organic materials where the importance of polaron effects has been found.[22,24]

Employing the Miller-Abrahams jump rate model [Eq. (2)], it follows that

$$\frac{W_{12}+W_{21}}{2} \cong \nu_0 \exp\left(-2\frac{r_{12}}{b}\right). \qquad (5)$$

Then, by neglecting the positional disorder, Eq. (1) yields the following for the effective Miller-Abrahams jump rate:

$$W_e = \langle W_{12}\rangle. \qquad (6)$$

In the case of polaron jump rate given by Eq. (3), one obtains

$$\frac{W_{12}+W_{21}}{2} \cong W_0 \exp\left(-2\frac{r_{12}}{b}\right)\exp\left(\frac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right). \qquad (7)$$

Upon ignoring the positional disorder and in the approximation iterative with respect to W_e, Eq. (1) yields the effective polaron jump rate

$$W_e = \frac{\left\langle W_{12}\exp\left(-\frac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)\right\rangle}{\left\langle \exp\left(-\frac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)\right\rangle}. \qquad (8)$$

Thus, in the case of polaron hopping transport, the EMA calculation of the effective jump rate W_e by Eq. (8) cannot be reduced to just a configuration averaging of the W_{12}. This is in contrast to the Miller-Abrahams model [cf. Eq. (6)].

III. CARRIER DENSITY EFFECT

We consider now the carrier density effect on charge mobility within our EMA formalism. We assume that double occupancy of a hopping site with carriers of equivalent sign is prohibited and that the DOS distribution is not affected by carrier density. The latter can be justified by the fact that the interaction between charges of the same sign is repulsive and, therefore, cannot create the Coulomb traps, and as a result, the broadening of the DOS distribution is much weaker than in the case of chemically doped materials. To calculate W_e for arbitrary carrier concentration n ($n<N$), one should account for the many-particle nature of the charge transport process by proper choice of the energy distribution functions for starting and target states: $P(\varepsilon_1)$ and $Q(\varepsilon_2)$ functions, respectively. If the intrinsic DOS distribution is a Gaussian with the width σ,

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{\varepsilon}{\sigma}\right)^2\right], \qquad (9)$$

then the normalized $P(\varepsilon_1)$ distribution can be presented as

$$P(\varepsilon_1) = \frac{g(\varepsilon_1)f(\varepsilon_1,\varepsilon_F)}{\int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)f(\varepsilon,\varepsilon_F)} \qquad (10)$$

and the normalized $Q(\varepsilon_2)$ distribution as

$$Q(\varepsilon_2) = \frac{g(\varepsilon_2)[1-f(\varepsilon_2,\varepsilon_F)]}{\int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)[1-f(\varepsilon,\varepsilon_F)]}. \qquad (11)$$

Here, $f(\varepsilon,\varepsilon_F)$ is given by the Fermi-Dirac statistics

$$f(\varepsilon,\varepsilon_F) = \frac{1}{1+\exp\left(\frac{\varepsilon-\varepsilon_F}{k_BT}\right)}. \qquad (12)$$

The value of the Fermi level ε_F can be determined from the following transcendental equation for the carrier concentration n:

$$n = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)f(\varepsilon,\varepsilon_F). \qquad (13)$$

In the limit of vanishing charge carrier concentrations ($n/N\to 0$), one obtains $(\varepsilon-\varepsilon_F)/k_BT \gg 1$. In such case of one-particle approximation, the position of the Fermi level is unimportant as the function $P(\varepsilon_1)$ has the form of the normalized equilibrium ODOS distribution function,

$$P(\varepsilon_1) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\varepsilon_1-\varepsilon_0}{\sigma}\right)^2\right], \tag{14}$$

At the same time, the function $Q(\varepsilon_2)$ takes the form of the DOS distribution function:

$$Q(\varepsilon_2) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\varepsilon_2}{\sigma}\right)^2\right]. \tag{15}$$

The drift mobility $\mu_e = ea^2 W_e / k_B T$ at arbitrary concentration of the charge carriers can be calculated by employing the concept of the *effective transport energy* ε_t, which has been proven to be especially efficient for calculating the carrier mobility in disordered materials.[16,27] The effective transport energy level implies the energy of a target site to which most of localized carriers make thermally activated jumps and which does not depend on the energy of a starting state ε_1 when $\varepsilon_1 < \varepsilon_t$. This approach accounts for changing the jump distance with changing temperature in the two-site transitions. By employing this concept, one can replace the $Q(\varepsilon_2)$ function by

$$Q(\varepsilon_2) = \delta(\varepsilon_2 - \varepsilon_t). \tag{16}$$

The ε_t level depends on the temperature and carrier concentration.

Substituting Eqs. (2), (10), and (16) into Eq. (6), for the Miller-Abrahams model, we obtain the following for the arbitrary carrier density:

$$W_e = \frac{\int_{-\infty}^{\varepsilon_t} d\varepsilon W(\varepsilon,\varepsilon_t) g(\varepsilon) f(\varepsilon,\varepsilon_F)}{\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon) f(\varepsilon,\varepsilon_F)}, \tag{17}$$

where

$$W(\varepsilon,\varepsilon_t) = \nu_0 \exp\left(-2\frac{r_t}{b}\right)\exp\left(-\frac{\varepsilon_t-\varepsilon}{k_B T}\right). \tag{18}$$

Here, $r_t = r(\varepsilon_t)$ is the jump distance at and below the transport energy level ε_t. In Eq. (17) and further, only hopping transitions to the transport energy level from the states below the ε_t have been taken into account at the configuration averaging. Then, Eq. (17) for the effective Miller-Abrahams jump rate can be rewritten as

$$W_e = \nu_0 \exp\left(-2\frac{r_t}{b}\right)\exp\left(-\frac{\varepsilon_t}{k_B T}\right) \times \frac{\int_{-\infty}^{\varepsilon_t} d\varepsilon \exp\left(\frac{\varepsilon}{k_B T}\right) g(\varepsilon) f(\varepsilon,\varepsilon_F)}{\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon) f(\varepsilon,\varepsilon_F)}. \tag{19}$$

In the case of the polaron model, the effective jump rate for the arbitrary carrier (polaron) density can be obtained by substituting Eqs. (3), (10), and (16) into Eq. (8),

$$W_e = \frac{\int_{-\infty}^{\varepsilon_t} d\varepsilon W(\varepsilon,\varepsilon_t) \exp\left(\frac{\varepsilon}{2k_B T}\right) g(\varepsilon) f(\varepsilon,\varepsilon_F)}{\int_{-\infty}^{\varepsilon_t} d\varepsilon \exp\left(\frac{\varepsilon}{2k_B T}\right) g(\varepsilon) f(\varepsilon,\varepsilon_F)}, \tag{20}$$

where

$$W(\varepsilon,\varepsilon_t) = W_1 \exp\left(-\frac{E_a}{k_B T}\right)\exp\left(-2\frac{r_t}{b}\right)\exp\left(-\frac{\varepsilon_t-\varepsilon}{2k_B T}\right). \tag{21}$$

Correspondingly, Eq. (20) can be rewritten as

$$W_e = W_1 \exp\left(-2\frac{r_t}{b}\right)\exp\left(-\frac{E_a}{k_B T}\right)\exp\left(-\frac{\varepsilon_t}{2k_B T}\right) \times \frac{\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon) \exp\left(\frac{\varepsilon}{k_B T}\right) f(\varepsilon,\varepsilon_F)}{\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon) \exp\left(\frac{\varepsilon}{2k_B T}\right) f(\varepsilon,\varepsilon_F)}. \tag{22}$$

The effective drift mobility μ_e for the arbitrary jump rate model can be calculated using the generalized Einstein equation, which can be written, as suggested recently by Roichman and Tessler,[28] as

$$\mu_e = e k_0 r_t^2 W_e / k_B T, \tag{23}$$

where k_0 can be obtained as

$$k_0 = 1 - \frac{\int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f^2(\varepsilon,\varepsilon_F)}{\int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon,\varepsilon_F)}. \tag{24}$$

In the case of negligible carrier concentration, i.e., $n/N \to 0$, Eq. (24) predicts $k_0 \to 1$.

In the framework of the Miller-Abrahams jump rate model, the effective charge carrier mobility μ_e can be calculated using Eqs. (9), (19), and (23) as

$$\mu_e = \mu_0 k_0 x \left(\frac{r_t}{a}\right)^2 \exp\left(-2\frac{r_t}{b}\right)\exp(-x x_t) \times \frac{\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2 + xt\right)}{1+\exp[x(t-x_F)]}}{\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2\right)}{1+\exp[x(t-x_F)]}}, \tag{25}$$

where $\mu_0 = ea^2\nu_0/\sigma$, $a = N^{-1/3}$, $x = \sigma/k_B T$, $x_t = \varepsilon_t/\sigma$, and $x_F = \varepsilon_F/\sigma$.

Within the polaron model, the effective carrier mobility μ_e can be obtained using Eqs. (9), (22), and (23) and the result reads

$$\mu_e = \mu_0 k_0 x \left(\frac{r_t}{a}\right)^2 \exp\left(-2\frac{r_t}{b}\right)\exp(-x x_a)\exp\left(-\frac{1}{2}x x_t\right) \times \frac{\displaystyle\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2 + x t\right)}{1+\exp[x(t-x_F)]}}{\displaystyle\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2 + \frac{1}{2}x t\right)}{1+\exp[x(t-x_F)]}}, \tag{26}$$

where $\mu_0 = ea^2 W_1/\sigma$ and $x_a = E_a/\sigma$.

In the case of infinitesimally low concentration of charge carriers ($n \ll N$) in the framework of the Miller-Abrahams model, Eq. (25) yields

$$\mu_e = \mu_0 x \left(\frac{r_t}{a}\right)^2 \exp\left(-2\frac{r_t}{b}\right) \frac{1+\mathrm{erf}\left(\frac{x_t}{\sqrt{2}}\right)}{1+\mathrm{erf}\left(\frac{x+x_t}{\sqrt{2}}\right)} \exp\left(-\frac{1}{2}x^2 - x x_t\right), \tag{27}$$

while in the framework of the polaron model, Eq. (26) leads to

$$\mu_e = \mu_0 x \left(\frac{r_t}{a}\right)^2 \exp\left(-2\frac{r_t}{b}\right) \frac{1+\mathrm{erf}\left(\frac{x_t}{\sqrt{2}}\right)}{1+\mathrm{erf}\left(\frac{x+2x_t}{2\sqrt{2}}\right)} \exp(-x x_a) \times \exp\left(-\frac{1}{8}x^2 - \frac{1}{2}x x_t\right). \tag{28}$$

IV. AVERAGING OF THE HOPPING RATE VERSUS HOPPING TIMES

In this section, we shall discuss the configurational averaging procedures used in theories on charge carrier transport in disordered organic solids. It should be mentioned that there has been a vivid discussion regarding the problem of a general approach to the calculation of the drift mobility in disordered organic systems (see, for instance, Refs. 11 and 29). In fact, the discussion concerns the validity of the use of two expressions for the calculation of the charge mobility within the variable range hopping approach accounting for the transport energy concept,[29] namely,

$$\mu_e \approx \frac{e}{k_B T} r_t^2 W_e, \tag{29}$$

where

$$W_e = \langle W \rangle, \tag{30}$$

and

$$\mu_e \approx \frac{e}{k_B T} r_t^2 W_e, \tag{31}$$

where

$$W_e = \langle W^{-1} \rangle^{-1}. \tag{32}$$

$r_t = r(\varepsilon_t)$ is the jump distance at and below the transport energy level ε_t and W is the jump rate between adjacent sites within the Miller-Abrahams model.[30] Nevertheless, this issue can be readily solved if one considers that there are two ways to do the configuration averaging using Eqs. (30) and (32).

Indeed, we mention that the effective jump rate can also be calculated by a different method than has been described in the previous section. It has been shown by Baranovskii and co-workers[12,27] that W_e can be obtained for the low carrier density limit within the Miller-Abrahams model by averaging times of hopping intersite transitions. Hence, instead of Eq. (6), the following equation was used:

$$W_e = \langle W_{12}^{-1} \rangle^{-1}, \tag{33}$$

where

$$\langle W_{12}^{-1} \rangle = \frac{\displaystyle\int_{-\infty}^{\varepsilon_t} d\varepsilon W_{12}^{-1} g(\varepsilon)}{\displaystyle\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon)}. \tag{34}$$

Here,

$$W_{12}^{-1} = \nu_0^{-1} \exp\left(2\frac{r_t}{b}\right)\exp\left(\frac{\varepsilon_t - \varepsilon}{k_B T}\right). \tag{35}$$

Upon averaging in Eq. (34), only transitions from the states below the transport energy level to this level have been taken into consideration.

In the general case of arbitrary charge carrier concentration, one should average times of hopping transitions over the distribution of empty (target) localized states, i.e., by using the function given by Eq. (11). Therefore, instead of Eq. (34), one obtains

$$\langle W_{12}^{-1} \rangle = \frac{\displaystyle\int_{-\infty}^{\varepsilon_t} d\varepsilon W_{12}^{-1} g(\varepsilon)[1 - f(\varepsilon, \varepsilon_F)]}{\displaystyle\int_{-\infty}^{\varepsilon_t} d\varepsilon g(\varepsilon)[1 - f(\varepsilon, \varepsilon_F)]}. \tag{36}$$

Substituting Eqs. (35) and (36) into Eq. (33), one obtains the expression for W_e which coincides exactly with Eq. (19). If the W_{12} is obtained within the polaron model [cf. Eq. (3)] and substituted into Eq. (36), then, by using also Eq. (33), the resulting expression for W_e is identical with Eq. (22).

It should be stressed, however, that configurational energy averaging has been performed in a *different way* when obtaining the above expressions. In Eq. (30), the calculation of the drift mobility implies averaging of the *hopping rates* over the normalized equilibrium energy distribution of charge carriers. However, when calculating the mobility by averaging of *hopping times*, as done in Eq. (32), averaging is performed over the normalized energetic distribution of the empty (target) states. Both approaches for the calculation of the zero-field effective drift mobility are eventually equivalent provided that the effective transport energy concept is used. The same problem has been also discussed recently in Ref. 22. Thus, the above consideration clearly shows that the recent criticism in Refs. 11, 27, and 29 regarding the validity of the configurational averaging of the hopping rates over the equilibrium energetic distribution of charge carriers[16] is actually unfounded. We should, however, emphasize that Eqs. (30) and (6) are only valid in the presence of energetic disorder. It is not valid for solely positionally disordered system, as it has been noticed correctly by Baranovskii *et al.*[11,27,29] In the latter case, the calculation of W_e should be performed using the general universal expression Eq. (1). Then, $W_{12}=W_{21}=W$, and from Eq. (1), the following known EMA expression can be derived:

$$\left\langle \frac{W-W_e}{W+2W_e} \right\rangle = 0. \tag{37}$$

Here, the angular brackets denote positional averaging.

The consistency of the results obtained by different methods justifies the validity of Eq. (1) obtained by the EMA theory for calculating the effective jump rate W_e, as well as the validity of their different forms given by Eqs. (6) and (8), deduced from Eq. (1) for calculating W_e in the framework of the Miller-Abrahams and polaron models, respectively.

V. EFFECTIVE TRANSPORT ENERGY

For further treatment of the charge mobility at large carrier densities, the effective transport energy level x_t ($x_t=\varepsilon_t/\sigma$) will be calculated employing both the Miller-Abrahams and polaron models. For the general case of the DOS distribution function $g(\varepsilon)$ and arbitrary concentration of charge carriers, the transport energy ε_t can be introduced as follows. One can roughly estimate the distance $r(\varepsilon_f)$ between the nearest neighbor sites for the charge carrier jump from a site with arbitrary energy ε_i to a site with energy $\varepsilon_f > \varepsilon_i$ using the following relation:

$$\frac{4\pi}{3B} r^3(\varepsilon_f) \int_{-\infty}^{\varepsilon_f} d\varepsilon g(\varepsilon)[1-f(\varepsilon,\varepsilon_F)] \cong 1. \tag{38}$$

Hence, we have

$$r(\varepsilon_f) \cong \left[\frac{4\pi}{3B} \int_{-\infty}^{\varepsilon_f} d\varepsilon g(\varepsilon)[1-f(\varepsilon,\varepsilon_F)] \right]^{-1/3}. \tag{39}$$

Here, parameter $B=2.7$ is determined according to percolation criteria.[12] Let us assume that all localized states participate in the transitions, i.e., $\varepsilon_t \to \infty$. Then, for the case of negligible charge carrier concentration, Eq. (39) yields the percolation radius $r(\infty)=0.86a$.[31] This implies that Eq. (39) is valid for arbitrary ε_t values and not only for $\varepsilon_t \leqslant -\sigma/2$, as it has been claimed in Ref. 12. It should be noted, however, that the theoretical results obtained below for the temperature dependence of the charge mobility in the framework of the Miller-Abrahams model and the transport energy concept show better agreement with available results of computer simulations when one assumes $B=1$ (by the way, the same value was also used before by Baranovskii *et al.*[27] for the case of zero carrier density limit and the typical ratio $b/a=0.1$). Thus, assuming $B=1$, $\ln(\mu_e) \propto -0.48(\sigma/k_BT)^2$ is derived, which is closer to the expression $\ln(\mu_e) \propto -(2\sigma/3k_BT)^2 \cong -0.44(\sigma/k_BT)^2$ obtained by previous computer simulation studies[1] compared to the relation $\ln(\mu_e) \propto -0.52(\sigma/k_BT)^2$ obtained assuming $B=2.7$. For this reason, we will use the value $B=1$ in our subsequent calculations.

In the case of the Miller-Abrahams jump rate model [Eq. (2)], the probability of carrier jump from a site with energy ε_i to the target site with energy ε_f (at $\varepsilon_f > \varepsilon_i$) is given by

$$W(\varepsilon_i,\varepsilon_j) = \nu_0 \exp\left[-2\frac{r(\varepsilon_f)}{b} - \frac{\varepsilon_f-\varepsilon_i}{k_BT} \right]. \tag{40}$$

The target site energy ε_f can be calculated by determining the maximum of the above jump rate function [Eq. (40)] as follows:

$$\frac{\partial W(\varepsilon_i,\varepsilon_f)}{\partial \varepsilon_f} = 0,$$

$$\text{or } [1-f(\varepsilon_f,\varepsilon_F)]g(\varepsilon_f)\left[\frac{4\pi}{3B} \int_{-\infty}^{\varepsilon_t} d\varepsilon [1-f(\varepsilon,\varepsilon_F)]g(\varepsilon) \right]^{-4/3} = \frac{1}{k_BT}\frac{3b}{2}\frac{3B}{4\pi}. \tag{41}$$

As one can see, ε_f value determined from the maximal jump rate does not depend on the energy of the starting site ε_i and defines the effective transport energy level ε_t. Taking into account the Gaussian shape of the DOS [Eq. (9)], one can rewrite Eq. (41) in the form the convenient for the calculation of the transport energy x_t ($x_t=\varepsilon_t/\sigma$) as

$$\frac{1}{\sqrt{2\pi}} \frac{\exp\left(-\frac{1}{2}x_t^2\right)}{1+\exp[-x(x_t-x_F)]} \times \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2\right)}{1+\exp[-x(t-x_F)]} \right]^{-4/3} = \frac{3}{2}\left(\frac{4\pi}{3B}\right)^{1/3} x\frac{b}{a}. \tag{42}$$

The concept of the transport energy can also be applied for the polaron jump rate model [Eq. (3)]. In this case, the probability of the carrier transition from a site with energy ε_i to the target site with energy ε_f (at $\varepsilon_f > \varepsilon_i$) can be written as

$$W(\varepsilon_i,\varepsilon_j) = W_0 \exp\left[-2\frac{r(\varepsilon_f)}{b} - \frac{\varepsilon_f-\varepsilon_i}{2k_BT} \right]. \tag{43}$$

In this case, $x_t=\varepsilon_t/\sigma$ value can be calculated from the following equation:

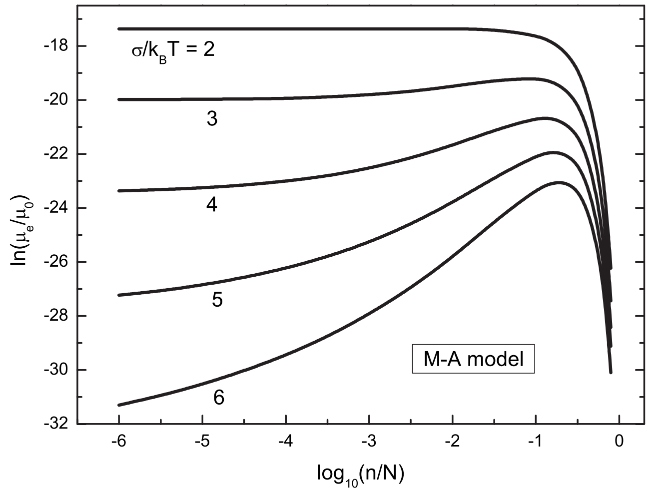

FIG. 1. Dependence of the drift charge carrier mobility μ_e on the carrier concentration n at different temperatures, calculated within the Miller-Abrahams jump rate model by Eq. (25) using Eqs. (42) and (45). Parameter $b/a=0.1$.

$$\frac{1}{\sqrt{2\pi}}\frac{\exp\left(-\frac{1}{2}x_t^2\right)}{1+\exp[-x(x_t-x_F)]}\times\left[\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x_t}dt\frac{\exp\left(-\frac{1}{2}t^2\right)}{1+\exp[-x(t-x_F)]}\right]^{-4/3}=\frac{3}{4}\left(\frac{4\pi}{3B}\right)^{1/3}x\frac{b}{a}. \tag{44}$$

For both jump rate models, we have

$$r_t=a\left[\frac{4\pi}{3B}\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x_t}dt\frac{\exp\left(-\frac{1}{2}t^2\right)}{1+\exp[-x(t-x_F)]}\right]^{-1/3}. \tag{45}$$

Equations. (42) and (44) for the different jump rate models differ only in the numeric coefficients in their right sides. However, as it will be demonstrated below, this difference proves to be of principal importance for the charge carrier mobility at high carrier concentrations.

VI. RESULTS AND DISCUSSIONS

A. Comparison of the carrier density effects calculated within the different jump rate models

Figure 1 shows the charge carrier mobility μ_e as a function of the carrier concentration n at different temperatures calculated for $b/a=0.1$ within the Miller-Abrahams jump rate model [see Eq. (25)] using Eqs. (42) and (45) for different values of σ/kT. The observed increase of charge carrier mobility with increasing carrier concentration presented in Fig. 1 agrees well with previous numerical experiments by the master equation approach.[10,14] N is the concentration of the localized states.

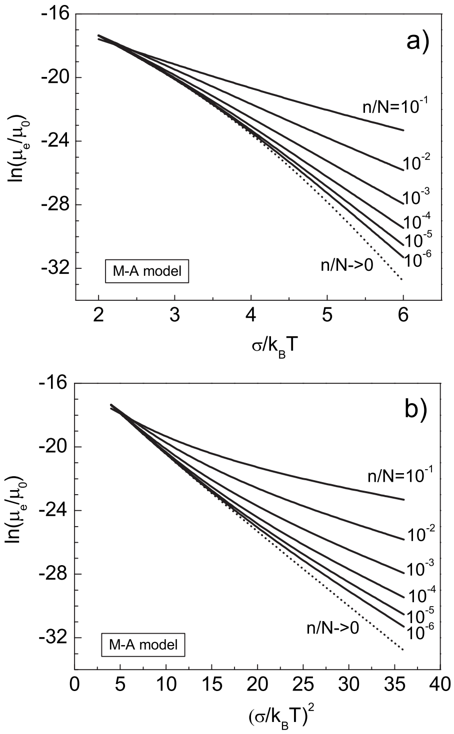

FIG. 2. (a) Temperature dependence $[\ln(\mu_e/\mu_o)$ vs $1/T]$ of the charge carrier mobility μ_e calculated within the Miller-Abrahams jump rate model for different carrier concentrations. (b) The data of $\ln(\mu_e/\mu_o)$ versus $1/T^2$.

Temperature dependences of the charge carrier mobility μ_e calculated within the Miller-Abrahams model for different carrier concentrations are plotted in Fig. 2 semilogarithmically versus $1/T$ and $1/T^2$ parametric in the carrier concentration. It should be noted that the curve in Fig. 2(b), which was calculated in the limit of zero carrier concentration $n/N\rightarrow 0$ using Eq. (27), can be approximated well by the relation $\ln(\mu_e)\propto -k_1(\sigma/k_BT)^2$, where $k_1=0.48$. As one can see, a typical sub-Arrhenius temperature dependence μ versus $1/T^2$ observed at low carrier concentration clearly changes to the Arrhenius-type dependence of the mobility (μ vs $1/T$) with increasing carrier concentration.

Figure 3 shows the carrier concentration dependences of the drift carrier mobility for different temperatures, which were calculated in the framework of the polaron jump rate model by Eq. (26) using Eqs. (44) and (45) at $b/a=0.1$ and moderately large polaron activation energy $E_a/\sigma=3$. Temperature dependence of the zero carrier concentration mobility $n/N\rightarrow 0$ calculated with Eq. (28) for the polaron jump rate can be approximated well by the relation $\ln(\mu_e)\propto -E_a/k_BT-k_2(\sigma/k_BT)^2$, where $k_2=0.12$. Note that $k_1/k_2=4$, which coincides with results of our previous calculations of polaron transport[22] where carrier jumps with variable range have not been considered. This implies that the ratio $k_1/k_2=4$ is a constant in the framework of the polaron transport model. Unfortunately due to lack of relevant computer simulation data, the obtained k_2 parameter cannot be verified independently.

Figure 4 shows the dependence of the effective transport energy ε_t on carrier concentration n calculated at $\sigma/k_BT=6$

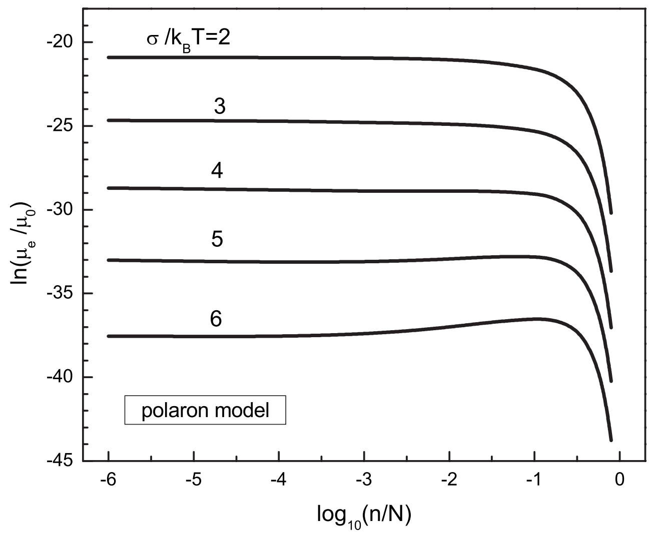

FIG. 3. Carrier concentration dependences of the drift charge carrier mobility at different temperatures calculated in the framework of the polaron model by Eq. (26) using Eqs. (44) and (45). Parameters $E_a/\sigma=3$ and $b/a=0.1$.

and $b/a=0.1$ within the Miller-Abrahams and polaron models. As one can see, in both cases, the transport energy is virtually a constant at small carrier concentrations but tends to increase considerably at very high carrier densities. Here, we should mention that charge carrier densities in an accumulation channel in a OFET is typically limited by $n/N < 0.01$, therefore, such a concentration range is obviously of most practical interest. However, for certain configurations, much larger accumulation charges can be attracted to the interface of an OTFT as, for instance, by using polarizable gate dielectrics. In the latter cases, one can reach charge density equivalent to that obtained by 10% chemical doping. Thus, besides for fundamental science, extreme concentration of charge carriers may prove relevant.

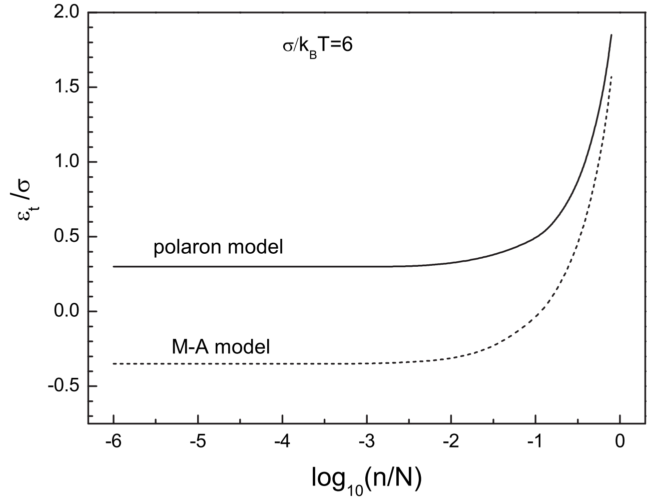

FIG. 4. Dependence of the transport energy ε_t on carrier concentration n calculated within the Miller-Abrahams and polaron models using Eqs. (42) and (44), respectively. Parameters $\sigma/k_BT=6$ and $b/a=0.1$.

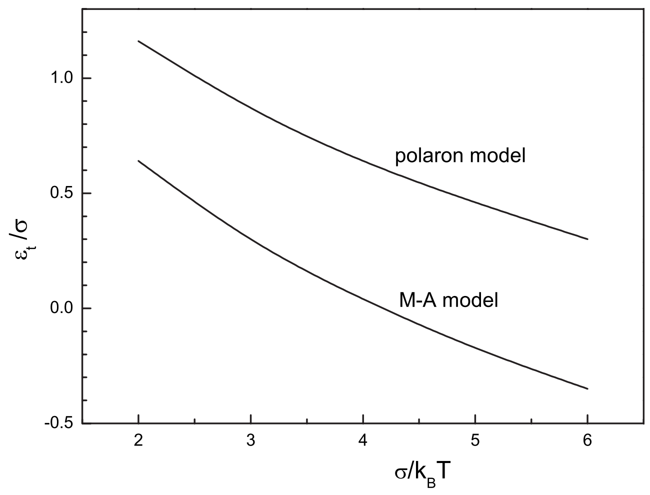

FIG. 5. Temperature dependences of the transport energy at a moderate carrier concentration as calculated within the Miller-Abrahams and polaron models with Eqs. (42) and (44), respectively.

It is remarkable that at low carrier concentrations, the effective transport energy level lies *below* the DOS center in the Miller-Abrahams model, but surprisingly, it is located slightly *above* the DOS center in the polaron model. As one can see from Fig. 5, at moderate carrier concentrations, the effective transport energy is very close to the DOS center and shifted by $\sim 0.3\sigma$ at $\sigma/k_BT=6$. Qualitatively similar carrier concentration dependence of the effective transport energy was obtained by Arkhipov *et al.*[16] employing the Miller-Abrahams jump rate, but the authors obtained that the transport energy always lies above the DOS center at all carrier concentrations. Implications of the effective transport energy position above the DOS center has been already thoroughly discussed elsewhere.[32,33]

We should further comment on the obtained difference in the effective transport energy for bare charge carriers and polarons. This difference basically comes from the difference in the "energy" terms in asymmetric Miller-Abrahams and symmetric polaron jump rate expressions W_{ij} [cf. Eqs. (2) and (3)]. The total activation energy for an elementary intersite carrier jump between hopping sites i and j (at $\varepsilon_j > \varepsilon_i$) with the rate $W_{ji} \propto \exp(-E_{ji}/k_BT)$ is $E_{ji}=\varepsilon_j-\varepsilon_i$ in the framework of the Miller-Abrahams model, but it consists of two components in the polaron model: $E_{ji}=E_a+(\varepsilon_j-\varepsilon_i)/2$ (at $E_a/\sigma \gg 1$). We note that the presence of considerable polaron effects has two important impacts, namely, (i) it results in the appearance of a polaron activation energy component in the total activation energy of the elementary carrier jump and (ii) the energetic disorder component in the total activation energy is twice as small as that for the Miller-Abrahams model for bare charge carriers. The latter effect gives rise to the different transport energies for bare and polaron carriers since the effective transport energy in both models is determined solely by the energetic disorder, as it follows from Eqs. (42) and (44). It should be also mentioned that the percolation threshold is also different in the Miller-Abrahams and polaron models as its value calculated using the variable range hopping formalism[31] shows that it is sensitive to the type of jump rate.

The carrier concentration dependence of the effective transport energy in Fig. 4 sheds light on the effect of the nonmonotonous behavior of mobility upon the carrier density presented in Fig. 1. The increase of the carrier mobility with increasing carrier density can be explained as follows. When the Fermi level ε_F approaches the mean equilibration energy ε_0 of the charge carriers, the number of localized carriers above ε_0 increases. Consequently, the density of vacant neighbor sites with a specific difference of energies within the intersite hopping distance will be, in average, larger. This results in an increase of mobility with increasing carrier concentration. In this case, the effective transport energy level ε_t calculated employing the Miller-Abrahams jump rate is (i) located below the DOS center in the considered range of carrier concentration n and (ii) is a constant value dependent on σ/kT except at very large charge concentration where a sharp increase of the ε_t is observed. This gives rise to a decrease of the drift mobility μ_e at very large carrier concentration and, consequently, to appearance of a maximum on the carrier concentration dependence of the charge mobility.

The temperature dependences of the drift mobilities presented in Fig. 2 agree qualitatively with results of recent numerical simulations.[7,14] They demonstrate that $\ln(\mu_e/\mu_0)$ in the framework of the Miller-Abrahams model can change either quadratically or linearly with respect to reciprocal temperature $1/T$ depending on the carrier concentration, i.e., it depends on experimental conditions.

A remarkable result of the present EMA calculations is that they predict a very different carrier density dependence of the charge mobility within the polaron and Miller-Abrahams jump rate models. As it follows from Fig. 3, within the polaron model, a large increase in carrier density has almost negligible effect on the polaron mobility, even at low temperatures ($\sigma/k_BT \gg 1$), provided that the polaron activation energy is moderately large ($E_a/\sigma \geqslant 3$). Consequently, the temperature dependence of the polaron mobility is also hardly sensitive to the increase of the carrier density. Such a behavior of the carrier density dependence of the charge mobility is due to the fact that, in this case, the effective transport energy level ε_t (see Fig. 5) lies above the center of the DOS, i.e., essentially higher than in the case of the Miller-Abrahams model.

For comparison of the above models, Fig. 5 shows temperature dependences of the effective transport energy at moderate carrier concentrations as calculated within the Miller-Abrahams and polaron jump rate models. As one can note, in the case of the polaron model, the transport energy level lies higher than that in the case of the Miller-Abrahams model over the whole range of considered temperatures. Thus, a notable increase of polaron mobility with increasing carrier concentration becomes possible only at considerably higher carrier concentrations or lower temperatures compared to the bare charge carriers obeying the Miller-Abrahams jump rate. This is because at the same temperature, the effective energy barrier ($\varepsilon_t - \varepsilon_F$) is larger in the former case and, consequently, its *relative* change due to the lifting of the Fermi level up with increasing carrier density is smaller. In the polaron model, the region of increasing mobility with increasing charge carrier density may actually never be reached. At sufficiently high carrier concentrations ($n \to N$), the transport energy level considerably shifts up to the upper DOS portion with low localized state density, which leads to an abrupt decrease of the carrier mobility at very large carrier density. In addition, the decrease of the parameter k_0 also results in the decrease of charge mobility with increasing carrier concentration. Further, we should note that, in reality, the polaron DOS is displaced with respect to the "bare" charge carrier DOS distribution by the polaron binding energy $E_p = 2E_a$, while their profile shapes are almost the same. However, for comparison of the temperature dependences of the effective transport energies, the above DOS distributions have been overlapped in Fig. 5 such that their DOS centers coincide.

Hence, the key result of the present study is that it suggests that in contrast to the Miller-Abrahams jump rate model, the considerable change of charge carrier mobility with increasing carrier concentration observed also in many experiments is incompatible with a moderately large polaron binding energy. On the other hand, this might suggest an interesting explanation why in some materials, the SCLC mobility is not much different from the FET mobility. It might not be the only explanation of such experimental finding but it might be true in materials with considerable polaron effects (large polaron binding energy). Systematic experimental studies in this direction could provide a straightforward test of the presented model. Finally, it should be noted that at very large carrier concentrations, the polaron mobility, however, shows similar strong decrease as in the case of the Miller-Abrahams model.

It should be noted here that our calculations employing the complete Marcus expression for the polaron jump rate led to similar results on the effect of a large carrier concentration on the polaron mobility. Moreover, the obtained strong difference in the carrier density dependence of the mobility for the Miller-Abrahams and polaron hopping models has also been supported by the EMA mobility calculations performed even without invoking the effective transport energy concept (such calculations are justified for a small-to-moderate degree of the energetic disorder).

Unfortunately, computer simulation data based on the Marcus jump rate [Eq. (3)] are, to our knowledge, currently not available, which precludes direct comparison with our results obtained in the framework of the polaron model. We hope that our results will stimulate such simulations studies.

B. Comparison with numerical calculations

In order to verify our approach, we compared the results of our analytical calculations with available results of computer calculations of charge carrier mobility at large carrier concentrations. Recently Pasveer and co-workers[10,14] calculated the dependence of the hopping charge carrier mobility on carrier concentration by a numerical solution of the master equation for hopping transport in a disordered solid with a Gaussian DOS using the Miller-Abrahams jump rate for a *regular cubic lattice* with lattice constant a. Their method takes into account variable range hopping but, as the authors stated, it was sufficient to consider hops with a maximum distance of $\sqrt{3}a$ for the considered range of parameters. In order to compare our results with their data, we set $r_t = a$ into the general equations Eqs. (25) and (27) and rewrite them as

$$\mu_e = \mu_0 k_0 x \exp\left(-2\frac{a}{b}\right)\exp(-xx_t)\frac{\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2+xt\right)}{1+\exp[x(t-x_F)]}}{\int_{-\infty}^{x_t} dt \frac{\exp\left(-\frac{1}{2}t^2\right)}{1+\exp[x(t-x_F)]}} \tag{46}$$

and

$$\mu_e = \mu_0 x \exp\left(-2\frac{a}{b}\right)\frac{1+\mathrm{erf}\left(\frac{x_t}{\sqrt{2}}\right)}{1+\mathrm{erf}\left(\frac{x+x_t}{\sqrt{2}}\right)}\exp\left(-\frac{1}{2}x^2 - xx_t\right). \tag{47}$$

For calculating the transport energy ε_t within the Miller-Abrahams model for a regular cubic lattice parameter [cf Eqs. (46) and (47)], we assume the term $\exp[-(1/2)x^2 - xx_t]$ in Eq. (47) to be equal to the convenient expression $\mu \propto \exp[-(4/9)x^2]$ obtained by computer simulation studies of the charge transport. Hence, we obtain

$$\frac{\varepsilon_t}{\sigma} = -\frac{1}{18}\frac{\sigma}{k_B T}. \tag{48}$$

Let us assume that under equilibrium, all carriers are located at the energy ε_0. In this case, Eq. (14) reduces to $P(\varepsilon_1) = \delta(\varepsilon_1 - \varepsilon_0)$. Consequently, the term $\exp[-x^2 - xx_t]$ arises in Eq. (47) and by the comparison, we obtain $\varepsilon_t/\sigma = -(5/9) \times (\sigma/k_B T)$. This corresponds to the value of the transport energy in the two-level model for the energetically disordered system.[34] Note that in this approximation, the transport energy ε_t does not depend on the carrier concentration.

The carrier concentration dependence of the charge mobility calculated with the use of Eqs. (13), (24), (46), and (48) for the Miller-Abrahams jump rate and at $a/b = 10$ is presented in Fig. 6(a) (solid curves) and results of the recent computer simulations of Pasveer *et al.*[10] are given by symbols for different degrees of the energetic disorder σ/kT. It should be noted that an iteration procedure similar to that suggested earlier by Yu *et al.*[35] has been used for solving the master equation in computer simulation studies of hopping transport.[10] The same procedure can be used also in the case of the Marcus jump rate. As one can see from Fig. 6(a), our analytical results are in very good quantitative agreement with computer simulation data within the carrier density range where charge mobility increases with increasing of charge carrier concentration.

The present EMA approach can be further supported by comparison with the recently developed variable range hopping (VRH) theory of Arkhipov *et al.*[16] Indeed, the VRH theory fits quantitatively very well numerical calculation data, as can be seen from Fig. 6(b). The calculated carrier density dependence of the charge mobility are presented by solid curves in Fig. 6(b) and compared to an equivalent set of numerical simulation data (symbols) as in Fig. 6(a). The charge mobility is calculated[16] by

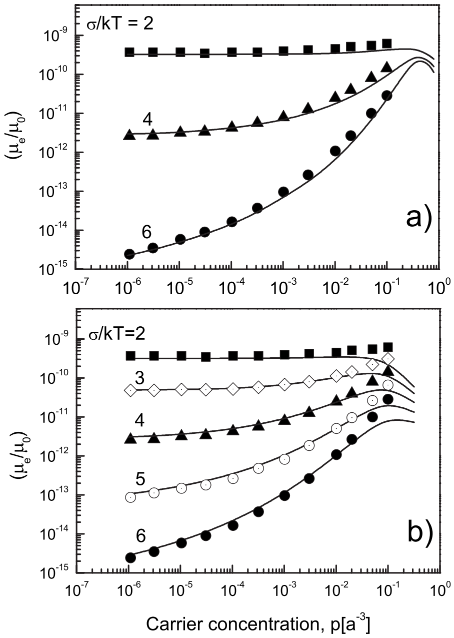

FIG. 6. (a) Carrier concentration dependence of the charge mobility calculated using Eqs. (13), (24), (46), and (48), for $a/b = 10$ (solid curves) and results of computer simulations (symbols) (Ref. 10). (b) Fitting results of the same set of numerical calculation data (symbols) as in Fig. 6(a) by the variable range hopping theory (solid curves) developed in Ref. 16.

$$\mu = \frac{e\nu_0}{kTn}\left[\int_{-\infty}^{0}\frac{g(\varepsilon)d\varepsilon}{1+\exp\left(-\frac{\varepsilon-\varepsilon_F}{k_B T}\right)}\right]^{-2/3} \times \int_{-\infty}^{\varepsilon_{tr}}\frac{g(\varepsilon)\exp\left(-\frac{\varepsilon_{tr}-\varepsilon}{k_B T}\right)}{1+\exp\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right)}d\varepsilon,$$

$$n = \int_{-\infty}^{\infty}\frac{g(\varepsilon)}{1+\exp\left(\frac{\varepsilon-\varepsilon_F}{k_B T}\right)}d\varepsilon. \tag{49}$$

The effective transport energy was derived within the above VRH theory from the following transcendental equation:

$$\frac{4\pi}{3}\int_{-\infty}^{\varepsilon_t}\frac{g(\varepsilon)}{1+\exp\left(-\frac{\varepsilon-\varepsilon_F}{k_B T}\right)}\left(\frac{\varepsilon_t-\varepsilon}{2\gamma k_B T}\right)^3 d\varepsilon = \beta, \tag{50}$$

where γ is the inverse localization radius $(\gamma = 10 \times N_t^{1/3} = 10/a$, $a = N_t^{-1/3}$, and $N_t = 10^{21}$ cm^{-3} is the total density of intrinsic sites) and $\beta = 5$ is a fitting coefficient.

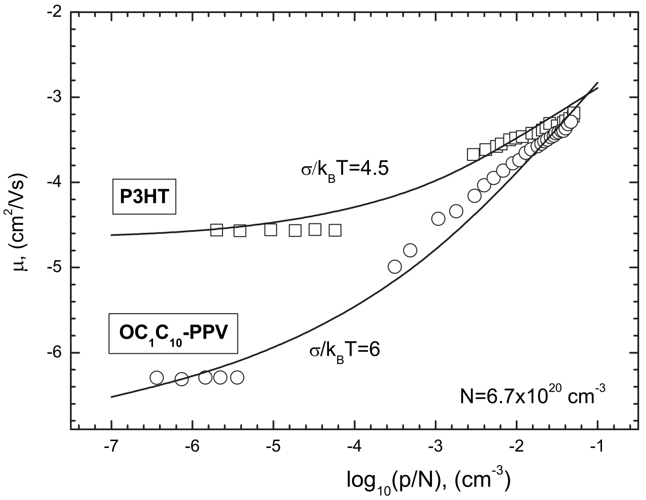

FIG. 7. The fitting of experimental data of the FET mobility measured in two different conjugated polymers P3HT and OC1C10-PPV (symbols) by Eqs. (25), (42), and (45) of the present EMA theory (solid curves).

As one can see from comparison of Figs. 6(a) and 6(b), the above analytical theories describe successfully the numerical simulation results of the charge mobility as a function of carrier density. It should be, however, noted that in contrast to the above numerical simulation results, our model predicts a decrease of the charge mobility at very high carrier densities. The maximum of mobility might still occur at somewhat lower charge carrier density than predicted by our theory (and presented in Figs. 1 and 3), since it follows from the maximum for conductance occurring exactly at $n/N = 0.5$ due to particle-hole symmetry in the master equation.[10] Thus, in the range of *very high carrier concentrations*, the present EMA theory provides just a qualitative description of the carrier density dependence of the charge mobility.

C. Comparison with experimental results

Figure 7 presents the fitting of experimental data of the FET mobility measured in two different conjugated polymers,[8] namely, poly-3-hexylthiophene (P3HT) and poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene) (OC1C10-PPV), by Eqs. (25), (42), and (45) of the present EMA theory. Here, we used the total density of the localized states $N = 6.7\times 6.4^{20}$ cm^{-3} for P3HT.[16] Parameter $\mu_0 = a^2\nu_0 e/\sigma$ [cf. Eq. (25)] due to Pasveer *et al.*[10] was $10^{6.4}$ and $10^{7.3}$ cm^2/V s for P3HT and OC1C10-PPV, respectively, which correspond to the conventional prefactors of mobility $\mu_0 = (a^2\nu_0 e/\sigma)\exp(-2a/b)$ to become 5.2×10^{-3} and 4.2×10^{-2} cm^2/V s for $a/b = 10$. The fitting parameter was the parameter of the energetic disorder σ/k_BT, which was 4.5 for P3HT and 6 for OC1C10-PPV. As one can see, a reasonably good agreement between the experiment and the EMA theory is observed.

VII. CONCLUSION

The present theoretical consideration bears out that the charge carrier mobility strongly depends on carrier density in disordered organic semiconductors with hopping charge transport obeying the Miller-Abrahams jump rate which neglects polaron effects and assuming a Gaussian DOS distribution. On the other hand, we demonstrated that the carrier concentration effect depends considerably on polaron formation. The theory predicts that the presence of a large polaron binding energy compared to the width of the distribution of states should result in much weaker carrier concentration dependence of the charge mobility. The physical reason for the latter is that the polaron activation energy, which contributes considerably to the polaron hopping transport, does not depend on the concentration of polarons.

We showed that the analytical calculations within both the present EMA and the VRH theory of Arkhipov *et al.*[16] (i) are able to describe quantitatively well the results of the numerical experiment of Pasveer *et al.*,[10] which are considered here as a reference for examining our models, and (ii) both analytical theories predict a decrease of the carrier mobility at very high carrier densities, hence predicting the existence of an optimal carrier concentration at which the mobility peaks. A nice agreement between the results of the above analytical theories justifies the basic premises of these models. We should, however, note that some difference between lateral (FET measurements) and transverse (diode) mobilities in organic solids can, at least partially, result from organic film anisotropy, as demonstrated recently in Ref. [36]

It is interesting to compare the above EMA analytical model to the VRH[16] model. Both models employ the same kind of configurational averaging over the equilibrium distribution of starting states for charge carriers. Also, both theories use the concept of the effective transport energy, although different approaches have been employed for its calculations, as can be seen from the comparison of Sec. V of the present paper and Ref. 16. Further, the VRH model suggested by Arkhipov *et al.*[7,16] is applicable for systems with sufficiently large energetic disorder and inevitably linked to the concept of the effective transport energy. The EMA formalism does use the effective energy concept for sufficiently large energetic disorder, however, it can be employed also for moderately disordered materials without invoking the transport energy level consideration.

Finally, we should mention that in certain organic disordered materials, a rather small difference in the FET and ToF mobilities has been observed, for instance, in different polyfluorene copolymers.[18] Although other factors cannot be excluded, for instance, an organic film anisotropy which might result in some difference between lateral and transverse mobilities,[36] the considerable polaron binding energy of charge carriers in polyfluorene-type of polymers or copolymers offers an explanation for this observation. Indeed, the determined polaron activation energy in these polymers from analysis of the charge transport data[24] is quite considerable and is in the range from 0.107 to 0.190 eV, while σ ranges within 0.051–0.075 eV depending on copolymer structure and the film morphology. The ratio E_a/σ was typically from 2 to 3 and implies that the effect of carrier density should indeed be relatively weak, as suggested by the present EMA theory. Nonetheless, the effect of the polaron binding energy on the carrier density dependence of the mobility clearly requires further experimental verification.

ACKNOWLEDGMENTS

This work was implemented within the framework of the program of fundamental research of the National Academy of Science of Ukraine, "Nanostructured systems, nanomaterials, nanotechnologies" through the Project No. 10/07-H, and by the Ministry of Education and Science of Ukraine through Project No. M/138-2007.

---

*Corresponding author. ifishch@kinr.kiev.ua

†Deceased.

[1] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).

[2] P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography* (Dekker, New York, 1998).

[3] P. W. M. Blom and M. C. J. M. Vissenberg, Mater. Sci. Eng., R. **27**, 53 (2000).

[4] V. I. Arkhipov, I. I. Fishchuk, A. Kadashchuk, and H. Bässler, in *Photophysics of Molecular Materials: From Single Molecules to Single crystals*, edited by G. Lanzani (Wiley-VCH, Weinheim, 2006).

[5] R. Jankowiak, K.-D. Rockwitz, and H. Bässler, J. Phys. Chem. **87**, 552 (1983).

[6] A. Kadashchuk, D. S. Weiss, P. M. Borsenberger, S. Nešpůrek, N. Ostapenko, and V. Zaika, Chem. Phys. **247**, 307 (1999).

[7] V. I. Arkhipov, P. Heremans, E. V. Emelianova, G. J. Adriaenssens, and H. Bässler, J. Phys.: Condens. Matter **14**, 9899 (2002).

[8] C. Tanase, E. J. Meijer, P. W. M. Blom, and D. M. deLeeuw, Phys. Rev. Lett. **91**, 216601 (2003).

[9] Y. Roichman, Y. Preezant, and N. Tessler, Phys. Status Solidi A **201**, 1246 (2004).

[10] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005).

[11] S. D. Baranovskii, O. Rubel, and P. Thomas, J. Non-Cryst. Solids **352**, 1644 (2006).

[12] O. Rubel, S. D. Baranovskii, P. Thomas, and S. Yamasaki, Phys. Rev. B **69**, 014206 (2004).

[13] O. Rubel, S. D. Baranovskii, P. Tomas, and S. Yamasaki, Phys. Status Solidi C **1**, 168 (2004).

[14] R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Rev. B **72**, 155206 (2005).

[15] N. Tessler and Y. Roichman, Org. Electron. **6**, 200 (2005).

[16] V. I. Arkhipov, P. Heremans, E. V. Emelianova, G. J. Adriaensses, and H. Bässler, Appl. Phys. Lett. **82**, 3245 (2003); V. I. Arkhipov, E. V. Emelianova, P. Heremans, and H. Bässler, Phys. Rev. B, **72**, 235202 (2005).

[17] Y. Roichman and N. Tessler, Synth. Met. **135-136**, 443 (2003).

[18] R. Rawcliffe, D. D. C. Bradley, and A. J. Campbell, Proc. SPIE **5217**, 25 (2003).

[19] V. M. Kenkre and D. H. Dunlap, Philos. Mag. B **65**, 831 (1992).

[20] D. H. Dunlap and V. M. Kenkre, Chem. Phys. **178**, 67 (1993).

[21] P. E. Parris, V. M. Kenkre, and D. H. Dunlap, Phys. Rev. Lett. **87**, 126601 (2001).

[22] I. I. Fishchuk, A. Kadashchuk, H. Bässler, and S. Nešpůrek, Phys. Rev. B **67**, 224303 (2003).

[23] I. I. Fishchuk, D. Hertel, H. Bässler, and A. K. Kadashchuk, Phys. Rev. B **65**, 125201 (2002); I. I. Fishchuk, A. K. Kadashchuk, H. Bässler, and D. S. Weiss, *ibid.* **66**, 205208 (2002); I. I. Fishchuk, A. Kadashchuk, H. Bässler, and M. Abkowitz, *ibid.* **70**, 245212 (2004); I. I. Fishchuk, A. K. Kadashchuk, A. Vakhnin, Yu. Korosko, H. Bässler, B. Souharce, and U. Scherf, *ibid.* **73**, 115210 (2006).

[24] T. Kreouzis, D. Poplavskyy, S. M. Tuladhar, M. Campoy-Quiles, J. Nelson, A. J. Campbell, and D. D. C. Bradley, Phys. Rev. B **73**, 235201 (2006).

[25] B. Movaghar, B. Pohlmann, and W. Schirmacher, Philos. Mag. B **41**, 49 (1980).

[26] I. I. Fishchuk, Philos. Mag. B **81**, 561 (2001).

[27] S. D. Baranovskii, H. Cordes, F. Hensel, and G. Leising, Phys. Rev. B **62**, 7934 (2000).

[28] Y. Roichman and N. Tessler, Appl. Phys. Lett. **80**, 1948 (2002).

[29] S. D. Baranovskii, O. Rubel, and P. Thomas, Thin Solid Films **487**, 2 (2005).

[30] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

[31] A. L. Efros and B. I. Shklovskii, *Electronic Processes in Doped Semiconductors* (Springer, Berlin, 1984).

[32] V. I. Arkhipov, J. Reynaert, Y. D. Jin, P. Heremans, E. V. Emelianova, G. J. Adriaenssens, and H. Bässler, Synth. Met. **138**, 209 (2003).

[33] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, Phys. Rev. B **64**, 125125 (2001).

[34] P. M. Borsenberger, W. T. Gruenbaum, U. Wolf, and H. Bässler, Chem. Phys. **234**, 277 (1998).

[35] Z. G. Yu, D. L. Smith, A. Saxena, R. L. Martin, and A. R. Bishop, Phys. Rev. Lett. **84**, 721 (2000); Phys. Rev. B **63**, 085202 (2001).

[36] S. Scheinert and G. Paasch, Phys. Status Solidi A **201**, 1263 (2004).