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Nondispersive polaron transport in disordered organic solids

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An analytical theory based on the effective medium approach is formulated to describe nondispersive hopping charge transport in a disordered organic material where polaron effects are important. The treatment of polaron transport in solids with superimposed disorder and polaron effects is based on the Marcus jump rate equation, while the conventional Miller-Abrahams formalism is used to describe charge mobility in polaron-free systems. It is shown that the Poole-Frenkel-type field dependence of mobility $\ln \mu \propto \sqrt{E}$ occurs for both the bare charge carrier and the polaron transport provided that energetic correlation effects have been taken into account. We show that our polaron model can quantitatively explain the observed magnitudes of temperature- and electric-field-dependent polaron mobilities assuming physically reasonable values of polaron binding energies and transfer integrals; it gives a background for the development of the method for estimation of polaron binding energy and the energetic disorder parameter from these dependences. The results of the calculations are found to be in good agreement with both experimental results obtained for some σ-conjugated polysilylenes where polaron formation was straightforwardly demonstrated and recent computer simulations of polaron transport.

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I. INTRODUCTION

It is generally accepted that charge transport in disordered organic solids occurs by hopping. Therefore mobilities of these materials are found to be, as a rule, very low and strongly electric-field and temperature dependent.[1–4] In the past decade, many results concerning the charge carrier transport in doped polymers, conjugated main-chain and pendant group polymers, and vapor deposited molecular glasses were published and described by a formalism based on disorder elaborated by Bässler and co-workers.[1–3] Recently the formalism has been extended by including intersite correlation.[5,6]

Despite of the success of the disorder formalism, there were during last two decades extensive discussions concerning the importance of polaron effects for charge transport in organic disordered solids.[1,7–15] The model of polaron formation has been used as an alternative description of charge carrier transport in several organic solids. The small polaron model,[7–9] which has often been employed, assumes that a localized carrier strongly interacts with some molecular vibrations of the molecule on which the carrier resides. The hopping quasiparticle (polaron) is thus a charge associated with a molecular distortion. The essential distinction between the pure polaron and disorder model consists in different values of the deformation and disorder energy. The disorder formalism assumes that the electron-phonon coupling is sufficiently weak and the activation energy of the charge transport reflects the static energetic disorder of the hopping sites. In contrast, the polaron model suggests a strong electron-phonon coupling and negligible contribution of the energetic disorder to the activation energy of charge mobility.

Purely polaron models are less used since they eventually can fail to consistently describe charge transport in organic disordered materials because of their principle limitation related to the magnitude of physical parameters such as polaron binding energies E_p and transfer integral J. Indeed, for small polaron models, the zero-field activation energy of the mobility E_a in diabatic limit is $E_p/2$. Thus, if the representative value of the activation energy of the mobility ranges from 0.3 to 0.6 eV, then the small polaron model must postulate the polaron binding energy from 0.6 to 1.2 eV. Such a large E_p value is hardly justifiable for small organic molecules, especially if one bears in mind that their crystalline counterparts usually show the value of 0.15 eV as an upper limit of polaron binding energy.[16] In addition, to explain a typical value of charge mobility μ in disorder-free materials of the order of 10^{-6} cm^2/V s, consistent with the measured activation energy $E_a \approx 0.5$ eV due to the polaron formation, one should postulate the nearest-neighbor transfer integral of about 1 eV.[8,9] This value is unacceptably large for organic solids with relatively weak van der Waals intermolecular coupling.[4] In addition, many basic experimental observations, such as the temporal features of photocurrent transients and the transition from nondispersive to dispersive transport regimes upon lowering temperature, are in contrast to the prediction of small polaron model. Indeed, as a consequence of the intramolecular nature of the structural distortion, E_p is a well-defined energy, hence the charge transport should obey Gaussian statistics and photocurrent transients should neither show a long tail nor become dispersive at any temperature (unless the transport becomes controlled by an energetically nonuniform distribution of traps).

However, it is believed that for some organic systems the deformation energy might be comparable with the disorder energy. In principle, upon adding or removing an electron from a molecule, the molecular skeleton must change because of the readjustment of the individual bond lengths. There are just a few reports where it was clearly demonstrated that polaron formation has to be taken into account and the observed temperature dependence of mobility is attributed to the superposition of disorder and polaron effects.[13–15] Bässler *et al.*[13] suggested that in such case the effective zero-electric-field ($E \to 0$) Arrhenius activation energy of the mobility E_{aeff} can be approximated by a sum of the disorder and polaron contributions $E^{\mu}_{\mathrm{aeff}}(E \to 0) = E^{\mathrm{pol}}_{a} + E^{\mathrm{dis}}_{\mathrm{aeff}} = E_p/2 + (8/9)\sigma^2/k_B T$, where E^{pol}_{a} and $E^{\mathrm{dis}}_{\mathrm{aeff}}$ are the polaronic and disorder contributions, respectively, and σ is the width of the DOS distribution. This approach, being a good starting point to account for polaron effects, avoids the abovementioned shortcomings related to the magnitudes of physical parameters and provides means for determination of both σ and E_p from a E_{aeff} vs $1/T$ plot. However, the simplified jump rate equation used in Ref. 13 for polaron hopping transport has no theoretical justification. It is worth noting that polaron formation can be detected also by thermally stimulated luminescence[17] since polaron strongly affects both low-temperature energy relaxation and thermally assisted hopping of charge in disordered organic materials.

An analytical disordered polaron model was suggested by Kenkre and Dunlap[10,11] to account for the polaron transport under the influence of energetic disorder. The calculations of transport characteristics were performed using the variable-range hopping technique[11] assuming that disorder plays the key role and polarons are always in diabatic limit. The results were mainly used to explain the dependence of the activation energy of mobility on the concentration of transport sites; it was assumed that competition between energetic disorder and spatial disorder is the limiting factor in polaron transport. The drawback of this approach is that it requires unacceptable large values of intersite transfer integrals and of the polaron binding energy. It is worth noting that recent computer simulations by Parris *et al.*[18] have demonstrated that the problem related to physical parameters can be solved assuming the small-polaron transport occurs in the presence of correlated energetic disorder. In this case the polaron transport with realistic values of J and E_p can be in good agreement with experimental observations.

Recently we applied the effective medium approach (EMA) to describe charge carrier transport in weakly disordered polaron-free three-dimensional (3D) organic media[19] as well as in disordered media containing traps.[20] In this work we present an analytical EMA theory to describe the charge transport in disordered materials where polaron formation takes place. We compare the theoretical results with experimental data obtained on poly[methyl(phenyl)silylene] (PMPSi) and poly[biphenylyl(methyl)silylene] (PBPMSi) for which considerable polaron binding energies of $E_p = 0.16$ and 0.22 eV, respectively, were recently reported.[21] The latter value is the largest among those reported so far and it is presumably due to a strong coupling of the charge to a torsional mode of the biphenyl unit[22] and a large polarizability of this substituent.[21]

II. THEORETICAL FORMULATION

A self-consistent theory based on the effective medium approach was recently formulated[19] to describe nondispersive charge carrier transport in disordered 3D organic systems for arbitrary electric fields $\mathbf{E} = \{E,0,0\}$ and has been applied to polaron-free materials. In general to case, the effective hopping drift mobility can be obtained from the following expression:

$$\mu_e = a\,\frac{W_e^+ - W_e^-}{E}, \tag{1}$$

where a is an average distance between neighboring hopping sites. W_e^+ and W_e^- is the effective charge carrier jump probability in the direction along and against the electric field, respectively. In two-site cluster approximation W_e^+ and W_e^- can be determined[19] as the following formulas:

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

where W_{12}^+ and W_{21}^- is a jump rate between two adjacent sites along and opposite to the electric field direction, respectively. The angular brackets denote energetic configuration averaging. Here positional disorder was neglected.

A crucial point for developing of any theory describing charge carrier transport in organic disordered solids is the choice of certain expression to describe W_{12}^+ and W_{21}^-. Generally speaking, an expression for jump rate W_{ij} might not be the same for the whole temperature range. Two types of expressions for jump rate W_{ij} are usually considered.

(1) For disordered materials with a weak electron-phonon coupling and/or low-temperature limit ($T < T_D/2$, where T_D is the Debye temperature) when polaron effects are unimportant, the Miller-Abrahams (MA) jump rate[23] can be used

$$W_{ij} = \nu_0 \exp\left(-2\,\frac{r_{ji}}{b}\right) \exp\left[-\frac{|\varepsilon_j - \varepsilon_i| + (\varepsilon_j - \varepsilon_i)}{2k_B T}\right], \tag{3}$$

where ν_0 is a frequency factor and b is the localization radius of a charge carrier.

(2) Polaron effects might be important in the high-coupling and/or high-temperature limit. In such case, the

nonadiabatic small polaron hopping rate given by Marcus theory[24,25] could be used (hereinafter Marcus jump rate):

$$W_{ij}=\frac{J^2}{\hbar}\sqrt{\frac{\pi}{4E_a k_B T}}\exp\left(-\frac{E_a}{k_B T}\right)\times\exp\left[-\frac{\varepsilon_j-\varepsilon_i}{2k_B T}-\frac{(\varepsilon_j-\varepsilon_i)^2}{16E_a k_B T}\right], \qquad (4)$$

where $J=J_0\exp(-r_{ji}/b)$ is the transfer integral between sites with separation of r_{ji} and E_a is the small polaron activation energy, which is equal to half of the polaron binding energy $(E_a=E_p/2)$. It should be noted that instead of Eq. (4), the so-called symmetrical jump rate is also often used [Eq. (5)]

$$W_{ij}=\frac{J^2}{\hbar}\sqrt{\frac{\pi}{4E_a k_B T}}\exp\left(-\frac{E_a}{k_B T}\right)\exp\left(-\frac{\varepsilon_j-\varepsilon_i}{2k_B T}\right). \qquad (5)$$

This expression is essentially similar to Eq. (4) with the exception of omission of the last term in the exponent. However, the usage of the symmetrical jump rate is limited by a relatively weak energetic disorder.

Under the applied electric field **E** in all the above expressions, the value of $\varepsilon_j-\varepsilon_i$ should be substituted by $\varepsilon_j-\varepsilon_i+e(\mathbf{r}_j-\mathbf{r}_i)\mathbf{E}$, where e is the unit charge. W_e^+ and W_e^- can be calculated by substituting Eqs. (3)–(5) into Eq. (2). To perform the configurational averaging, one should choose the distribution functions for the starting state ε_1 and the target state ε_2. As we demonstrated before,[19] in thermodynamic equilibrium, the target and starting states are described by the density-of-states (DOS) distribution $P(\varepsilon_2)$ and the asymptotic occupational density-of-states (ODOS) distribution of carriers after establishing of thermal equilibrium $P(\varepsilon_1)$, respectively. Thus, for calculation of W_e^+ in the case of Gaussian DOS distribution with the width σ, one should use the following expressions:

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

$$P(\varepsilon_2)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{\varepsilon_2}{\sigma}\right)^2\right], \qquad (6)$$

where $\varepsilon_0=-\sigma^2/k_B T$. To calculate W_e^- one should use ε_1 and ε_2 instead of ε_2 and ε_1, respectively, in Eq. (6).

A. EMA treatment of charge transport in a polaron-free system

First, for the sake of completeness, let us start with the MA jump rate given by Eq. (3). Substituting Eq. (3) into Eq. (2) and assuming $r_{ji}=a$ for the case of $\sigma/k_B T\gg 1$, one can get the following expressions:

$$Y_e^+=\left\langle \exp\left[-\frac{|\varepsilon_2-\varepsilon_1-eaE|+(\varepsilon_2-\varepsilon_1-eaE)}{2k_B T}\right]\right\rangle,$$

$$Y_e^-=\left\langle \exp\left[-\frac{|\varepsilon_1-\varepsilon_2+eaE|+(\varepsilon_1-\varepsilon_2+eaE)}{2k_B T}\right]\right\rangle, \qquad (7)$$

where $Y_e^{\pm}=W_e^{\pm}/W_0$ and $W_0=\nu_0\exp(-2a/b)$. Configurational averaging in Eq. (7) using Eq. (6) yields

$$Y_e^{\pm}=\frac{1}{2}\left\{\exp\left(-\frac{1}{2}x^2\pm xf\right)\left[1-\mathrm{erf}\left(\frac{\pm f}{\sqrt{2}}\right)\right]+\left[1-\mathrm{erf}\left(\frac{x\mp f}{\sqrt{2}}\right)\right]\right\}, \qquad (8)$$

where $x=\sigma/k_B T$, $f=eaE/\sigma$, and $\mathrm{erf}(z)=(2/\sqrt{\pi})\int_0^z dt e^{-t^2}$ is the error function. In the present treatment we use the transport energy level ε_p which, when only energetic disorder is considered, is located at $\varepsilon_p\cong-\sigma/2$.[19] As it was shown before,[19,26,27] for $\sigma/k_B T\gg 1$, one can consider $\varepsilon_p\cong 0$, i.e., the transport level is located at the maximum of the DOS distribution. Therefore, one can put in Eq. (6) $P(\varepsilon_2)=\delta(\varepsilon_2)$. The result for effective mobility [see Eq. (1)] reads

$$\mu_e=\mu_0\frac{Y_e^+-Y_e^-}{xf}, \qquad (9)$$

where $\mu_0=(ea^2\nu_0/k_B T)\exp(-2a/b)$. In the limiting case of zero-field $(E\to 0)$, one can get from Eqs. (8) and (9) the relation

$$\mu_e=\mu_0\exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2\right]. \qquad (10)$$

Equations (8) and (9) can be used for the calculation of the field dependence of μ_e over a broad field range for arbitrary electric fields. We will limit our consideration by the electric-field range important for experiments; thus, we assume $1/x\ll f\ll x$. Combining Eqs. (8) and (9), one obtains

$$\mu_e=\mu_3\exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2+\frac{\sigma}{k_B T}\frac{eaE}{\sigma}-\frac{1}{2}\left(\frac{eaE}{\sigma}\right)^2\right], \qquad (11)$$

where $\mu_3=\mu_0/\sqrt{2\pi}xf^2$ is the power function of only the electrical field. We can neglect this dependence assuming, for instance, $f=1$. One could take into account correlation effects using the method described in Ref. 19. Doing so, eaE/σ should be substituted by $\sqrt{x/2}\sqrt{eaE/\sigma}$ in Eq. (11); then one gets[19]

$$\mu_e=\mu_3\exp\left[-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2+\frac{1}{\sqrt{2}}\left(\frac{\sigma}{k_B T}\right)^{3/2}\sqrt{\frac{eaE}{\sigma}}-\frac{1}{4}\frac{\sigma}{k_B T}\frac{eaE}{\sigma}\right]. \qquad (12)$$

Here we kept the abbreviation σ for the correlated value of σ_d as well. Analysis shows that in the considered electric field range, Eq. (12) can be well extrapolated by the following expression:

$$\mu_e=\mu_3\exp\left\{-\frac{1}{2}\left(\frac{\sigma}{k_BT}\right)^2+\frac{1}{\sqrt{2}}\left[\left(\frac{\sigma}{k_BT}\right)^{3/2}-\left(\frac{\sigma}{k_BT}\right)^{1/2}\right]\sqrt{\frac{eaE}{\sigma}}\right\}. \tag{13}$$

Equation (13) is in a good agreement with the expression derived from computer simulations[28–30]

$$\mu_e\propto\exp\left\{-\frac{9}{25}\left(\frac{\sigma}{k_BT}\right)^2+0.78\left[\left(\frac{\sigma}{k_BT}\right)^{3/2}-2\right]\sqrt{\frac{eaE}{\sigma}}\right\}. \tag{14}$$

Thus, the obtained Eqs. (12) and (13) agree well with both results of computer simulations [see Eq. (14)] of charge transport in materials devoid of polaron effects and with experimental data of the dependence of charge carrier mobility on electric field which obey the well-known Poole-Frenkel-type dependence $\ln\mu\propto\sqrt{E}$.

B. EMA treatment of polaron transport in a disordered organic system

Let us consider polaron transport using the Marcus jump rate given by Eq. (4) in disordered systems. Substituting Eq. (4) into Eqs. (1) and (2), one can obtain the expression for the effective polaron mobility

$$\mu_e=\mu_1\exp\left(-\frac{E_a}{k_BT}\right)\frac{1}{fx}\left(\frac{Y_e^+}{Z_e^+}-\frac{Y_e^-}{Z_e^-}\right), \tag{15}$$

where

$$\mu_1=\frac{ea^2}{k_BT}W_1,\quad W_1=\frac{J^2}{\hbar}\sqrt{\frac{\pi}{4E_ak_BT}}, \tag{16}$$

$$Z_e^+=\left\langle\exp\left[-\frac{|\varepsilon_2-\varepsilon_1-eaE|}{2k_BT}+\frac{(\varepsilon_2-\varepsilon_1-eaE)^2}{16E_ak_BT}\right]\right\rangle,$$

$$Z_e^-=\left\langle\exp\left[-\frac{|\varepsilon_1-\varepsilon_2+eaE|}{2k_BT}+\frac{(\varepsilon_1-\varepsilon_2+eaE)^2}{16E_ak_BT}\right]\right\rangle. \tag{17}$$

It should be noted that starting states of ODOS in the expressions for Z_e^+ and Z_e^- are ε_1 and ε_2, respectively. Substituting Eq. (6) into Eq. (17) and performing calculation under the same approximation as used in calculation of $Y_e^\pm$, one obtains

$$Z_e^\pm=\frac{\exp\left[-\frac{1}{2}(x\mp f)^2\right]}{q}\times\frac{1}{2}\left\{\exp\frac{1}{2}\left(\frac{x\mp 2f}{2q}\right)^2\left[1+\mathrm{erf}\left(\frac{x\mp 2f}{2\sqrt{2}q}\right)\right]+\exp\frac{1}{2}\left(\frac{3x\mp 2f}{2q}\right)^2\left[1-\mathrm{erf}\left(\frac{3x\mp 2f}{2\sqrt{2}q}\right)\right]\right\}, \tag{18}$$

where $q=\sqrt{1-xy/8}$, $y=\sigma/E_a$. Equation (18) is valid when $(\sigma/E_a)(\sigma/k_BT)/8<1$. In the limiting case of zero electric field $(E\to 0)$, one obtains from Eqs. (15), (8), and (18)

$$\mu_e=\mu_1\frac{1}{2q}\exp\left[-\frac{E_a}{k_BT}-\frac{1}{8q^2}\left(\frac{\sigma}{k_BT}\right)^2\right]. \tag{19}$$

Drift mobility of polarons calculated using the symmetrical jump rate [see Eq. (5)] can also be described by Eq. (19) provided that $q=1$,[31] which corresponds to the condition when $(\sigma/E_a)(\sigma/k_BT)/8\ll 1$. In such case, one can derive the apparent effective Arrhenius activation energy of the polaron mobility as

$$E_{\text{eff}}=-k_B[d\ln\mu_e/d(1/T)]=E_a+\frac{1}{4}\frac{\sigma^2}{k_BT}. \tag{20}$$

E_{eff} is the sum of contributions from the energetic disorder and the polaron formation (polaron activation energy). As one may see, this equation differs somewhat from the conventional expression $E_{\text{eff}}=E_a+(8/9)\sigma^2/k_BT$,[13] which was used for estimating of the material parameters E_a and σ from the temperature dependence of the mobility. Employment of Eq. (20) for the analysis of experimental data gives a twice larger parameter σ than that obtained using the above conventional expression. This is due to the suggestion that polaron formation and disorder effects are independent and additive processes. When this is the case, the conventional expression for E_{eff} consists of the activation energy E_a of small polaron [which appears in Eq. (4) only at relatively high temperatures] and the activation energy of hopping due to the energetic disorder [which is calculated at relatively low temperatures using of Eq. (3)].

Thus, Eq. (19) derived from the Marcus jump rate seems to be the most appropriate approach to estimate material parameters E_a and σ from the experimental temperature dependence of the zero-field mobility. It should be noted that in this case E_{eff} is no longer a simple sum of activation energies due to the polaron formation and energetic disorder [see Eq. (20)] since in general case [when q in Eq. (19) is not equal to unity], the value E_{eff} is not a linear function of $1/T$. Therefore, Eq. (20) is inappropriate for estimating the the polaron binding energy by extrapolating E_{eff} to the infinite temperature. Solution of this problem for general case of the Marcus jump rate is described below.

Equations (15), (8), and (18) can be used for calculating the electric-field dependence of polaron mobility in a broad range of arbitrary fields (as mentioned above, we will limit ourselves to the field range $1/x\ll f\ll x/2$). It should be mentioned that this field range is at least twice smaller than that considered above for the derivation of Eq. (11). From Eqs. (15), (8), and (18) one obtains

$$\mu_e=\mu_4\exp\left[-\frac{E_a}{k_BT}-\frac{1}{8q^2}\left(\frac{\sigma}{k_BT}\right)^2+\frac{1}{2q^2}\frac{\sigma}{k_BT}\frac{eaE}{\sigma}-\frac{1}{2q^2}\left(\frac{eaE}{\sigma}\right)^2\right], \tag{21}$$

where $\mu_4 = \mu_1 q/\sqrt{2\pi} x f^2$. Here we assume, as in the case of μ_3, $f=1$.

After taking into account the correlation effects, the result reads

$$\mu_e = \mu_4 \exp\left[-\frac{E_a}{k_B T} - \frac{1}{8q^2}\left(\frac{\sigma}{k_B T}\right)^2 + \frac{1}{2\sqrt{2}q^2}\left(\frac{\sigma}{k_B T}\right)^{3/2}\sqrt{\frac{eaE}{\sigma}} - \frac{1}{4q^2}\left(\frac{\sigma}{k_B T}\right)\frac{eaE}{\sigma}\right]. \tag{22}$$

In the case of a symmetrical jump rate [see Eq. (5)], we should put $q=1$ into Eqs. (21) and (22). Analysis of these equations shows that in the considered electric field range, Eq. (22) can be approximated well by the following expression:

$$\mu_e = \mu_4 \exp\left\{ -\frac{E_a}{k_B T} - \frac{1}{8q^2}\left(\frac{\sigma}{k_B T}\right)^2 + \frac{1}{2\sqrt{2}q^2}\left[\left(\frac{\sigma}{k_B T}\right)^{3/2} - \left(\frac{\sigma}{k_B T}\right)^{1/2}\right]\sqrt{\frac{eaE}{\sigma}}\right\}. \tag{23}$$

Note that the electric field range where the Eq. (23) is valid is at least twice smaller than that for which Eq. (13) is applicable. It should be stressed that Eq. (23) agrees well with the empirical expression derived from recent computer simulations[18]

$$\mu_e = \mu_0 \exp\left\{ -\frac{E_a}{k_B T} - 0.31\left(\frac{\sigma}{k_B T}\right)^2 + 0.78\left[\left(\frac{\sigma}{k_B T}\right)^{3/2} - 1.75\right]\sqrt{\frac{eaE}{\sigma}}\right\}. \tag{24}$$

The value $\mu_4 = 2.45\times 10^{-3}$ cm^2/V s determined for the parameters from Ref. 18 is close to the value of $\mu_0 = 3.60 \times 10^{-3}$ cm^2/V s calculated in Ref. 18. Other information from the above treatment is that according to our calculations, μ_e is only slightly sensitive to the correlation effects [see Eqs. (22) and (21)]. The obtained Eqs. (22) and (23) agree reasonably well with the computer simulation results of Eq. (24) and correspond to the Poole-Frenkel type of the dependence $\ln \mu \propto \sqrt{E}$.

C. Treatment of charge and polaron transport based on the percolation path approximation

The results obtained by the present EMA theory can be supported by another method based on the idea of percolation path approximation (PPA),[32] which can be applied in the case of strong disorder. The PPA assumes that the charge carrier motion in three-dimensional (3D) strongly disordered system occurs along the actual one-dimensional (but not straight line) conduction paths. In a random system those paths include only sites with energy $\varepsilon < \varepsilon_t$, where ε_t is a percolation (transport) energy level of the 3D random system. Since one-dimensional charge carrier motion is considered and bonds are connected sequentially, the exact expression for the effective probability of charge hopping can be obtained by inverse of the average hopping times. In this case, instead of Eq. (2), values of W_e^+ and W_e^- can be expressed as

$$W_e^+ = \langle \tau_{12}^+ \rangle^{-1}, \quad W_e^- = \langle \tau_{21}^- \rangle^{-1}, \tag{25}$$

where

$$\langle \tau_{12}^+ \rangle = \frac{\int_{-\infty}^{\varepsilon_t} P(\varepsilon_1)\{W_{12}^+(\varepsilon_t,\varepsilon_1)\}^{-1} d\varepsilon_1}{\int_{-\infty}^{\varepsilon_t} P(\varepsilon_1) d\varepsilon_1},$$

$$\langle \tau_{21}^- \rangle = \frac{\int_{-\infty}^{\varepsilon_t} P(\varepsilon_2)\{W_{21}^-(\varepsilon_t,\varepsilon_2)\}^{-1} d\varepsilon_2}{\int_{-\infty}^{\varepsilon_t} P(\varepsilon_2) d\varepsilon_2}. \tag{26}$$

Here

$$P(\varepsilon) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\varepsilon}{\sigma}\right)^2\right]. \tag{27}$$

In the limiting case of zero-electric field, Eqs. (26) are coincident with results on the average hopping time obtained by Baranovskii *et al.*[33]

Let us consider two situations of the MA and Marcus jump rate.

(a) For the MA type of the jump rate the result reads

$$W_{12}^+(\varepsilon_t,\varepsilon_1) = W_0 \exp\left[-\frac{|\varepsilon_t - \varepsilon_1 - eaE| + (\varepsilon_t - \varepsilon_1 - eaE)}{2k_B T}\right], \tag{28}$$

$$W_{21}^-(\varepsilon_t,\varepsilon_2) = W_0 \exp\left[-\frac{|\varepsilon_t - \varepsilon_2 + eaE| + (\varepsilon_t - \varepsilon_2 + eaE)}{2k_B T}\right]. \tag{29}$$

After substitution of Eqs. (26)–(29) into Eq. (25) and assuming $\varepsilon_t \cong 0$, as stated above for ε_p, one obtains

$$H_e^{\pm} = \left\{ \exp\left(\frac{1}{2}x^2 \mp xf\right)\left[1 + \mathrm{erf}\left(\frac{x \mp f}{\sqrt{2}}\right)\right] + \mathrm{erf}\left(\frac{\pm f}{\sqrt{2}}\right)\right\}^{-1}, \tag{30}$$

where $H_e^{\pm} = W_e^{\pm}/W_0$. Then, instead of Eq. (9), one has the relation

$$\mu_e = \mu_0 \frac{H_e^+ - H_e^-}{xf}. \tag{31}$$

For the limiting case of a weak electric field ($E \to 0$), using Eqs. (30) and (31), one obtains Eq. (10). In the important field range when $1/x \ll f \ll x$, taking into account the correlation effects one derives an approximate Eq. (13) with slightly modified prefactor μ_3.

(b) In the case of polaron hopping, we have

$$W_{12}^{+}(\varepsilon_t,\varepsilon_1)=W_1\exp\left(-\frac{E_a}{k_BT}\right)\exp\left[-\frac{\varepsilon_t-\varepsilon_1-eaE}{2k_BT}-\frac{(\varepsilon_t-\varepsilon_1-eaE)^2}{16E_ak_BT}\right], \tag{32}$$

$$W_{21}^{+}(\varepsilon_t,\varepsilon_2)=W_1\exp\left(-\frac{E_a}{k_BT}\right)\exp\left[-\frac{\varepsilon_t-\varepsilon_2+eaE}{2k_BT}-\frac{(\varepsilon_t-\varepsilon_2+eaE)^2}{16E_ak_BT}\right]. \tag{33}$$

After substitution of Eqs. (26), (27), (32), and (33) into Eq. (25) and assuming $\varepsilon_t \cong 0$ as above, the result reads

$$Q_e^{\pm}=\frac{q\exp\left(-\frac{x^2}{8q^2}\right)\exp\left(\pm\frac{xf}{2q^2}-\frac{xyf^2}{16q^2}\right)}{1+\mathrm{erf}\left[\frac{x}{2q\sqrt{2}}\left(1\mp\frac{yf}{4}\right)\right]}, \tag{34}$$

where $Q_e^{\pm}=W_e^{\pm}/W_1$. Then, instead of Eq. (15), one obtains

$$\mu_e=\mu_1\exp\left(-\frac{E_a}{k_BT}\right)\frac{1}{fx}(Q_e^{+}-Q_e^{-}). \tag{35}$$

From Eqs. (34) and (35) one obtains Eq. (19) for a limiting case of weak electric field $(E\rightarrow 0)$. In the experimentally important field range, taking into account correlation effects, one derives an approximation expression (23) with slightly modified prefactor μ_4.

Thus we showed that the employment of either the effective medium approach or the transport energy method gives—provided that $\sigma/k_BT \gg 1$—the same results for temperature dependence of the mobility and fairly similar results for the field dependences of the mobility, the only difference relating to the magnitude of prefactors in the experimentally important field range. This applies to both the bare charge carrier and polaron transport.

Finally we should mention that some suspicion has been recently cast[33] on the validity of the configurational averaging of hopping rates as it was used by Arkhipov *et al.*[34] for calculation of charge carrier drift mobility. Baranovskii *et al.*[33] argue that the averaging used in Ref. 34 should lead to exponentially wrong results. At first glance this might look plausible since, indeed, when one performs configurational averaging of the MA hopping rates using Eq. (26) in the case of strong disorder and low-field limit, the result reads $\mu_e = \mu_0\sqrt{2/\pi k_BT/\sigma}$, i.e., is at variance with Eq. (10). Hence, the surmised exponentially wrong result is actually derived. However, it should be emphasized that such averaging over the distribution of starting states in Eq. (26) was done using the DOS function [Eq. (27)]. A key point of the EMA approach we developed is that the configurational averaging of hopping rates is performed provided that the ODOS function [Eq. (6)] is used for averaging over the distribution of starting states, which leads to the correct result given by Eq. (10). In fact, the ODOS function has been also used for averaging in the mentioned Ref. 34 [see, for instance, Eq. (3) in Ref. 34b], which justifies the approach used by Arkhipov *et al.*[34] and reinforces their results.

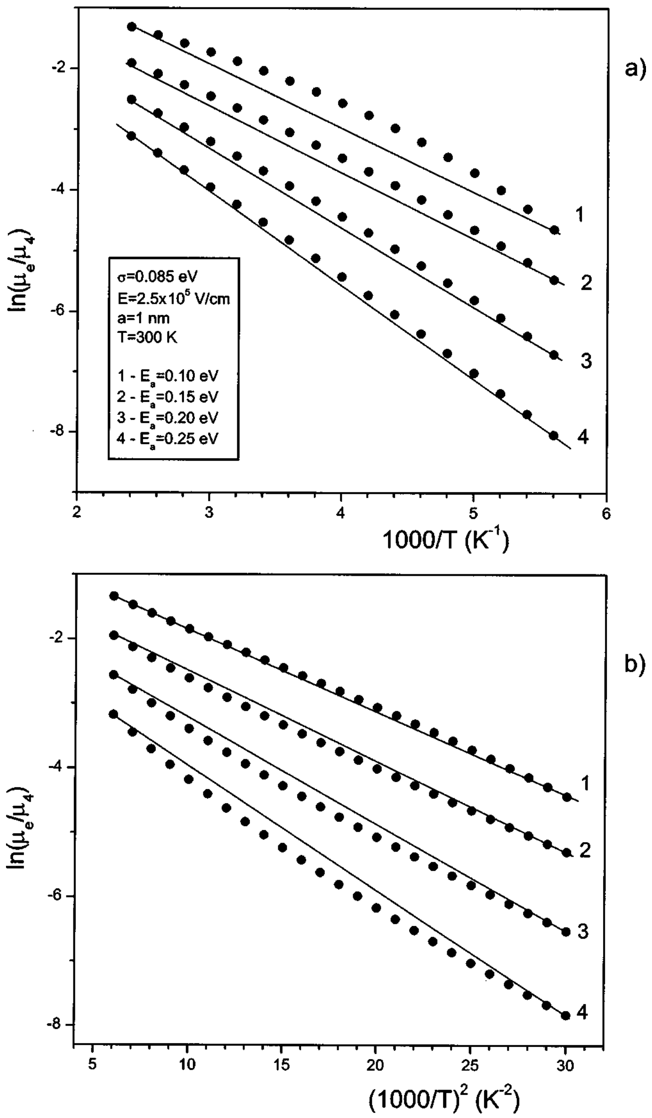

FIG. 1. (a) The Arrhenius plot of the temperature dependences of the polaron mobility calculated from Eq. (23) for several values of polaron activation energies E_a. Solid straight lines are given for linearity comparison. (b) The same data but replotted in the sub-Arrhenius coordinates, i.e., $\ln\mu$ vs T^{-2}.

III. RESULTS AND DISCUSSION

A. General predictions

Figure 1(a) shows Arrhenius plots of the temperature dependences of the polaron mobility calculated using Eq. (23) for several values of polaron activation energies E_a. Solid straight lines are given for linearity comparison. As one can see, these dependences are nonlinear for small polaron activation energies (see curve 1). This suggests a dominant role of the disorder effects in such a situation. This conclusion is supported by good linear dependence of the same data in the sub-Arrhenius coordinates, i.e., $\ln\mu$ vs T^{-2} [curve 1 in Fig.

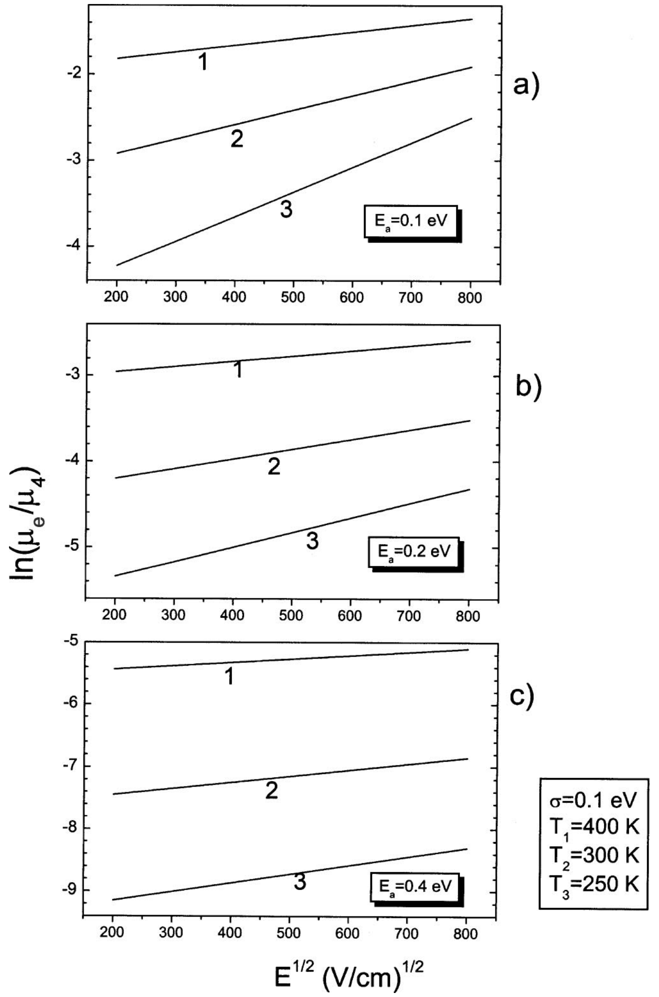

FIG. 2. Field dependences of the polaron mobilities in a disordered material for different temperatures and polaron activation energies of 0.1, 0.2, and 0.4 eV [(a), (b), and (c), respectively].

1(b)] as expected for disorder-dominated transport. As long as polaron activation energy is larger, the Arrhenius temperature dependence of the mobility tends to be closer to a straight line [Fig. 1(a), curve 4] while the deviation from the linear dependence in sub-Arrhenius coordinates becomes more pronounced [curve 4 in Fig. 1(b)]. Thus, an apparently linear Arrhenius plot is an unambiguous evidence for both the presence of polaron effects and a relatively large polaron binding energy. At the same time, the linear temperature dependence of mobility in $\ln \mu$ vs T^{-2} representation could reflect either a polaron-free charge carrier transport in a disordered system or a polaron transport with polaron activation energy relatively small with respect to the width of the DOS; so the disorder effects play a dominant role here. It should be noted that these two transport regimes are usually indistinguishable from the temperature dependence of the charge carrier mobilities only, e.g., the field dependence of the mobility must be taken into account in order to analyze experimental results properly.

Field dependences of the polaron mobilities in a disordered material for different temperatures and polaron activation energies are shown in Fig. 2. As expected, polaron mobility strongly decreases as polaron activation energy increases in the sequence of 0.1, 0.2, and 0.4 eV [Figs. 2(a), 2(b), and 2(c), respectively]. However, the slopes of the field dependences of the polaron mobilities become are relatively less sensitive to temperature in the case of large polaron activation energies [see, e.g., Figs. 2(a) and 2(c)].

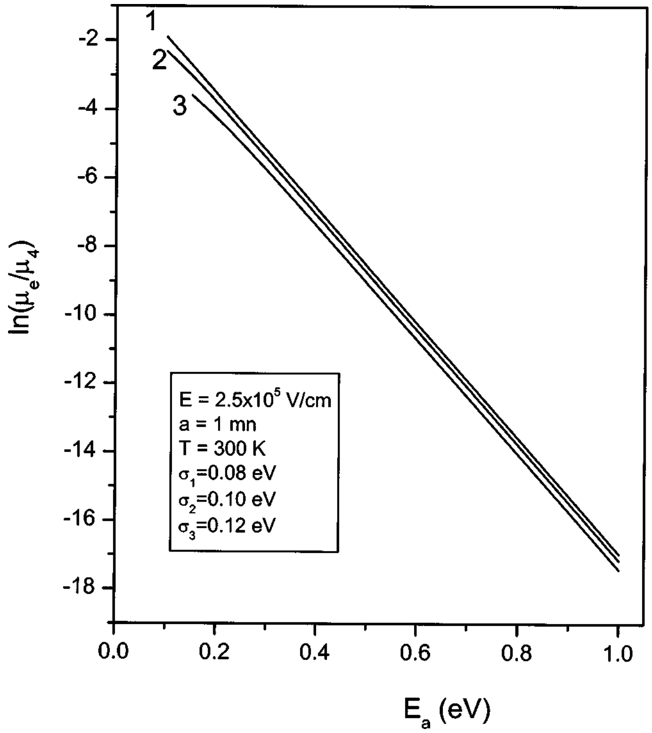

FIG. 3. Dependence of the polaron mobility in a disordered organic system on polaron activation energy for different values of σ.

Figure 3 shows the dependence of the polaron mobility in a disordered organic system on polaron activation energy for several values of σ. It bears out the expected linear decrease in $\ln \mu$ with increasing polaron activation energy.

As it was discussed above, the observation of the linear dependence $\ln \mu \propto 1/T^2$ for zero-field mobility does not necessary mean the absence of polaron formation. This dependence conventionally stems from the MA formalism; however, a similar dependence could result also from the polaron model for a certain set of parameters. Therefore, generally speaking, the temperature dependence cannot be considered as a crucial test for the existence of polaron effects.

From the analysis of the present theory, an important test follows, which, in principle, could be used for distinguishing between polaron and polaron-free transport. It appears that slopes of the electric field dependence of the mobility [Poole-Frenkel (PF) factors], defined as $\beta' = \partial \ln(\mu_e/\mu_3)/\partial\sqrt{E}$, varies almost linearly with $T^{-3/2}$ in the case of polaron-free transport when the MA formalism is applicable [curve 1 in Fig. 4(b)]. Alternatively, the dependence of the PF factor in representation $\beta = \partial \ln(\mu_e/\mu_4)/\partial\sqrt{E}$ vs $T^{-3/2}$ notably deviates significantly from a straight line in the case of polaron model [curve 2 in Fig. 4(b)]. Thus, the presence of such deviation should imply

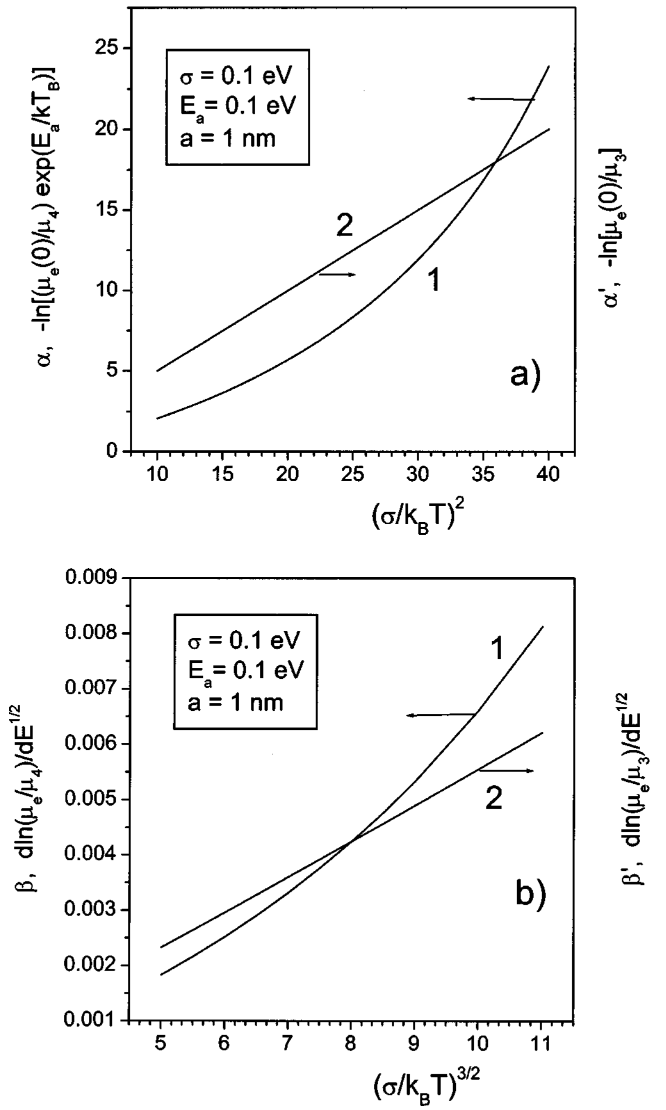

FIG. 4. (a) Temperature dependences of parameters α and α' (see text for explanation) for polaron and polaron-free transport in a disordered system (curves 1 and 2, respectively). (b) Temperature dependences of PF factors β and β' for polaron and polaron-free hopping transport in a disordered system (curves 1 and 2, respectively).

the presence of polarons in the system under study. Moreover, it appears that in zero electric field the value $\alpha' = -\ln[\mu_e(0)/\mu_3]$ depends linearly on T^{-2} in the case of MA approximation [curve 2 in Fig. 4(a)], whereas the dependence $\alpha = -\ln[(\mu_e(0)/\mu_4)\exp(E_a/k_BT)]$ on T^{-2} deviates from a straight line in the case of the polaron model.

B. Comparison with experiment

To compare our theory with experimental results for systems where polaron effects are important we have taken the data from Ref. 13 obtained for poly[methyl(phenyl)silylene] (PMPSi) films. The superposition of the disorder and polaron effects was demonstrated in a straightforward way from the specific temperature dependence of the mobility measured over a broad temperature range. First, we consider zero-field mobility values of PMPSi (see Fig. 3 in Ref. 13) measured at temperatures $T_1 = 333$ K, $T_2 = 250$ K, $T_3 = 200$ K. Solving the set of two equations for $\ln[\mu_e(T_1)/\mu_e(T_2)]$ and $\ln[\mu_e(T_2)/\mu_e(T_3)]$ obtained using Eq. (19) and experimental data, one obtains $E_a = 0.139$ eV and $\sigma = 0.0930$ eV. It should be taken into account that proper extrapolation of experimental data to zero field could be sometimes problematic and reduces the accuracy of the analysis. Therefore we used the experimental data of the temperature dependence of the mobility measured at $E = 2.5\times10^5$ V/cm (see Fig. 4 in Ref. 13) and Eq. (22) or (23). Here we assumed $a = 1.2$ nm. The calculation yields $E_a = 0.145$ eV and $\sigma = 0.0886$ eV. Further, we have used these values as material parameters for the calculation of the temperature and field dependence of the effective polaron mobility in PMPSi.

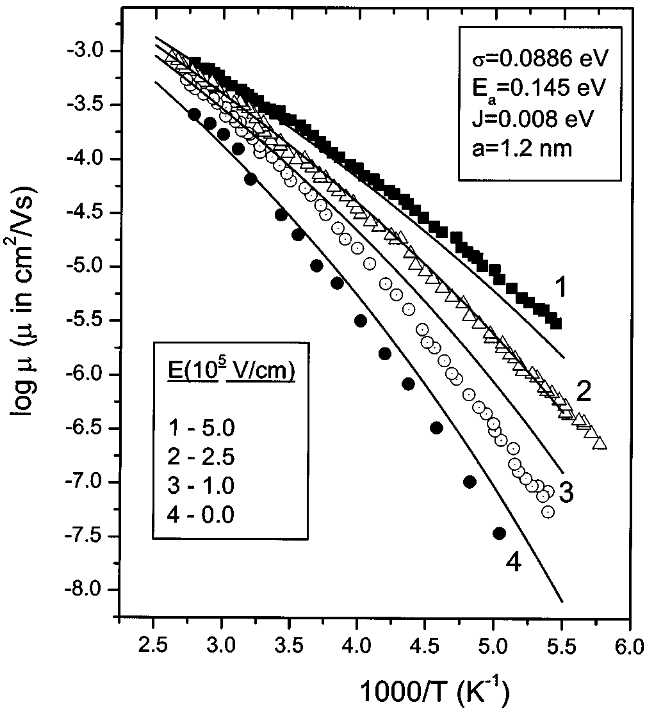

FIG. 5. Temperature dependences of the drift mobility μ_e in PMPSi calculated using Eq. (23) for several electric fields (solid lines). Experimental data from Ref. 13 are given by symbols.

Figure 5 shows the temperature dependences of the drift mobility μ_e calculated using Eq. (23) for several electric fields. Experimental data[13] are shown by symbols. It should be stressed that apart from parameters $E_a = 0.145$ eV and $\sigma = 0.0886$ eV discussed above, the only fitting parameters were (i) average hopping distance $a = 1.2$ nm and (ii) nearest-neighbor transfer integral $J = 0.008$ eV. Such values are quite appropriate for this polymer.

Figure 6 presents field dependences of the drift mobility μ_e in PMPSi calculated using Eq. (23) for several temperatures. All parameters used in the calculations were the same as in Fig. 5. The symbols show the experimental data, and the calculated dependences. One can see quite good agreement between the theory and experiment. It is essential that both the temperature and field dependences of the mobility

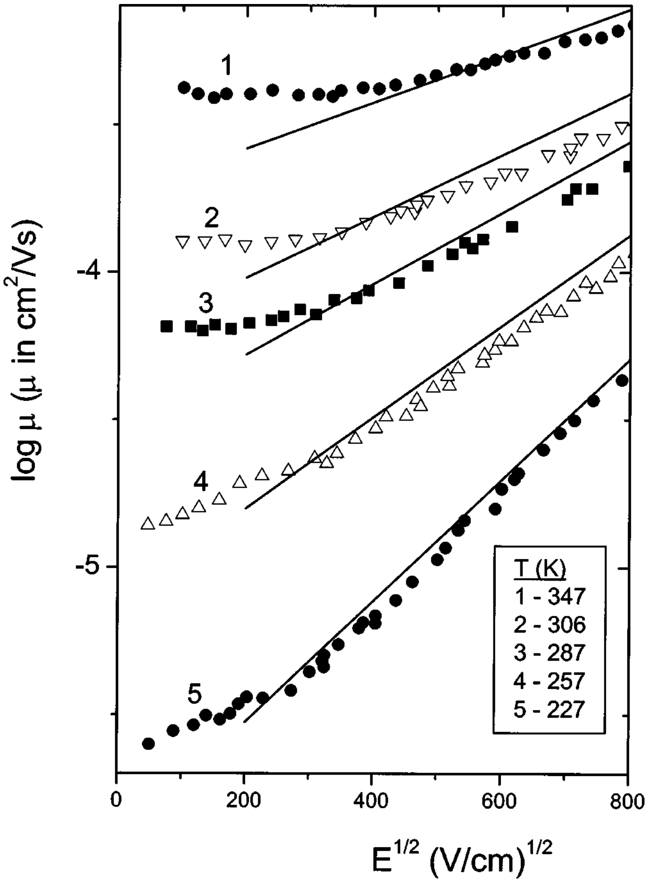

FIG. 6. Field dependences of the drift mobility μ_e in PMPSi calculated from Eq. (23) for several temperatures. All parameters used in the calculations were the same as in Fig. 5. Symbols show the experimental data, lines the calculated dependences.

were calculated with the same set of material parameters ($E_a = 0.145$ eV, $\sigma = 0.0886$ eV, $a = 1.2$ nm, $J = 0.008$ eV).

Dependences of the charge mobility on the electric field measured in PBPMSi films at different temperatures are shown in Fig. 7 (symbols). In general, the charge mobility in PBPMSi is about an order of magnitude lower than in PMPSi. It is a consequence of larger polaron binding energy in this polymer as found in Ref. 21. This conclusion was recently supported also by comparative thermally stimulated luminescence (TSL) studies[17] in PMPSi and PBPMSi. Fitting of experimental data of the mobility in PBPMSi by Eq. (23) (Fig. 7, straight lines) actually gives a larger polaron activation energy $E_a = 0.22$ eV, while the rest of parameters are similar to that of PMPSi ($\sigma = 0.096$ eV, $a = 1.3$ nm) except a larger transfer integral (by a factor of 2), $J = 0.016$ eV. This can be expected since it is known[35] that the larger is a conjugated system with attached side groups the larger is the localization radius of the charge.

Figure 8 shows a comparison of the results of our theoretical calculations (solid lines) and computer simulations (taken from Ref. 18; symbols) for the polaron transport in a disordered solid. All the used material parameters were the same.

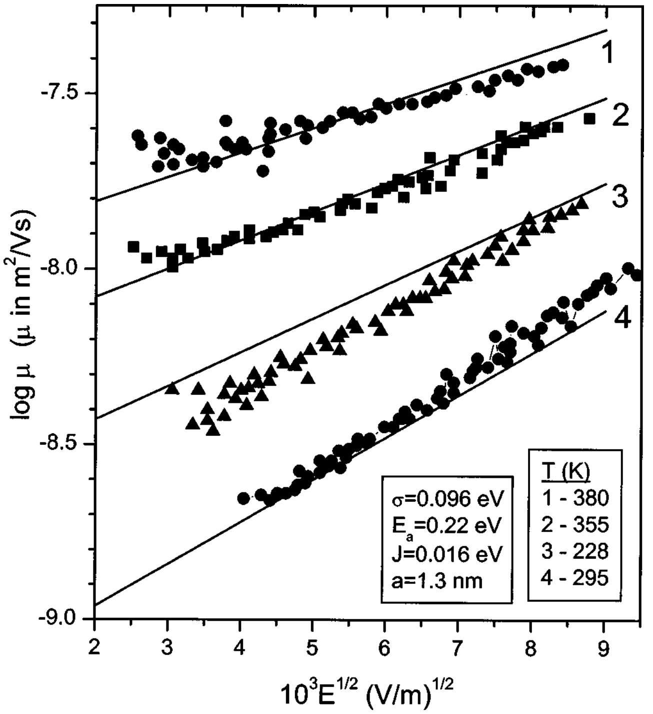

FIG. 7. Field dependences of the drift mobility μ_e in PBPMSi calculated from Eq. (23) for several temperatures (solid lines). Experimental data are given by symbols.

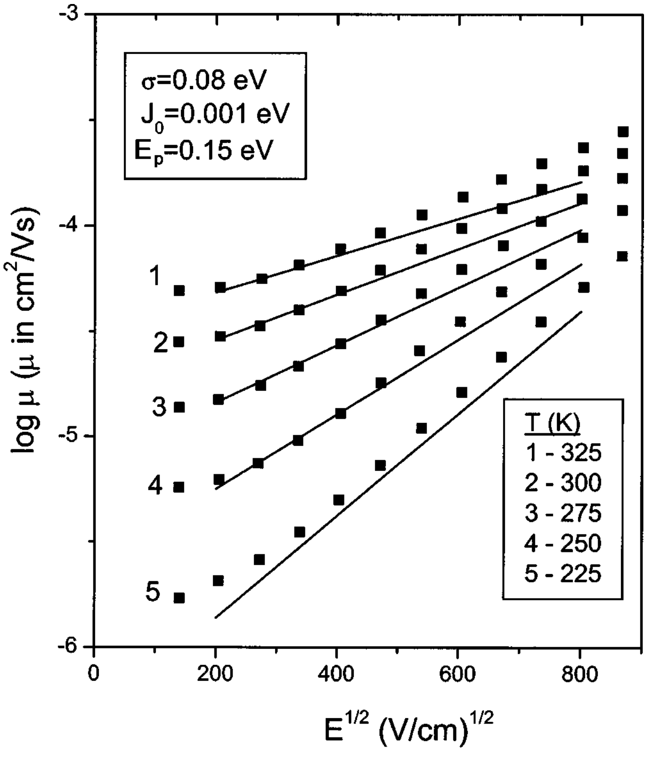

FIG. 8. Theoretical calculations (solid lines) of the field dependences of the polaron mobility in a disordered solid and the results of computer simulations (taken from Ref. 18; symbols) for the polaron transport. All the used material parameters were the same.

IV. CONCLUSION

An approach based on the Marcus jump rate equation is developed analytically to describe polaron transport in a disordered organic solid with superimposed disorder and polaron effects. It allows more precise estimation of the energetic disorder parameter and polaron binding energy (polaron activation energy) from the fitting of experimental temperature and field dependences of the mobility. Our polaron model can quantitatively explain the observed magnitudes of temperature and electric-field dependent polaron mobilities assuming reasonable values of polaron binding energies and transfer integrals. It is shown that the Poole-Frenkel-type field dependence of mobility $\ln\mu\propto\sqrt{E}$ occurs for both the bare charge carrier and the polaron transport provided that energetic correlation effects have been taken into account. Also the super-Arrhenius type temperature dependence of the drift mobility $\ln\mu\propto 1/T^2$ can be observed for polaron transport provided that the polaron activation energy is relatively small. Our model suggests a possible test for distinguishing between polaron and polaron-free transport since the PF factor is predicted to vary linearly with $T^{-3/2}$ in polaron-free systems, deviating from linearity for the polaron transport. Finally, the results of the calculations are found to be in good agreement with both experimental results obtained for some σ-conjugated polysilylenes where polaron formation was straightforwardly demonstrated and with recent computer simulations of polaron transport.

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