Photoinduced charge transport in molecular solids: the question of polaron formation

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ABSTRACT

A long standing issue for transport in molecularly doped polymers is the compatibility of the small polaron hopping rate. It has been recently shown that the Poole-Frenkel field dependence of the mobility of injected charges in molecularly doped polymers arises as a natural consequence of the charge-dipole interaction. In this paper we address the extent to which the Poole-Frenkle behavior is compatible with and dependent upon the size of the polaron binding energy.

1. INTRODUCTION

From the first time-of-flight mobility measurements on molecularly-doped polymers (MDP's) there has been considerable debate regarding the nature of the charge carriers that are photoinjected into these systems. In particular, there has often been disagreement as to whether the strongly activated field and temperature dependence of the observed mobility is related more to properties associated with the carrier and its interaction with phonons (e.g., the magnitude of the polaron binding energy, the degree and type of polaron formation), to static properties of the material (e.g., the amount and characteristics of energetic and spatial disorder), or to some combination of both. In the disorder formalism by Bässler, Borsenberger, and coworkers, it has been assumed that observed activation energies arise from activated hopping of carriers in an energetically disordered medium possessing a Gaussian density of localized transport states characterized by an energetic width $\sigma \approx 0.1$ eV. Within the context of this Gaussian disorder model (GDM), numerous simulations have been carried out using a specific functional form of the hopping rate in which polaron formation and multiphonon processes are assumed to be minimal (i.e., Miller-Abrahams rates\textsuperscript{1}). In much of the work of Schein and coworkers, by contrast, significant effort has gone into explaining the concentration dependence of observed activation energies in terms of the polaron binding energy $\Delta$ of the carriers, the electron transfer integral $J$, and a crossover that has been suggested to occur between adiabatic and nonadiabatic small polaron.\textsuperscript{2} Others have attempted to combine these two viewpoints by considering hopping with small polaron-like rates among energetically disparate sites.\textsuperscript{3,4}

Until recently, however, quantitative difficulties have hampered the internal consistency of many of the polaron models. For example, in the absence of disorder, to predict mobilities of the right order of magnitude ($\mu \sim 10^{-3}$ to $10^{-4}$ cm$^2$/Vs) using a polaron binding energy $\Delta$ big enough to give typical activation energies ($E_a = \Delta/2 \approx 0.5$ eV), it is necessary to assume transfer integrals $J$ considerably larger than the bandwidth of an organic crystal.\textsuperscript{5} On the other hand, if the polaron binding energy is actually rather small, ostensibly allowing for a reasonable value of $J$, there would then need to be substantial energetic disorder to get an effective activation energy of the order of 0.5 eV. If the width $\sigma$ of the energetic disorder needed to make up the difference represents actual energy jumps encountered in typical hops (as it does in the GDM and other models with uncorrelated energetic disorder), then an additional problem arises; the small polaron hopping rate tends to become "inverted". Inversion, in this context, refers to the strong suppression of the jump probability that occurs with small polaron type rates$^5$

$$R = \frac{J^2}{\hbar} \sqrt{\frac{\pi}{2\Delta kT}} e^{-\Delta/2kT} \exp \left( -\frac{\Omega}{2kT} - \frac{\Omega^2}{8\Delta kT} \right)$$

for hops between sites with large intersite energy difference $\Omega$, and arises as a result of the exponential factor $\exp\left(-\Omega^2/8\Delta\right)$ occurring in those rates which expresses the diminishing probability of having a "coincident event"

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when $|\Omega|$ is significantly greater than the polaron binding energy.\(^5\) Such a reduction of the hopping rate for energetically disparate jumps makes it again difficult to obtain mobilities of the right order of magnitude without taking an unreasonably large value of $J$. In numerical work on the GDM such difficulties do not arise; the hopping rate is assumed to be of the Miller-Abrahams, single phonon-assisted type, having asymmetric detailed balance.\(^6\) Indeed, numerical simulations of the Gaussian disorder model using symmetric rates are not consistent with formulae that have been extensively employed in the disorder formalism.\(^4\) For this combination of reasons, it has been assumed by some that photoinjected charge carriers in molecularly-doped polymers are not polarons, but are implicitly associated with bare, disorder-localized electronic states.

In recent years, however, it has been recognized that disorder models with appropriate spatial correlations characterizing the random potential energy landscape\(^3\) can explain most of the features associated with transport in these materials.\(^8\) In particular, recent theoretical work has successfully explained the Poole-Frenkel field dependence, $\mu \propto \exp \gamma \sqrt{E}$, of photoinjected charge carrier drift mobilities commonly observed in these materials on the basis of spatial correlations naturally occurring as a result of the long-range charge-dipole interaction between charge carriers and permanent electric dipoles in the material.\(^9\)\(^10\) Moreover, this picture offers a natural explanation for the relationship that empirically exists between observed activation energies and dipole moments of the molecular constituents in a wide class of molecularly doped polymers, and organic molecular glasses.\(^11\)\(^-\)\(^17\)

In this paper we point out that correlated disorder models (CDM's) of this type also offer the possibility of reconciling difficulties that have traditionally hindered polaron-based explanations of transport in these systems. Such a reconciliation is possible because, as pointed out previously, in correlated disorder models large potential energy fluctuations typically occur only over very large length scales. As a result, energy differences associated with nearest neighbor hops are typically much smaller than would be expected based upon the full width of the energetic disorder. Indeed, the activation energies that emerge in such models are the net result of many hops over spatially extended energetic hills and valleys.\(^18\) In this paper we show using an analytical extension of the approach developed in Refs. 9 and 19 (the details of which will be presented more fully in a subsequent paper), that the field and temperature dependence of the mobility in molecularly doped polymers is generally consistent with small polaron motion in a random energy landscape having correlations of the appropriate type. Through numerical studies based upon our theoretical expressions we are able to establish upper and lower bounds on the magnitude of polaron binding energies consistent with typical experimental data. Within the context of a 1D analysis of the underlying transport, we find that acceptable Poole-Frenkel-type behavior can be achieved with polaron binding energies in the range $\Delta = 0.1 - 0.5$ eV, and corresponding electron transfer integrals in the range $J = 0.01 - 0.1$ eV.

### 2. CALCULATIONAL APPROACH

A formal extension of the theory presented in Refs. 9 and 19 makes it applicable to a rather general form of the hopping rate, including, as a special case, hopping rates of the type (1) that arise in the theory of molecular polarons. As in our earlier paper, the starting point of the analysis is an exact expression for the drift velocity\(^9\)\(^20\)

$$v = \frac{\rho}{\sum_{n=1}^{\infty} e^{-\beta(n-1)\epsilon E \rho} \left(\beta u_n - u_{n+1}\right) R_{n,n+1}^{-1}}$$

(2)

for a particle moving along a one-dimensional transport path of sites separated by mean intersite spacing $\rho$ through a 3-dimensional energetically disordered medium. In this expression $\beta^{-1} = kT$ is the mean thermal energy, $\epsilon E \rho$ is the potential energy drop induced by the field between neighboring sites, $u_n$ is the site energy of the $n$th site along the path, and $R_{n,n+1}$ is the hopping rate connecting the $n$th site to its neighbor. The ensemble average in (2) was calculated in Ref. 9 by assuming a simple exponential dependence of the hopping rate $R_{n,n+1}$ on the energy difference $\Omega_n = u_{n+1} - u_n - \epsilon E \rho$. In the present circumstance we take advantage of the fact that the hopping rate between two sites typically arises from a microscopic calculation as the Fourier transform of a memory function.\(^21\) Thus, if the electron-phonon interaction is translationally invariant, the rate may be expressed in the general form

$$R_{n,n+1} = e^{-\beta \Omega_n/2} \tilde{W}(\Omega_n) = e^{-\beta \Omega_n/2} \int_{-\infty}^{\infty} dt e^{i\Omega_n t} \tilde{W}(t)$$

(3)
where the memory function \( W(t) \) and its Fourier transform \( \tilde{W}(\Omega) \) contain all model specific information about the electron phonon coupling. Following Ref. 22, we take advantage of this structure and formally introduce a function

\[
\tilde{f}(\Omega) = \frac{1}{\tilde{W}(\Omega)} = \int_{-\infty}^{\infty} \, dt \, f(t) e^{i\Omega t}
\]

in terms of which the drift velocity can be written

\[
v = \frac{\rho e^{\beta e E_{0}/2}}{\sum_{n=1}^{\infty} e^{-\beta(n-1) e E_{0}} \int_{-\infty}^{\infty} \, dt \, f(t) e^{-i\Omega t} e^{-\beta E_{0}} \left( e^{-\beta(n+1) u_{n}} e^{i\Omega t} e^{eta n u_{n}} + e^{-\beta u_{n-1}} e^{-\beta n u_{n}} \right).}
\]

(5)

For concentration, temperature, and field ranges of interest, the site energy distributions of the dipolar disorder model\(^7\) are well approximated by a Gaussian,\(^{33}\) and the ensemble average of the product of exponentials in the denominator is straightforward to compute using the techniques of Refs. 9 and 19. The essential result is that

\[
\left\langle e^{-\beta(n-1) u_{n}} e^{i\Omega t} e^{-\beta n u_{n}} \right\rangle = e^{\beta^{2} \sigma^{2} a_{n} e^{i\beta^{2} b_{n} \Omega t} e^{\beta^{2} c_{n} \Omega t}}
\]

(6)

where \( \sigma^{2} = \langle u_{n}^{2} \rangle \) is the variance of the energetic distribution associated with the dipolar disorder, and the quantities \( a_{n}, b_{n}, \) and \( c_{n} \) are defined through the relations

\[
a_{n} = \frac{1}{4} \left[ \frac{\delta_{n,1}(\rho - a)}{\rho} + (1 - \delta_{n,1}) \left( \frac{3\rho + 1}{\rho} - \frac{2a}{\rho n(n-1)} \right) \right]
\]

(7)

\[
b_{n} = \frac{\delta_{n,1}(\rho - a)}{\rho} + (1 - \delta_{n,1}) \frac{a}{n \rho}
\]

(8)

\[
c_{n} = \frac{(1 - \delta_{n,1})(\rho - a)}{\rho}
\]

(9)

in which \( a \), representing a minimal molecular radius, is typically about one-half the mean intersite spacing, a relationship that we assume in what follows.

For the small polaron rate \((1)\), we have, through Eqs. (3 and 4), the specific result that

\[
f(t) = \sqrt{\frac{\Delta kT}{2\pi^{2} J_{0} \eta}} \exp \left( -\tau^{2}/4\eta \right)
\]

(10)

where \( \eta = -8\Delta kT \). Because \( \eta \) is negative in this instance, we perform the integral resulting from the substitution of (10) and (6) into the denominator of (5) by formally treating \( \eta \) as a complex variable and analytically continuing the result to the value of \( \eta \) appropriate for the small polaron rate. After dividing by the field, the final result of the calculation is the following exact expression for the small polaron mobility

\[
\mu = \frac{J^{2} \rho}{\hbar E_{0} \Delta \sqrt{8} (4\Delta - \beta \sigma^{2})} \frac{e^{\beta e E_{0}/2} e^{-\beta \Delta/2}}{\sum_{n=1}^{\infty} e^{-\beta e E_{0} n(1-n)} e^{\beta^{2} \sigma^{2} a_{n}} \exp \left[ 2 \left( \frac{\beta^{2} \sigma^{2} b_{n} - \beta e E_{0} n}{4 \Delta \sigma^{2} e^{2} a_{n}} \right) \right]}
\]

(11)

Equation (11) allows, through a numerical evaluation of the sum in the denominator, calculation of the mobility for small polaron hopping rates as an explicit function of the transfer integral \( J \), the polaron binding energy \( \Delta \), the width \( \sigma \) of the energetic disorder, and the temperature \( T = 1/k_{B} \).

3. NUMERICAL RESULTS AND DISCUSSION

In Fig. 1 we present calculations of the field dependent mobility using Eq. (11) for a specific set of microscopic parameters, demonstrating that hopping rates of the small polaron type are indeed consistent with a strongly activated Poole-Frenkel mobility of the right magnitude over the range of temperatures \( T = 230 - 330 \) K and fields \( E = 2.5 \times 10^{5} - 1.5 \times 10^{6} \) V/cm typically probed in experiment. The filled data points in these figures were produced using (11) with polaron parameters \( J = 10 \) meV and \( \Delta = 0.15 \) eV that are reasonable for molecular solids. In addition we have assumed a mean intersite spacing \( \rho = 10 \) Å, a molecular radius \( a = 5 \) Å, and have included correlated energetic
Figure 1. Field dependent mobility for the model described in the text. Filled circles are calculated from Eq. (11) using $\sigma = 80$ meV, $a = 5\, \text{Å}$, $\rho = 10\, \text{Å}$, $\Delta = 0.15$ eV, and $J = 10$ meV, for temperatures ranging from 231 to 331 K; the lines are the result of least-square fits in the range $\sqrt{E} = 3-9$ (V/µm)$^{1/2}$.

disorder characterized by a width parameter $\sigma = 80$ meV. For the data points shown, numerical convergence of the sum in the denominator of (11) occurs within about $10^3$ terms of the series. The straight lines accompanying the numerical data are the results of linear least-square fits performed in the restricted range $\sqrt{E} = 300-900$ (V/cm)$^{1/2}$.

In Figs. 2 and 3 we present additional data derived from the linear fits appearing in Fig. 1. Specifically, we present in Fig. 2 the Poole-Frenkel factors $\gamma = \partial \ln (\mu/\mu_0)/\partial \sqrt{E}$, representing the slope of each fit in Fig. 1, and in Fig. 3 the extrapolated zero field mobility, representing the intercepts of those fits. In the analytic theory of Ref. 9 and the recent numerical work of Ref. 10, these quantities are predicted to scale with temperature in a way which has been characterized through the empirical relation

$$\mu = \mu_0 e^{-A_1 \beta^2 \sigma^2 e^{A_2 (\beta^2 \sigma^3/3 - A_3)} \sqrt{E} \sigma/\sigma},$$

where $A_1$, $A_2$, and $A_3$ are empirical parameters that depend upon dimensionality and the degree of spatial disorder of the system. According to these predictions, the Poole-Frenkel factor $\gamma$ should scale with temperature as $T^{-3/2}$ and the zero-field extrapolated mobility $\mu(0)$ should display the quadratic activation with temperature $\ln \mu(0) \propto (\sigma/kT)^2$ that it shares with the uncorrelated Gaussian disorder model. The data in Figs. 2 and 3, which have been plotted accordingly, clearly support the predicted scaling laws. By fitting the relationships in Figs. 2 and 3 to the corresponding functional form (12) proposed by Novikov, et al. in Ref. 10, we obtain the empirical coefficients $\mu_0 = 1.8 \times 10^{-2}$ cm$^2$/Vs, $A_1 = 1.02$, $A_2 = 2.24$, and $A_3 = 0.99$ characterizing the small polaron model described by Eq. (11) for this particular set of polaron parameters.

In addition to the data presented in Figs. 1-3, we have performed a more extensive investigation of the mobility predicted from (11) over a wide range of polaron and disorder parameters. For the same values of $\sigma$, $a$, and $\rho$, and polaron binding energies in the range $\Delta = 0.1 - 0.5$ eV, the quality of the fits to (12) remains undiminished, but with Poole-Frenkel parameters $A_2$ and $A_3$ increasing very slightly (by about 2%) with increasing $\Delta$. The prefactor
Figure 2. Poole-Frenkel factor $\gamma$, as determined from the slopes in Fig. 1, plotted as a function of $T^{-3/2}$.

parameter $A_1$ increases monotonically with increasing $\Delta$, from $A_1 = 0.99$ to $A_1 = 1.34$, reflecting the polaronic contribution to the activated behavior; Nevertheless, even for $\Delta = 0.5$ eV, no significant deviation from a $T^{-2}$ dependence was observed in the temperature range examined. Thus aside from a slightly increasing value of $A_1$, there is no perceptible qualitative effect of having a large polaron binding energy, although the actual magnitude of the mobility drops precipitously as $\Delta$ exceeds 0.5 eV; to maintain reasonable values for the mobility, it is therefore necessary to increase the value of $J$ to 100 meV for $\Delta = 0.5$ eV. Higher values of $\Delta$ are incompatible because they must be accompanied by values of $J$ which are too large for molecular solids. For $\Delta$ smaller than 0.1 eV, we also begin to see significant deviations from the Poole-Frenkel law which arise when a large enough fraction of the hopping rates becomes extremely slow in the "inverted" regime. These deviations are naturally exaggerated in our one dimensional calculation, where it is impossible to avoid a slow hop, to the extent that a steady state mobility does not exist for $4\Delta \leq \beta \sigma^2$. Such a transition to an anomalous transport regime is well-known in this context, and has been discussed previously. A more complete analysis of this transition, along with a more comprehensive discussion of other aspects of the present model will appear in a subsequent publication.

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REFERENCES

Figure 3. Extrapolated zero-field mobility \( \mu(0) \), as determined from the intercepts in Fig. 1, plotted as a function of \( T^{-2} \). A linear relationship is expected for hopping in a Gaussian density of states.