

Disordered polaron transport: a theoretical description of the motion of photoinjected charges in molecularly doped polymers

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We present a model for the description of the temperature and concentration dependence of the mobility of photoinjected charge carriers in molecularly doped polymers on the basis of polaron transport in disordered media. We develop an existing variable range hopping technique to incorporate excluded volume effects which can be of importance in molecularly doped polymers, use the technique in conjunction with a Gaussian distribution of site energies in the polymeric solid, apply the formalism to calculate the mobility and address recent observations on hole motion in TPD and TTA in polycarbonate matrices. We show that the competition between spatial and energetic disorder can provide a reasonable mechanism for the observed concentration dependence of the activation energy for charge transport. Our theory thus provides an alternative to a recently proposed explanation based on an adiabatic-diabatic polaron transition.

1. Introduction

Charge transport in molecular solids has proved to be a fertile area of solid state research in the last fifteen years [1-3]. Because intermolecular van der Waal forces in these materials are weak, the energies associated with intermolecular charge transfer are *not* disparately large with respect to energies pertinent to the static and dynamic disorder. For this reason, traditional transport ideas developed for materials such as metals and inorganic semiconductors break down severely in molecular solids, making it necessary to develop new approaches to the problem. The nature of the transport processes in molecular *crystals* has indeed been examined thoroughly in the last ten years, and a unified explanation of the behavior of the mobility been provided [4], in terms of an intermediate polaron theory, at least in one prototypical system, viz. naphthalene. However, new questions of a fundamental nature have arisen in recent years. They concern transport in statically *disordered* materials such as molecularly doped polymers [5,6]. Two models have been proposed to address the observations: one based on the transport of ordered polarons, the other on that of disordered nonpolaronic

carriers. In this article, we present a theory based on a transport of carriers which are both polaronic and disordered: the former as a result of strong interactions with the vibrations of the solid, and the latter as a result of the nonperiodic environment of the polymers.

Three important aspects of charge transfer in molecular solids are: the nature of the charge carriers, the role of static disorder, and the effects of high electric fields. In this paper, we will consider transport in the presence of low fields, and focus only on the role of static disorder. While we refer the reader to refs. [7-10] for a detailed discussion on the nature of carriers in the absence of disorder, it will be helpful to summarize the essential elements of the picture that has emerged in the ordered environment.

Naphthalene has served as the prototype system for investigations of the nature of charge carriers in molecular crystals. Photoinjected charge carriers in naphthalene exhibit peculiar transport behavior: in the *c'* direction, the mobility is found to decrease as the temperature *T* is raised from 30 to 100 K but then to be independent of *T* from 100 K onwards [11-13]. Much theoretical effort has been spent on the explanation of this behavior [4,7-10,14-18]. The

qualitative behavior of the observations is reproduced by almost all the theoretical studies. However, a systematic program of quantitative comparison of the observations with theoretical predictions has shown most theoretical approaches to fail such *quantitative* tests.

A quantitative as well as qualitative explanation has been provided by a more recently developed approach [4]. It is based on the ideas that (i) the charge carriers are polaronic, (ii) the important phonon branch is the librational one with a frequency of 16 meV in energy units and with a dispersion, found from independent (neutron diffraction) experiments, of 0.7, 1.4 and 0.24 meV in the three principal axes directions, (iii) there is a small but nonzero static energy fluctuation typified by the value of 0.17 meV in the site energies, and that (iv) the calculational technique to be employed is one similar to that developed earlier for the treatment of exciton transport via generalized master equations [19], which uses a consistent site-state perturbation approach. A comparison of theory and experiment produces excellent fits and perfectly reasonable values of the parameters [4], and leads to the conclusion that the transport is polaronic in all three directions in the crystal. In the light of these studies, it can be said that the nature of charge carriers in molecular solids with an ordered environment is clearly polaronic and that no fundamental questions remain in crystal transport in the low-field regime.

In contrast to the molecular crystals described above, the effects of static disorder on transport are large for the molecularly doped polymers. Here we will focus attention on the systems of TPD, TTA and DEH in polycarbonate, which have been investigated in recent experiments [20,21]. The details of the experiments and their interpretation may be summarized as follows. If the extrapolated low-field data are analyzed through a mobility expression which is the product of a prefactor and an exponential $\exp(-\Delta/k_B T)$, both the prefactor and the activation energy Δ are seen to exhibit different behavior than that expected for activated diabatic polarons in an ordered crystal: Δ shows dependence, and the prefactor shows lack of dependence, on the average distance between dopant molecules. For TPD, the observed activation energy increases as a function of increasing dopant separation, and the prefactor tends to be constant. On

the other hand, for DEH, the prefactor is an exponentially decreasing function of dopant separation, but the activation energy is a constant. A transition from one tendency to the other is observed for TTA.

It has been proposed [21] that these observations are indicative of a transition between adiabatic polaron hopping at small dopant spacing and diabatic polaron hopping at large dopant spacing. As the distance between dopant molecules decreases, the intermolecular transfer integral J increases. If J is so large that it does not provide the limiting rate for transport, the mobility is proportional to the product of the vibration frequency ω and an Arrhenius factor with an activation energy which depends on J . This is a consequence of adiabatic ordered polaronic theory [22]. In the diabatic limit for small transfer integral, on the other hand, the prefactor is proportional to J^2 , and the activation energy is J independent [23]. No expressions valid in the intermediate regime appear to be available but fits to the data on TTA have been provided via an interpolation between the two limits [21]. In each limit, the mobility μ is the product of $(ea^2/k_B T)$, an exponential $\exp(-\Delta/k_B T)$, and a factor F . In the diabatic limit, $F = (J^2/\hbar)\sqrt{\pi/2E_p k_B T}$ and $\Delta = \frac{1}{2}E_p$. In the adiabatic limit, $F = \omega$, and $\Delta = \frac{1}{2}E_p - J$. Values have been extracted from these fits for the following parameters: J , assumed to vary exponentially on the intersite distance a through $J = V_0 e^{-a/\lambda}$, where V_0 and λ are constants, the polaronic binding energy E_p , and the vibrational frequency ω . For TTA, these have been found [21] to be of the order of 0.25, 0.5, and 1 eV respectively.

2. Theoretical description via disordered polarons

The description given in ref. [21] is based on the assumptions that the charge carriers are polarons and that the key features of the data arise from a polaronic transition from adiabatic behavior to diabatic behavior. Since theoretical descriptions of transport in ordered solids such as the naphthalene crystal lend support to the idea the carriers in molecularly doped polymers are polaronic [4,9], we believe that it is a reasonable and natural starting point to take the carriers in molecular doped polymers also to be polaronic. On the other hand, we also believe that disor-

der plays a very important role in determining the features of charge transport in these solids, and that it is necessary, as others have done [24-27], to incorporate disorder in the transport description. What is called for is, therefore, a combination of the concepts of disorder with polaronic ideas. In the following analysis, we have assumed that the charge carriers are polarons (in the usual adiabatic limit), and that disorder plays the key role in the observed features. We will see that the prominent features of the data can be explained as a consequence of a competition between energetic disorder and spatial disorder to become the limiting factor in the transport.

The starting point of the theory is the expression for the polaron jump rate F_{ij} between any two dopant molecules i and j in the high-temperature and/or high-coupling limit [23],

$$F_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{2E_p k_B T}} \exp[-(E_p/2k_B T) - (W_{ij}/2k_B T) - (W_{ij}^2/8E_p k_B T)]. \quad (1)$$

In eq. (1), W_{ij} is the difference in carrier energies at molecules i and j . These energies vary from location to location as a result of static differences in the local environment. We note that the activation energy for the jump rate has a positive contribution $\frac{1}{2}E_p$ from the polaron formation, and a contribution $\frac{1}{2}W_{ij} + \frac{1}{8}W_{ij}^2/E_p$ from the energetic disorder which may be positive or negative. Following normal practice [28], we assume that the transfer matrix element J_{ij} depends exponentially on the spatial separation r_{ij} between molecules i and j ,

$$J_{ij} = V_0 \exp(-\alpha r_{ij}), \quad (2)$$

and rewrite eq. (1) as

$$F_{ij} = \frac{V_0^2}{\hbar} \sqrt{\frac{\pi}{2E_p k_B T}} \exp(-E_p/2k_B T) \exp(\mathfrak{R}_{ij}), \quad (3)$$

where

$$\mathfrak{R}_{ij} = 2\alpha r_{ij} + \frac{W_{ij}}{2kT} + \frac{W_{ij}^2}{8E_p kT}. \quad (4)$$

Our procedure consists of following standard methods of disordered transport to replace the disordered system above by an ordered system with a single effective rate F , given by

$$F = \frac{V_0^2}{\hbar} \sqrt{\frac{\pi}{2E_p k_B T}} \exp(-E_p/2k_B T) \exp(-\mathfrak{R}_p), \quad (5)$$

where \mathfrak{R}_p is the value of \mathfrak{R}_{ij} at the peak of the distribution of nearest-neighbor distances \mathfrak{R}_{ij} . From eq. (5), we calculate the zero-field mobility μ as

$$\mu = e^2 a^2 F / kT, \quad (6)$$

where a is taken to be the average separation between dopant molecules.

The methods of disordered transport we use here are based on a variable range hopping technique [29,30]. Our analysis proceeds as follows. First we sketch the technique, particularly as described by Apsley and Hughes [29], and show briefly how the effective rate F or the mobility μ may be calculated and the results used to explain the dependence of activation energy on dopant concentration. We then present our modification of the theory to account for excluded volume of the individual dopant molecules. Next we assume a Gaussian distribution of site energies and calculate \mathfrak{R}_p . Finally, we compare the modified theory with experiment.

The variable range hopping technique may be sketched as follows. The effective rate for hopping in a disordered arrangement of impurity sites is the average (or most probable) nearest-neighbor distance in a four-dimensional space consisting of three spatial dimensions, and a fourth dimension describing the energetic disorder. The distribution $P(\mathfrak{R})$ which specifies the probability that \mathfrak{R}_{ij} is a nearest-neighbor distance, is calculated as follows. If $\mathcal{N}(\mathfrak{R})$ is the average number of dopant molecules in the four-dimensional volume within a radius \mathfrak{R} , then the probability per interval $d\mathfrak{R}$ that no dopant molecules will be found at a radius less than \mathfrak{R} , but that one molecule will be found at \mathfrak{R} , is given by [29]

$$P(\mathfrak{R}) = \frac{\partial \mathcal{N}(\mathfrak{R})}{\partial \mathfrak{R}} \exp[-\mathcal{N}(\mathfrak{R})], \quad (7)$$

where $\mathcal{N}(\mathfrak{R})$ is calculated by integrating over the 4D volume:

$$\mathcal{N}(\mathfrak{R}) = \frac{kT}{W_{\max}(2\alpha\alpha)^3} \int_0^{W_{\max}/kT} dw \int_{2\alpha\alpha}^{\mathfrak{R}-w} 4\pi r^2 dr. \quad (8)$$

Here a_0 is the diameter of a dopant molecule, and a is the mean dopant separation. The technique of calculating the effective rate is to substitute (8) into (7), solve for the extremum of $P(\mathfrak{R})$, and use \mathfrak{R}_p , the corresponding value of \mathfrak{R} , in (5).

We recall results from Apsley and Hughes [29] for the case where W_{ij} is taken from a uniform distribution such that $0 \leq W_{ij} \leq W_{\max}$. For a low density ρ ($\rho = 1/a^3$) of dopant molecules, or impurity sites, we see that

$$\mathfrak{R}_p \approx \frac{W_{\max}}{3k_B T} + \frac{\alpha}{\sqrt[3]{\pi\rho}} \quad \left(\frac{\alpha}{\sqrt[3]{\rho}} \gg \frac{W_{\max}}{k_B T} \right). \quad (9)$$

On the other hand, Mott's $T^{1/4}$ law is recovered in the high-density limit,

$$\mathfrak{R}_p \approx \sqrt[4]{\frac{W_{\max} 36\alpha^3}{k_B T \pi\rho}} \quad \left(\frac{\alpha}{\sqrt[3]{\rho}} \ll \frac{W_{\max}}{k_B T} \right). \quad (10)$$

Although in the molecularly doped polymers we do not observe a $T^{1/4}$ dependence as expressed by eq. (10), the theory of Apsley and Hughes is still applicable in the narrow temperature range over which the experiment is performed. The mobility will appear to be activated, even in the regime where the $T^{1/4}$ law is appropriate. Thus, we define an effective activation energy Δ given by

$$\Delta = \frac{1}{2}E_p + \frac{d}{d(1/kT)} \mathfrak{R}_p, \quad (11)$$

and observe from (9) that, in the low-density limit, the contribution to Δ from the disorder is

$$\Delta_{\rho \rightarrow 0} - \frac{1}{2}E_p = \frac{1}{4}W_{\max}. \quad (12)$$

On the other hand, from (10), we find a high-density "effective" activation energy such that,

$$\Delta_{\rho \rightarrow \infty} - \frac{1}{2}E_p = \sqrt[4]{\frac{36W_{\max}kT^3\alpha^3}{\pi\rho}}. \quad (13)$$

We observe from eqs. (12) and (13) that $\Delta_{\rho \rightarrow 0} > \Delta_{\rho \rightarrow \infty}$, so that as the concentrations of sites decreases, the effective activation energy also increases. This transition from low activation energy to high activation energy may be understood quite simply. For high dopant concentrations, the carrier has a choice of many sites to which it may hop. Thus it makes its selection in favor of (lower) activation barriers. For low concentrations, on the other hand, location de-

termines the site selected. Whatever energetic barrier presents itself must be surmounted. Thus, the effective activation is higher for lower dopant concentrations. This behavior describes the tendency observed in the molecularly doped polymers. This is the primary feature of the variable range hopping technique which has suggested to us that it could be applied to molecularly doped systems. In order to develop a quantitative theory, we have found it necessary to make several modifications to the technique. The first of these modifications is the inclusion of excluded volume.

In the treatment of Apsley and Hughes, $P(\mathfrak{R})$, the probability distribution of nearest-neighbor distances, is calculated under the assumption that the location of a particular localized state is independent of the locations of the others. For example, as applied to disordered semiconductors, variable range hopping describes transport among localized states at the band edges. The states are assumed to be independent, like particles in a noninteracting gas. This assumption is reasonable in semiconductors because the concentration of impurities is low. In molecularly doped polymers, however, the localized site-basis consists of the dopant molecules themselves. Site locations are therefore correlated by dopant-dopant interactions, which are especially important for the high dopant concentrations studied in experiment. As we will see, $P(\mathfrak{R})$ is modified significantly even by the simple constraint that no two dopant molecules may occupy the same space. To calculate the probability distribution $P(\mathfrak{R})$ of nearest neighbor distances for high dopant concentrations, it is necessary to account for the volume which is excluded by the molecules themselves. Since excluded-volume considerations should concern only real space, we will carry out the calculations without involving the energy dimension. This will simplify the calculations. Also, to facilitate counting, we will regard the dopant molecules as occupying points on a simple cubic lattice such that the points are separated by the diameter of a dopant molecule, a_0 . Let us consider an example of a chain of specific sites at which dopant molecules may be located, extending in one direction from a molecule sitting at the origin. Assume that, the chain is 11 sites long, so that there are 10 sites besides the origin where molecules may sit. Assume that besides the molecule at the origin, there are 2

other molecules in the system. Suppose we wish to calculate the probability P_E that the 5 closest sites to the origin are empty. First, we calculate the number of ways of putting the two molecules on the 10 remaining sites. This number is 10×9 . There are 5 ways of putting the first molecule outside the 5-site empty region, and therefore there are 4 remaining ways of putting the second molecule outside the 5-site empty region. Thus there are 5×4 ways of putting down the two molecules outside the 5-site region. The probability that the 5-site region will be empty if the molecules are placed at random is therefore $(5 \times 4) / (10 \times 9)$, which we write in the suggestive form

$$P_E = \frac{11-6}{11-1} \frac{11-7}{11-2} \quad (14)$$

If we ask more generally for the probability that an M -site region will be empty if there are L molecules and N total sites, the answer is

$$P_E = \frac{N-M-1}{N-1} \frac{N-M-2}{N-2} \frac{N-M-3}{N-3} \dots \frac{N-M-L}{N-L} \\ = \frac{(N-M-1)!(N-L-1)!}{(N-1)!(N-M-L)!} \quad (15)$$

In the limit of large N and L , we can replace the factorials in (14) by Stirling's formula. This leaves us with the simple expression

$$P_E = \left(1 - \frac{L}{N-1}\right)^m \quad (16)$$

In the continuum limit we substitute $(r-a_0)/a_0 = M$ and $L/(N-1) = \rho a_0$. Then

$$P_E = (1 - \rho a_0)^{(r-a_0)/a_0} \\ = \exp\left(-\frac{r-a_0}{a_0} |\ln(1 - \rho a_0)|\right) \\ = \exp\left[-\frac{(r-a_0)}{a_0} \left|\ln\left(1 - \frac{a_0}{a}\right)\right|\right] \quad (17)$$

Therefore, the normalized probability that \mathfrak{R} is a nearest-neighbor distance is given by eq. (7), with

$$\mathcal{N}(\mathfrak{R}) = \frac{\mathfrak{R} - 2\alpha a_0}{2\alpha a'} \quad (18)$$

where a' is a modified average molecular distance, given by

$$a' = \frac{a_0}{|\ln(1 - a_0/a)|} \quad (19)$$

The above result holds for our one-dimensional chain. Similarly, in three dimensions,

$$\mathcal{N}(\mathfrak{R}) = \frac{4\pi}{3(2\alpha a')^3} [\mathfrak{R}^3 - (2\alpha a_0)^3] \quad (20)$$

where

$$a' = \frac{a_0}{\sqrt[3]{|\ln(1 - a_0^3/a^3)|}} \quad (21)$$

If we compare eq. (20) with the results obtained by simply integrating over volume as suggested by (8), we see that the excluded volume modification of the theory is to replace the mean site-spacing a by a' as specified in eq. (21). We note that, for $a \gg a_0$ (dilute systems) the excluded volume correction is unimportant, as expected.

We now make the specific assumption that the distribution of site energies is a Gaussian. In addition, we neglect the quadratic term $\frac{1}{8} W_{i,j}^2 / E_p kT$ in the energetic dependence of $\mathcal{P}_{i,j}$ for polaron binding energies which are large compared to the width of the disorder. In order to fit the data, we have found it necessary to assume that the distribution of carriers is non-thermal. Therefore we take the energy differences $W_{i,j}$ to be symmetrical with respect to $W=0$. For this case, the peak of the nearest-neighbor distribution may be extracted from

$$2 \int_{-\infty}^{\mathfrak{R}_p} dx \exp(-x^2/4\sigma_1^2) (\mathfrak{R}_p - x) \\ + \frac{1}{2\sigma_1^2} \int_0^{2\alpha a_0} dx x^2 (\mathfrak{R}_p - x) \exp[-(\mathfrak{R}_p - x)^2/4\sigma_1^2] \\ = \sqrt{\frac{\pi}{8}} (\alpha a)^{-3} \frac{1}{\sqrt{2}\sigma_1} \left(\int_{-\infty}^{\mathfrak{R}_p} dx \exp(-x^2/4\sigma_1^2) \right. \\ \left. \times (\mathfrak{R}_p - x)^2 - \int_0^{2\alpha a_0} dx x^2 \exp[-(\mathfrak{R}_p - x)^2/4\sigma_1^2] \right)^2 \quad (22)$$

Here, $\sigma_1 = \sigma/k_B T$, where σ is the width of the distribution of site energies. In order to compare (5) with

experiment, it is necessary to obtain \mathfrak{R}_p numerically as a function of temperature and concentration. We have carried out such numerical solutions in the context of molecularly doped polymers and have described the results in section 3 below.

We have thus constructed a theory based on polaron hopping in the molecularly doped polymers which has the essential structure necessary for the description of the experiments. Our theoretical contribution in the present paper begins with expression (5) for the mobility of a diabatic polaron and arrives at expression (22) for \mathfrak{R}_p , which, when substituted in (5), yields the mobility in a disordered environment. We have assumed that the distribution of dopant energies is a Gaussian, have taken the hops upward in energy to be equally likely as hops downwards in energy, and have explicitly taken into account the excluded volume of the individual dopant molecules.

3. Comparison with experiments

We have compared our disordered polaronic results (22) with the experiments on TTA and TPD [20,21]. For TTA, we found the intersite transfer integral J and the polaron binding energy E_p to be 0.2 and 1.7 eV respectively, and the width of the disorder σ to be 0.34 eV. Our simultaneous fits to the activation energy as a function of concentration and to the mobility as a function of concentration are shown in fig. 1. For TPD, we found the intersite transfer integral J and the polaron binding energy E_p to be 0.14 and 2.2 eV respectively, and the width of the disorder σ to be 0.36 eV. Our fits to the data from TPD are shown in fig. 2. For both TTA and TPD we find reasonable agreement with experiment. We find specifically in both cases that the theory is compatible with an activation energy which increases as the concentration of dopant molecules decreases. We have not shown the data and our fits for DEH-doped polycarbonate, which shows a constant activation energy of 0.6 eV for all dopant concentrations. This behavior is easily understood if we assume that the static disorder is simply an order of magnitude smaller for DEH-doped polycarbonate than for the case of the two dopants TTA and TPD. In such a case, the description for carrier transport in DEH is that of polaron hopping in essentially an energetically ordered

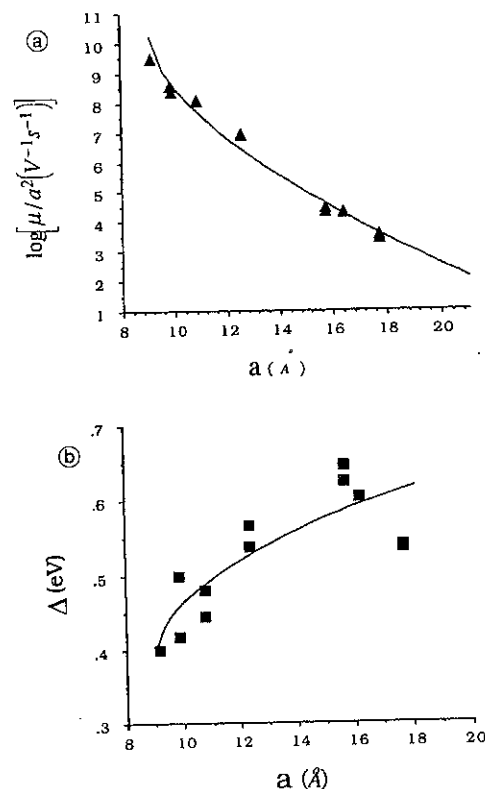


Fig. 1. In (a) is shown the extrapolated zero-field mobility of photoinjected holes in TTA-doped polycarbonate as a function of the mean dopant separation. Shown in (b) is the extrapolated zero-field activation energy as a function of the mean dopant separation. The data are from ref. [20]. The solid curves are produced from the theory, using parameters which were determined by fitting the two data sets simultaneously. The values of the fitted parameters are: $E_p = 1.7$ eV, $J = 0.2$ eV, and $\sigma = 0.34$ eV. The minimum dopant separation, a_0 , was taken to be 9 Å.

environment. Such transport is described by a concentration-independent activation energy which is equal to half the polaron binding energy.

In fig. 3 we show the data from TTA for the extracted activation energy along with the fits provided by our expression (5) as well as that given in ref. [21] as an interpolation between ordered polaron results in the diabatic and adiabatic regimes. While no qualitative considerations allow one to choose between the two fits, the theoretical curves have quite different shapes. Whereas the adiabatic-diabatic theory suggests that the saturated value of the activation energy is essentially obtained at a mean dopant separation of 15 Å, our theory suggests that the activation

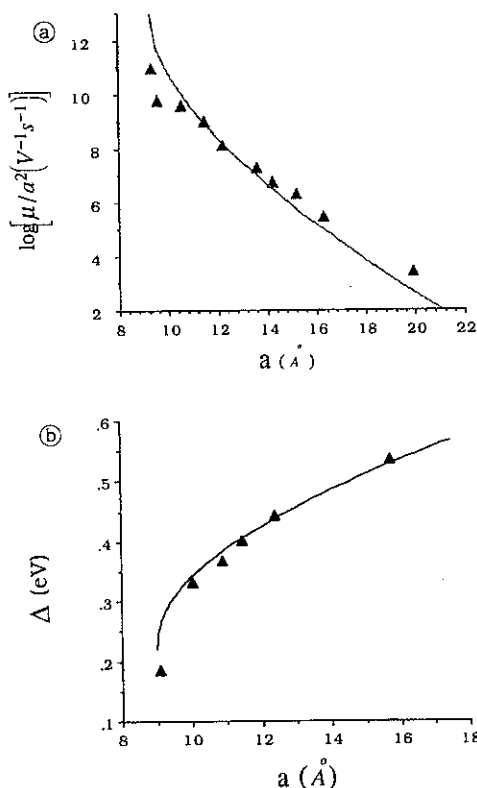


Fig. 2. In (a) is shown the extrapolated zero-field mobility of photoinjected holes in TPD-doped polycarbonate as a function of the mean dopant separation. Displayed in (b) is the extrapolated zero-field activation energy as a function of the mean dopant separation. The data are from ref. [21]. The solid curves are produced from the theory, using parameters which were determined by fitting the two data sets simultaneously. The values of the fitted parameters are: $E_p = 2.2$ eV, $J = 0.14$ eV, and $\sigma = 0.36$ eV. The minimum dopant separation, a_0 , was taken to be 9 Å.

energy has not yet reached its saturated value for the mean dopant separation of 20 Å. While, in principle, our theory contains a mechanism for a "transition" from the regime where an increasing dopant separation increases the activation energy, to a regime in which the activation energy is saturated, the extracted physical constants for the molecularly doped polymers are such that the system is not in this transition regime. The reason is as follows. In order to explain the change in activation energy as a function of dopant concentration, the distribution of the site energies must have a width of about 0.25 eV. For experiments at room temperature, this gives rise to a hopping rate with a highly energy-dependent Arrhen-

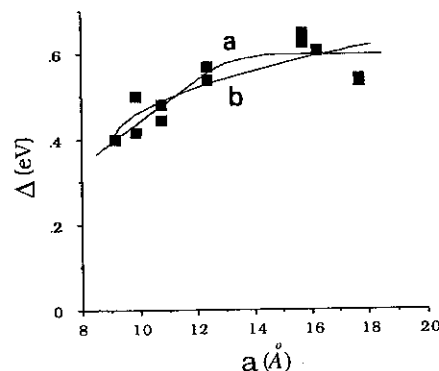


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ius factor. In such a case, the nearest-neighbor distance in the four-dimensional space depends much more strongly on the energy than it does on the dopant separation. Consequently, rather than describing a transition to a regime in which the activation energy is saturated, our theory describes a gradual increase in activation energy as a function of dopant separation over the entire range of experimental data. It is interesting that our theory agrees so well with the data, especially for the high concentrations of dopant molecules, where both experiment and theory show a sharp rise in the activation energy as a function of dopant separation. We find, however, that the sharp rise in activation energy predicted by the theory is caused by excluded volume considerations at high concentrations. At high dopant concentrations, the effective nearest-neighbor distance tends to zero quickly as a function of the mean lattice spacing.

Despite the satisfactory fits provided by our theory, there are problems with the values of parameters extracted from the fits. These problems are similar to those one encounters in the application of the ordered polaronic theory given in ref. [21]. The parameters we extract are J , E_p and the disorder width σ . The parameters in ref. [21] are J , E_p , and the fre-

experiment, it is necessary to obtain \mathfrak{R}_p numerically as a function of temperature and concentration. We have carried out such numerical solutions in the context of molecularly doped polymers and have described the results in section 3 below.

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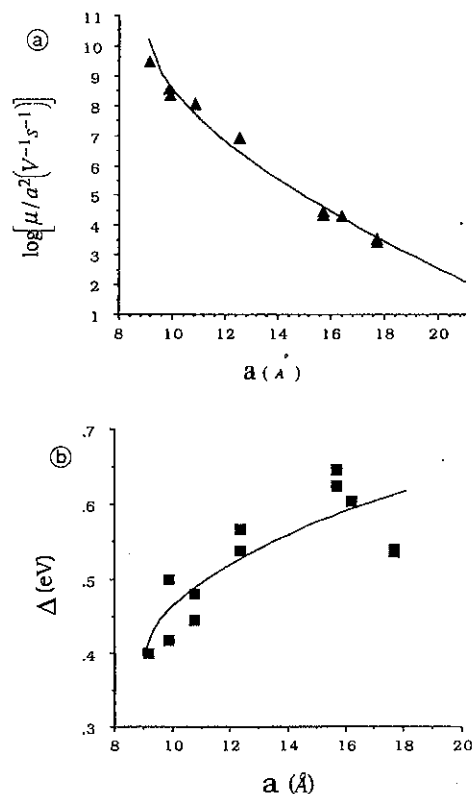


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In fig. 3 we show the data from TTA for the extracted activation energy along with the fits provided by our expression (5) as well as that given in ref. [21] as an interpolation between ordered polaron results in the diabatic and adiabatic regimes. While no qualitative considerations allow one to choose between the two fits, the theoretical curves have quite different shapes. Whereas the adiabatic-diabatic theory suggests that the saturated value of the activation energy is essentially obtained at a mean dopant separation of 15 Å, our theory suggests that the activation

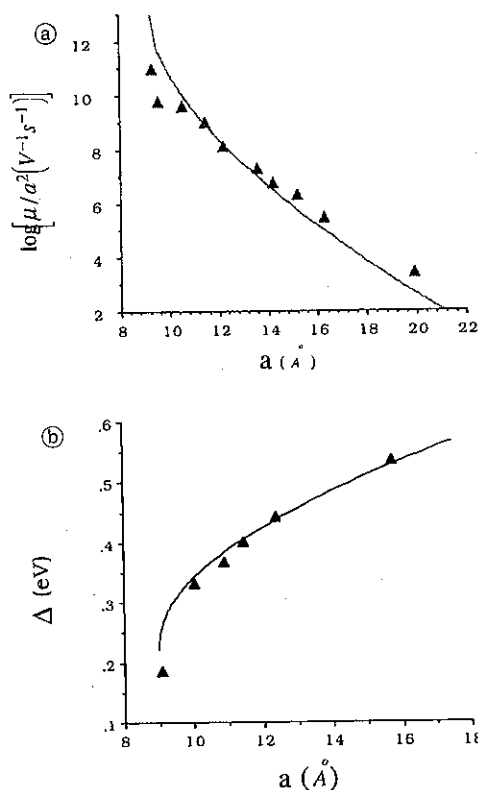


Fig. 2. In (a) is shown the extrapolated zero-field mobility of photoinjected holes in TPD-doped polycarbonate as a function of the mean dopant separation. Displayed in (b) is the extrapolated zero-field activation energy as a function of the mean dopant separation. The data are from ref. [21]. The solid curves are produced from the theory, using parameters which were determined by fitting the two data sets simultaneously. The values of the fitted parameters are: $E_p = 2.2$ eV, $J = 0.14$ eV, and $\sigma = 0.36$ eV. The minimum dopant separation, a_0 , was taken to be 9 Å.

energy has not yet reached its saturated value for the mean dopant separation of 20 Å. While, in principle, our theory contains a mechanism for a "transition" from the regime where an increasing dopant separation increases the activation energy, to a regime in which the activation energy is saturated, the extracted physical constants for the molecularly doped polymers are such that the system is not in this transition regime. The reason is as follows. In order to explain the change in activation energy as a function of dopant concentration, the distribution of the site energies must have a width of about 0.25 eV. For experiments at room temperature, this gives rise to a hopping rate with a highly energy-dependent Arrhen-

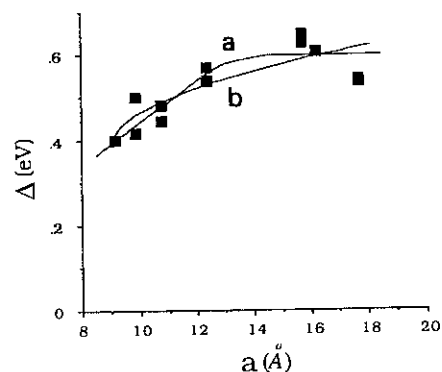


Fig. 3. The data from TTA for the extrapolated zero-field activation energy are shown as a function of the mean dopant separation, along with theoretical fits: fit (a) as provided by the interpolation of ref. [21] between ordered polaron results in the diabatic and adiabatic regimes, and fit (b) as given by our expression (5). The theoretical curves have quite different shapes. Whereas the adiabatic-diabatic theory suggests that the saturated value of the activation energy is essentially obtained at a mean dopant separation of 15 Å, our theory suggests that the activation energy has not yet reached its saturated value for the mean dopant separation of 20 Å.

ius factor. In such a case, the nearest-neighbor distance in the four-dimensional space depends much more strongly on the energy than it does on the dopant separation. Consequently, rather than describing a transition to a regime in which the activation energy is saturated, our theory describes a gradual increase in activation energy as a function of dopant separation over the entire range of experimental data. It is interesting that our theory agrees so well with the data, especially for the high concentrations of dopant molecules, where both experiment and theory show a sharp rise in the activation energy as a function of dopant separation. We find, however, that the sharp rise in activation energy predicted by the theory is caused by excluded volume considerations at high concentrations. At high dopant concentrations, the effective nearest-neighbor distance tends to zero quickly as a function of the mean lattice spacing.

Despite the satisfactory fits provided by our theory, there are problems with the values of parameters extracted from the fits. These problems are similar to those one encounters in the application of the ordered polaronic theory given in ref. [21]. The parameters we extract are J , E_p and the disorder width σ . The parameters in ref. [21] are J , E_p , and the fre-

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quency ω . Our value of the extracted disorder parameter σ appears to be reasonable. The value of the frequency ω obtained from the fits in ref. [21] is 1 eV and is therefore unacceptably large. If our values of J and E_p were reasonable, we could claim to have offered a better explanation of the data than in ref. [21]. However, our extracted values of J and E_p are also too large as are those in ref. [21]. We conclude that, before an adequate explanation of the observations can be said to have been provided, further work is required in both the ordered and disordered polaronic theories.

4. Discussion

While we have applied here a theoretical description of transport in the molecularly doped polymers which is based on polaron hopping in a disordered environment, ours is not the first attempt to use a disorder-based theory to explain these experiments. Baessler and co-workers [24-27] have developed a theory in which the observations of concentration-dependent activation energies and the high electric field effects are entirely based on disorder. The premise is the same, namely, that the carriers hop amongst dopant molecules which are disordered in energy and in their spatial arrangement. However, the assumed nature of the carriers is not polaronic as in our present theory, and the underlying hopping rate is that of Miller and Abrahams [31]. The hopping rates are independent of temperature when they describe a transition to an energetically lower site, but are suppressed by an Arrhenius factor $\exp(-\Delta/kT)$ when the hop is to an energetically higher site. By contrast, the polaronic hopping rates used in our theory are thermally assisted: enhanced by the factor $\exp(-\Delta/2kT)$ when the hop is to a site of lower energy, and suppressed by the factor $\exp(-\Delta/2kT)$ when the hop is to a site of higher energy. With the Miller-Abrahams hopping rate as a starting point, the time of flight experiments are reproduced by numerical simulations [26]. In order to make the conclusion drawn from the numerical simulations more transparent, we reproduced our calculation, incorporating the assumptions of ref. [24-26], and compared the results to experiment in the extrapolated low-field regime. In this case we found it impossible to fit the observed

dependence on dopant concentration and sample temperature. It is not inconceivable that this is a consequence of our particular calculation rather than that of the assumptions in the disordered nonpolaronic theory [27].

In summary, we have developed a theory to describe the drift mobility of photo-injected carriers in certain molecularly doped polymers. In keeping with successful descriptions [4,9] of transport in ordered molecular solids, our theory is based on the idea that the charge carriers are polaronic. However, in contrast to a recent attempt [21], we have adopted the point of view that the observed concentration dependence of the activation energy is an effect brought about by disorder, rather than by an adiabatic-diabatic polaron transition. We take this point of view from the treatment of refs. [24-26] but differ from the latter in assuming the carriers to be polaronic and in carrying out an analytic rather than a computer calculation of the mobilities. We have also seen that our theoretical fits to the experiments appear to be quite good, but result in parameter values which are in part unsatisfactory. In particular, as in ref. [21], the value of the transfer matrix element J which is required to fit the data is an order of magnitude larger than that which is found for the case of ordered molecular solids.

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