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Effect of dynamic disorder on charge transport along a pentacene chain

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The lattice equation of motion and a numerical solution of the time-dependent Schrödinger equation provide us with a microscopic picture of charge transport in highly ordered molecular crystals. We have chosen the pentacene single crystal as a model system, and we study charge transport as a function of phonon-mode time-dependent fluctuations in the intermolecular electron transfer integral. For comparison, we include similar fluctuations also in the intramolecular potentials. The variance in these energy quantities is closely related to the temperature of the system. The pentacene system is shown to be very sensitive to fluctuation in the intermolecular transfer integral, revealing a transition from adiabatic to nonadiabatic polaron transport for increasing temperatures. The extension of the polaron at temperatures above 200 K is limited by the electron localization length rather than the interplay between the electron transfer integral and the electron-phonon coupling strength.

I. INTRODUCTION

The theoretical understanding of charge transport mechanisms in ordered organic semiconductors is still far from satisfactory.[1] Despite decades of studies, several contradictions between experimental results and theoretical studies suggest that neither molecular-based charge transfer (or hopping) models nor band transport models are fully adequate when applied to these types of systems.[2] A recent approach, dealing with a combination of these two transport phenomena and applied to naphthalene crystals, has contributed to our understanding of charge-carrier transport in highly ordered organic materials,[3–5] but the enigmatic nature of the charge-carrier transport is not yet fully understood. The most important interactions that are involved in the dynamic process of moving electronic charge through the system of more or less well-aligned molecules are the intermolecular transfer integral (J), the electron-phonon coupling (λ), and the temperature ($k_B T$). It is well known from the work of Holstein[6,7] that electron-phonon coupling leads to the formation of polarons in molecular crystals, and that these polarons are candidates as charge carriers in the transport process. The polaron formation energy (E_P), which is related to both J and λ, is therefore an important quantity to consider in the context of charge transport. In addition, we also note that the intermolecular transfer integral depends on the electron-phonon coupling (or E_P) and on temperature since the polaron electronic bands narrow as a result of the electron-phonon coupling.[4]

From the basic arguments of the Holstein theory, we can notice that in order for the nonadiabatic charge-transfer process to be strictly valid, the polaron formation energy has to be much larger than the intermolecular transfer integral. Since typical values for the polaron formation energy are of the order of 100 meV,[2,8] this relation applies to very weakly coupled molecules, typically molecules in a polymer matrix,[9] and is of less relevance to molecular crystals.

For molecular crystals, the relation between J and E_P is instead close to unity. If we take pentacene as an ex-

ample, the reported values for J along the direction of strongest coupling are 50–80 meV.[10] The calculated polaron formation energies for pentacene reported in the literature range from 50 meV up to $\gtrsim$ 100 meV.[2] Therefore, in the case of pentacene (and molecules of similar size and structure, such as rubrene and perylene), the stable charge carrier in the ideal uniform system with constant J is a polaron localized to a few (three to four[11]) molecular units in the system. It should be noted that the result of a localized polaron is the ground state for a single excess electron (or hole) in the atomistic model we are using (see below).

In addition to these energy scales, we also have to consider the effect of the disorder, which inevitably exists in the molecular crystals, both in terms of intermolecular vibrational modes that, to first order, affect the intermolecular interactions, that is, J, and in terms of static defects such as crystal imperfections and the presence of impurities. In this work, we focus on the former, that is, dynamic disorder. We will show here that, despite the fact that the fluctuations are small compared to the absolute energies of J and E_P, they have a large effect on the charge transport process. In particular, we note that the localization of the charge carrier in the presence of dynamical disorder is less influenced by the electron-phonon coupling as compared to the polaron in the ideal system. Instead, to a large extent, the charge carriers are localized as a result of the effect disorder has on the localization of the wave functions. This localization is, however, not restricted to single molecular units. The localization also varies in time as a result of intermolecular vibrations, which cause variation in the intermolecular transfer integrals.[12]

In this work, we use a method capable of covering the intermediate range of intermolecular interactions.[11] We introduce a time-varying J, thus getting a model consistent with behavior of the system at finite temperatures. For comparison, we also perform simulations with similar time variations in the on-site, molecular potential.

II. CALCULATIONAL METHODS

In the derivation of the Hamiltonian, π- and σ-electron separability is invoked, and only the π electrons associated with carbon $2p_z$ orbitals are treated quantum mechanically.

$$t_{\mathrm{nn'}}(t) = \begin{cases} t_0 - \alpha[r_{\mathrm{nn'}}(t) - r_0] & \text{if n and n' belong to the same molecule,} \\ [k_0 + k_{\mathrm{nn'}}(t)]S_{\mathrm{nn'}}^{(0)} & \text{if n and n' belong to different adjacent molecules,} \end{cases} \quad (2)$$

where t_0 is the hopping integral at the mean nearest-neighbor atomic distance r_0, α is the electron-lattice displacement coupling constant, and $r_{\mathrm{nn'}}$ is the actual nearest-neighbor atomic distance. $S_{\mathrm{nn'}}^{(0)}$ are the overlap integrals between $2p_z$ Slater-type atomic orbitals on site n and n' on adjacent molecules of the ordered system.[11] The time step in the time evolution is 1 fs. The mean value and the fluctuations in time of the intermolecular interactions are imposed on the system via the quantities k_0 and $k_{\mathrm{nn'}}(t)$, respectively. These quantities scale the overlap integral between sites n and n' on adjacent molecules. The details on how this scaling is performed are described below. The different treatment of the intra- and intermolecular hopping integrals in terms of the electron-phonon coupling is motivated by the fact that the π-π intermolecular bond order is much weaker than the π-π contribution to the bond order associated with an intramolecular covalent bond. A change in the density matrix caused by, for example, the presence of an additional charge, has a strong effect on the force acting on a particular covalent bond, which motivates α in Eq. (2), but has hardly any effect on the intermolecular overlap and the force acting between two molecules. Thus, the description of the electron-phonon coupling is in line with the Holstein model rather than a Peierls-type of model such as the Su-Schrieffer-Heeger (SSH) model.[13,14] On the contrary, the fluctuations caused by the thermal motion of the molecules, here treated in the quantity $k_{\mathrm{nn'}}(t)$, are crucial for the description of the intermolecular hopping integrals.

We expand the σ bonding energy to second order around the undimerized state. Supplemented with the constraint of fixed total bond length in the system,[2] we denote this contribution H_{lattice},

$$H_{\mathrm{lattice}} = \frac{K_1}{2}\sum_{\mathrm{nn'}}(r_{\mathrm{nn'}} - r_0)^2 + \frac{K_2}{2}\sum_{\nu}(\phi_\nu - \phi_0)^2 + \frac{K_3}{2}\sum_{\nu}(\theta_\nu - \theta_0)^2. \quad (3)$$

Summations are over all unique intramolecular distances ($r_{\mathrm{nn'}}$), angles (ϕ_ν), and dihedral angles (θ_ν). The notations θ_ν, ϕ_ν are simply a counting of the angles. Spring constants K_i were determined empirically by fitting to ground-state geometries obtained from *ab initio* calculations.[6]

This contribution is denoted H_π,

$$H_\pi = \sum_{\mathrm{n}} \varepsilon_{\mathrm{n}}(t)\hat{c}_{\mathrm{n}}^\dagger \hat{c}_{\mathrm{n}} + \sum_{\mathrm{nn'}} t_{\mathrm{nn'}}(t)(\hat{c}_{\mathrm{n}}^\dagger \hat{c}_{\mathrm{n'}} + \hat{c}_{\mathrm{n'}}^\dagger \hat{c}_{\mathrm{n}}), \quad (1)$$

with the hopping integrals,

Finally, we allow for the contribution of an external electric field $\mathbf{E}(t)$ to the Hamiltonian in the form

$$H_E(t) = -|e|\sum_{\mathrm{n}} \mathbf{r}_{\mathrm{n}}\mathbf{E}(t)(\hat{c}_{\mathrm{n}}^\dagger \hat{c}_{\mathrm{n}} - 1), \quad (4)$$

where e is the value of the electron charge.

Thus, the total Hamiltonian in our model consists of three parts,

$$\hat{H} = \hat{H}_\pi + \hat{H}_{\mathrm{lattice}} + \hat{H}_E. \quad (5)$$

A quantum-mechanical description of the charge-carrier dynamics is readily derived from the simultaneous numerical solution to the time-dependent Schrödinger equation,[2]

$$i\hbar|\dot{\Psi}(t)\rangle = \hat{H}_\pi|\Psi(t)\rangle, \quad (6)$$

and the lattice equation of motion,

$$M\ddot{\mathbf{r}}_{\mathrm{n}} = -\nabla_{\mathbf{r}_{\mathrm{n}}}\langle\Psi(t)|\hat{H}|\Psi(t)\rangle - \gamma\dot{\mathbf{r}}_{\mathrm{n}}. \quad (7)$$

The lattice equation of motion has, in this case, a viscous damping term introduced to simulate dissipation of energy, gained from the electric field, to the surrounding medium. All parameters involved in the equations above are summarized in Table I.

The intermolecular transfer, J, is uniquely defined by the atomistic hopping integrals [see Eq. (2)]. The relation is, however, not explicit and the value of J is defined here as

TABLE I. Hamiltonian parameter set.

Parameter		Dimension
Reference hopping integral:	$t_0 = 2.66$	(eV)
Reference bond length:	$r_0 = 1.412$	(Å)
Reference bond angle:	$\phi_0 = 2\pi/3$	(rad)
Reference torsion angle:	$\theta_0 = 0$	(rad)
Electron-phonon coupling constant:	$\alpha = 6.8$	(eV/Å)
Harmonic distance spring constant:	$K_1 = 72.0$	(eV/Å^2)
Harmonic bond-angle spring constant:	$K_2 = 70.0$	(eV/rad^2)
Harmonic torsion-angle spring constant:	$K_3 = 200.0$	(eV/rad^2)
Damping constant:	$\gamma = 1.0 \times 10^5$	(eV as/Å^2)
Mass of a CH group:	$M = 1349312601.0$	[eV(as)^2/Å^2]

half the energy splitting between the two lowest unoccupied orbitals obtained from a time-independent solution of the Schrödinger equation for a pentacene dimer, the so called dimer-splitting approach.[15] The use of the lowest unoccupied orbitals is related to the fact that we study an electron added to the system. In this work, the value of k_0 is set in such a way that the intermolecular transfer integral for the ideal system is $J = 50$ meV.[10] The polaron binding energy is, given the parameters presented in Table I, $E_P = 97$ meV. Furthermore, with these parameters, we obtain a polaron extended over three to four pentacene molecules in the case of no disorder. As shown below, this situation will change when dynamical disorder is included.

The equation of motion for the atomic displacements may now be derived by differentiating the total energy of the system with respect to the atomic coordinates $\mathbf{r}_n$, unraveling the interdependence with Eq. (6) through the density-matrix elements $\rho_{nn'}(t)$. If we then make the mean-field ansatz[16] $\rho_{nn'}(t) = \sum_p \psi_{np}(t) f_p \psi^*_{n'p}(t)$, where p is the molecular-orbital (MO) index, $\psi_{np}(t)$ is the time-dependent MO, and $f_p \in [0,1,2]$ is the time-independent occupation number of the pth MO, $\{\psi_{np}(t)\}$ will be solutions to the time-dependent Schrödinger equation,

$$i\hbar \dot{\psi}_{np}(t) = \sum_{n'} H_{\pi(nn')}(t) \psi_{n'p}(t). \tag{8}$$

As stated in the Introduction, the main purpose of this work is to study how variations in time of the intermolecular transfer integrals (J) affect the electron transport processes. The fluctuations in J can be obtained in different ways.

The most direct way is to use the time-dependent geometries obtained from a molecular-dynamics simulation,[12,17] and from these geometries calculate the time evolution of J.[18,19] The calculation of J can be done using, for example, the dimer splitting method[15] or other methods that include also the polarization effect of surrounding molecules.[20–22]

Another simpler but yet realistic approach, which we have adopted, is to synthesize the time dependence of J by generating random white noise and filtering this noise in accordance with the relevant frequencies of the molecular motions. We do this by including the time-dependent noise quantity, $k_{nn'}(t)$, in Eq. (2). The time average of $k_{nn'}(t)$ is zero and the fluctuation strength is determined by the standard deviation of J. This methods allows an almost perfect fit to the time dependence of J as obtained from molecular-dynamics simulations,[12] but it also allows for studies of how filtering at different frequencies affects transport. We also have the possibility to introduce spatial correlations in J to study how the effect of spatial changes in J affects transport. Thus, besides the fact that the synthetic method is far less time-consuming, it is also more flexible and can provide information that is useful for a more complete understanding of the effects that limit charge mobility.

In addition to disorder in the (of-diagonal) intermolecular transfer integrals, we also perform simulations including on-site disorder, that is, disorder in the quantity ε_n in Eq. (1). The same basic ideas as for the studies of the intermolecular disorder are used in these studies, namely, we only include dynamical disorder in an otherwise perfect crystalline sample.
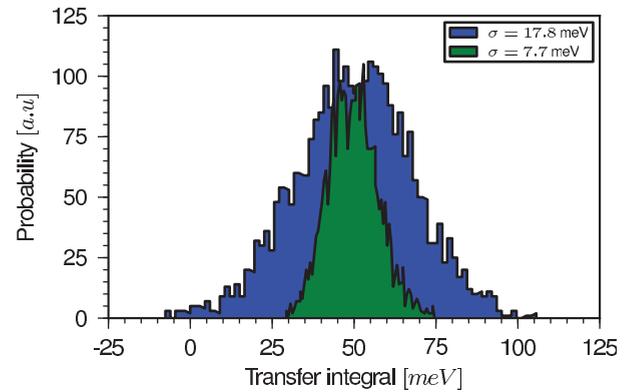

FIG. 1. (Color online) Distribution of the transfer integrals in solid pentacene at different standard deviations (σ).

It should be noted that one part of the on-site (intramolecular) fluctuations is already included in the model via the intramolecular vibrations obtained from the solution of Eq. (7). These vibrations occur, however, at a time scale much shorter than the time the charge carrier resides on a molecule, and they have a very small effect on the charge transport. Therefore, the origin of the relevant dynamical disorder, also in the case of the on-site energies, is mostly intermolecular and is due to the polarization effect from the molecules surrounding a particular molecule.[23]

The distribution of J for two different standard deviations (σ) is shown in Fig. 1. The two values ($\sigma = 7.7$ and 17.8 meV) are chosen to fit the standard deviations based on molecular-dynamics simulations for the same type of system at 100 and 200 K, respectively.[12] Similarly, the time dependence for a particular time period shown in Fig. 2 is a result of the filtering of a white noise signal to mimic the time dependence of the intermolecular transfer integral.[12]

The simulations including dynamical disorder in on-site energies are performed for exactly the same distributions and time dependence as shown in Figs. 1 and 2, respectively. The studies of the on-site disorder is only qualitative and shown below simply for comparison with the same disorder strength in J. We do not attempt to relate the amount of disorder to temperature, since this requires detailed studies of the polarization effects. However, as stated above, the
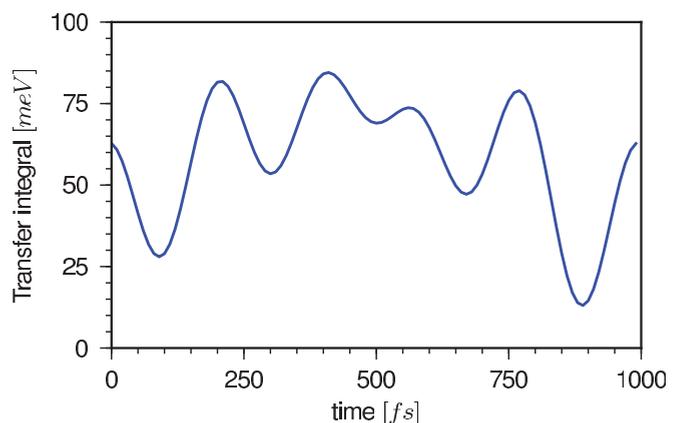

FIG. 2. (Color online) Time modulation of the transfer integrals for $\sigma = 17.8$ meV.

fluctuations in both the on-site energies and in J are both related to intermolecular interactions. This motivates, at least qualitatively, the present treatment of similar distributions in the intermolecular hopping integrals and the on-site energies. It should be stressed, however, that the main focus of this work is on the effect of the dynamical disorder in the intermolecular hopping integrals and that we hope to return in the near future to a similar quantitative treatment of the on-site energies.

III. RESULTS

The simulations carried out on chains of pentacene molecules provide us with detailed information concerning both the electronic and the geometrical structure of the system during charge transport. In the simulation data presented here, one electron was added to a chain of 20 pentacene molecules. The direction of the chain corresponds to the C-direction in Ref. 12. Fixed end boundary conditions were used, that is, a polaron approaching the end of the system bounces and changes its direction of motion.

We adopt a procedure used previously in which an initial potential is used to localize the electron to one end of the system and then switch off this potential and instead introduce the electrostatic potential due to the electric field.[11] We have chosen to collect data from the solutions of Eqs. (6) and (7) every fs during a total simulation time of up to 1 ps. In Fig. 3 is shown the time evolution of the net charge density per pentacene molecule.

The geometric structure is not shown here but follows closely the charge density, that is, the individual carbon atoms in the pentacene molecules distort from their neutral ground-state positions as a response to changes in the net charge density. The three panels show the results for three different distributions of the intermolecular transfer integral, J; the left panel corresponds to the ideal case of constant and uniform values of J ($J = 50$ meV), the middle and right panels display results with disorder in J as described in Fig. 1 with standard deviations of 7.7 and 17.8 meV, respectively. In comparison with earlier published distributions of the transfer integral as a function of temperature,[12] these standard deviations correspond to temperatures around 100 and 200 K, respectively. In all three panels, the electric-field strength is

5×10^4 V/cm. It should be noted, however, that the displayed behavior holds for field strengths in a range around this value.

It is clear from the ideal case that the extra electron inserted in the system is localized and, due to the electron-phonon interaction, forms a polaron that moves through the system under the influence of the external electric field. The polaron velocity is high, and after some 250 fs it hits the end of the pentacene chain, where it bounces. After a few cycles of interplay between the effects of the electric field and the chain ends, the polaron comes to rest at the end of the chain. During the drift process, the polaron extends over three to four pentacene molecules and moves with a velocity of 40×10^5/cm/s. The mobility in this system is thus ~ 80 cm^2/V s, which is considerably larger than what has been measured in any molecular-based systems. However, circumstances under which this simulation is performed are also unrealistic in the sense that there are no fluctuations at all in the transfer integral, and no extrinsic source of disorder is present.

The simulations become more interesting when we turn to the middle panel, which shows the polaron under the influence of weak dynamic disorder ($\sigma = 7.7$ meV corresponding to a temperature $T = 100$ K). As a result of the disorder, the polaron motion is more irregular, and during some instances it is less pronounced. The transport process is, however, still dominated by the same type of adiabatic drift motion as in the ideal case, even though, initially, it takes some time for the polaron to gain energy from the electric field and to overcome the trapping potential due to disorder.

The situation changes completely when we turn to the case with stronger disorder (right panel). The transport is first of all considerably slower, it takes approximately 1 ps to cross the system of 20 pentacene molecules. For the present field strength, the mobility is ~ 20 cm^2/V s. Even though this value is close to what has been observed experimentally, it should be kept in mind that we do not include the additional static disorder due to grain boundaries, etc. The effect of such disorder would be to reduce the mobility further but also to introduce temperature-activated processes.[24,25] Thus, there are many issues concerning the mobilities, and these numbers should be considered more quantitative than qualitative.
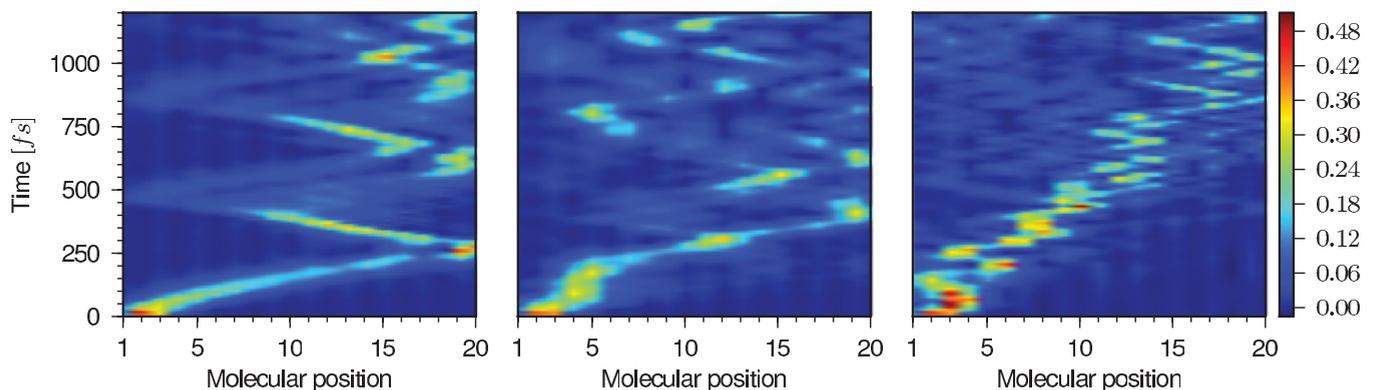

FIG. 3. (Color online) Excess charge density as a function of time in a linear system of 20 pentacene molecules, with a transfer integral standard deviation of 0 meV (left panel), 7.7 meV (middle panel), and 17.8 meV (right panel).
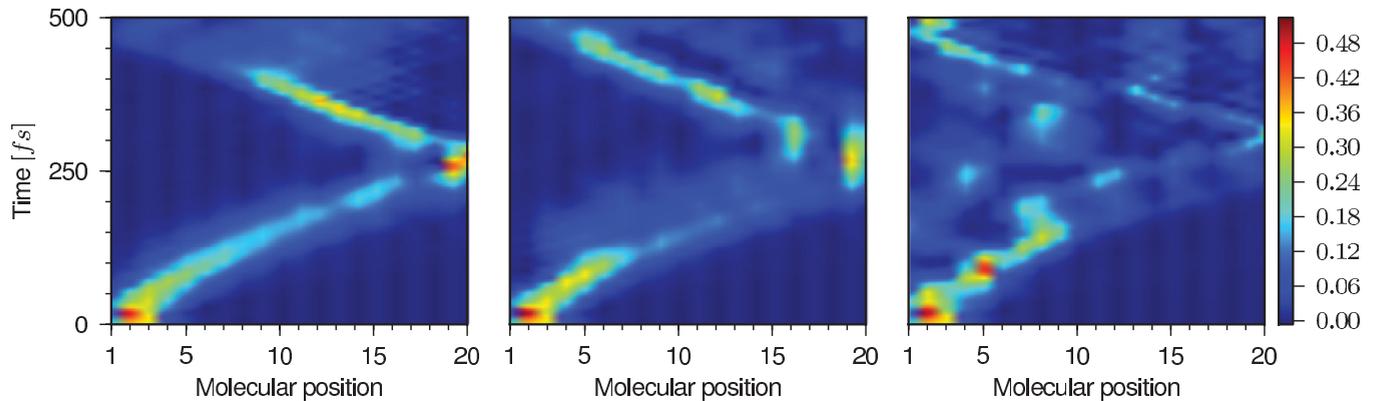
FIG. 4. (Color online) Excess charge density as a function of time in a linear system of 20 pentacene molecules, with an on-site potential standard deviation of 0 meV (left panel), 7.7 meV (middle panel), and 17.8 meV (right panel).

The transport pattern shown in the right panel in Fig. 3 combines short moments of drift motion similar to the adiabatic drift motion displayed in the two other panels with hopping events. The latter are sudden events and also include motion in the direction against the electric field separated in time with periods during which the polaron is *trapped* by the distortions in the transfer integral. The sudden change in position is accompanied by a change in the occupation of the time-independent solutions to the Schrödinger equation, which is the signature of the nonadiabatic hopping process. From a comparison between the transport pattern and the values of the transfer integral, we clearly observe (not shown here) a correlation between regions of (non)uniform values of J and typical (non)adiabatic polaron motion.

Despite the nonadiabatic character of the transport, it should be noted that the polaron very seldom localizes to a single molecule; it strongly prefers to delocalize over at least two neighboring molecules. Typically, such a pair of molecules has a larger transfer integral connecting them as compared to the transfer integral between the molecules surrounding the pair. Due to the changes in the transfer integral with time, this situation changes and the location of the polaron becomes unfavorable with respect to neighboring (pairs of) molecules, which stimulates the event of hopping. Due to the presence of the electric field in the direction along the molecular chain, such events occur in a majority of cases toward the right in Fig. 3.

We now turn to the corresponding results for fluctuations in the on-site energies. As described in Sec. II, these energies are generated in a similar way as the fluctuations in J. Simulation results are presented in Fig. 4 for standard deviations of 0, 7.7, and 17.8 meV, respectively. Again, we point out that these numbers are not given any relation to the temperature in this work. It is clear by comparing Figs. 3 and 4 that the transport effect of disorder on the transfer integrals and on the on-site energies is quite different. The overall picture is that the transition into a nonadiabatic behavior occurs for more narrow distributions in J as compared to the on-site energies. In the latter case, we have to go up to a Gaussian distribution with

a standard deviation around 50 meV to reach the nonadiabatic regime. As stated above, this work is not intended to relate the disorder in the on-site energies to temperature or other sources of fluctuations that might occur in the system. It is highly unlikely, however, that such fluctuations will be larger than those in the transfer integral[23,26] since, as pointed out above, both these types of fluctuations result from intermolecular interactions. Consequently, the major effect of dynamical disorder in molecular crystals comes from fluctuation in the transfer integral in the way described in Fig. 3.

IV. CONCLUSIONS

In summary, we have improved upon our earlier approach to study the transport of charge carriers in perfectly ordered molecular crystals by varying the intermolecular transfer integral in a way that simulates the effect of a large number of uncorrelated low-frequency intermolecular phonon modes. Using pentacene as a model system, we have seen how the introduction of disorder changes the transport process from an adiabatic polaron drift process to a combination of sequences of adiabatic drift and nonadiabatic hopping events. The hopping transport is associated with time intervals for which the polaron appears in a region where the variations in the intermolecular transfer integral are large between neighboring molecules. This leads to localization of the electronic wave functions occupied by the excess charge, in contrast to the usual electron-phonon coupling induced self-localization of the polaron. Finally, we conclude that the major effect of dynamical disorder in molecular crystals comes from fluctuation in the transfer integral, and that the fluctuations in the on-site energies have a minor influence on the transport-limiting processes.

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