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Polaron dynamics in a two-dimensional Holstein-Peierls system

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A semiclassical model for studying charge transport in a two-dimensional molecular lattice is presented and applied to both a well ordered system and a system with disorder. The model includes both intra- and inter-molecular electron-lattice interactions and the focus of the studies is to describe the dynamics of a charge carrier in the system. In particular, we study the dynamics of the system in which the polaron solution is dynamically stable. It is found that the parameter space for which the polaron is moving through the system is quite restricted and that the polaron is immobile for large electron-phonon coupling and weak intermolecular electron interactions and dynamically unstable and disassociates into a delocalized electronic state decoupled from the lattice for small electron-phonon coupling and strong intermolecular electron interactions. Disorder further limits the parameter space in which the polaron is mobile. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4803691>]

I. INTRODUCTION

Charge transport in molecular crystals has been a subject of study for many years and the research within this area is today more active than ever. The main reason for the interest is the use of organic compounds such as oligoacenes,¹⁻⁴ and rubrene⁵ in electronic devices. Charge transport, and charge carrier mobility in particular, is one of the fundamental physical processes that determine the device performance. The main challenge for today's research is to improve this performance and for that we need a better understanding of the underlying physical processes.

The physical description of charge transport in molecular crystals is rather complicated and there is no single transport process that applies to the different organic compounds used in electronic devices. The complications in the description of charge transport are related to the fact that both intra- and inter-molecular properties affect the transport mechanism and that the inter-molecular interactions are strongly affected by molecular vibrations, morphology, and disorder. A detailed knowledge of the disorder, in particular, is not available and also very difficult to control experimentally.

We can distinguish between three different intrinsic transport processes, the band model, the adiabatic (large) polaron model, and the non-adiabatic (small) polaron model.⁶ The basic theory of a moving polaron, i.e., an excess charge plus its self-induced polarization, was first presented in pioneering papers by Holstein^{7,8} in 1959. The Holstein model in its original formulation is restricted to a one-dimensional system and is focused on the intra-molecular electron-lattice interactions. In 1976, Emin and Holstein presented a study on an adiabatic electron motion in a deformable continuum.⁹ In their work they stated that both the characteristics of the electron-lattice interaction and also the dimensionality of the system are important for the polaron characteristics. The im-

portance of the dimensionality for the stability of polarons has been further studied by Kalosakas *et al.*¹⁰

The role of the dimensionality is complicated by the fact that molecular crystals both have intra- and inter-molecular degrees of freedom. The crystals are held together by (weak) Van der Waals forces, while the molecular building blocks contain covalently bonded atoms and the intra- and inter-molecular phonons have quite different characteristics. Nevertheless, we shall assume that the electron-lattice coupling involves both of these phonons. This means that the original Holstein model has to be extended to include also the inter-molecular (non-local) electron-lattice coupling, which usually is referred to as the Peierls coupling. This model was pioneered by Munn and Silbey¹¹ who concluded that the non-local coupling will enhance the hopping behaviour. The Holstein-Peierls model has later on been used by several groups.¹²⁻¹⁹ In particular in the pioneering work by Hannewald *et al.*,^{13,15} it is shown that the model is able to grasp several of the charge transport features exhibited by the molecular crystals.

A semi-classical treatment to study carrier dynamics is well suited for studies of large polaron dynamics^{17,20} in which the time-dependent polaron wavefunction moves along with the charge and the geometrical deformation. The limitation to large polaron transport restricts the validity of the studies to the case of well ordered structures in which the wavefunction has the possibility to move across the whole system without hindrance from localization effects induced by disorder. Nevertheless, such studies are of fundamental importance from the point of view of understanding the Holstein-Peierls model, which is the focus of the present work. Our studies are focussed on the polaron drift process in a two-dimensional system including an external electric field and how the drift process is affected by the parameters describing the various interactions in the system. We note from these studies that polaron transport is possible only in a rather limited range of such parameter values. Outside this range the polaron

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either becomes unstable and band-transport takes over or the polaron becomes a small polaron, which moves via a hopping process between molecular sites. We also discuss how the polaron dynamics is affected by disorder. It is well known that disorder induces electron localization and it has been confirmed by several groups that disorder reduces the spatial extension of the polaron, so the polaron is more localized and hence less mobile.^{21–23} This is also observed in our studies in which we have been able to quantify the relation between the disorder strength and the dynamical behaviour of the polaron.

II. METHODOLOGY

Since many of the molecular crystals are highly anisotropic with relatively strong in-plane electronic overlap but a weaker overlap perpendicular to these planes, we restrict our system to two dimensions (see Fig. 1).²⁴ Each molecule is represented by a site with index i (x-direction) and j (y-direction) with a potential energy, $\varepsilon_{i,j}$, which could be subject to disorder, and a single internal phonon mode with displacement $u_{i,j}$ which is coupled to the electronic system with the coupling strength A . In addition to the intra-molecular interactions we also introduce the molecular electronic transfer integrals $J_{i,j;i',j'}^{x,y}$ between two neighbouring sites (i,j) and (i',j'), the inter-molecular displacements $v_{i,j}^{x,y}$ (see Fig. 1) and the (Peierls) intermolecular electron-phonon coupling α .

The electronic part of the combined Holstein-Peierls model in two dimension is described via the Hamiltonian

$$H = H_{intra} + H_{inter}, \quad (1)$$

with

$$H_{intra} = \sum_{i,j} (\varepsilon_{i,j} + Au_{i,j}) \hat{c}_{i,j}^\dagger \hat{c}_{i,j} \quad (2)$$

and

$$H_{inter} = \sum_{i,j} (J_{i+1,j;i,j}^x \hat{c}_{i+1,j}^\dagger \hat{c}_{i,j} + H.C.) + \sum_{i,j} (J_{i,j+1;i,j}^y \hat{c}_{i,j+1}^\dagger \hat{c}_{i,j} + H.C.). \quad (3)$$

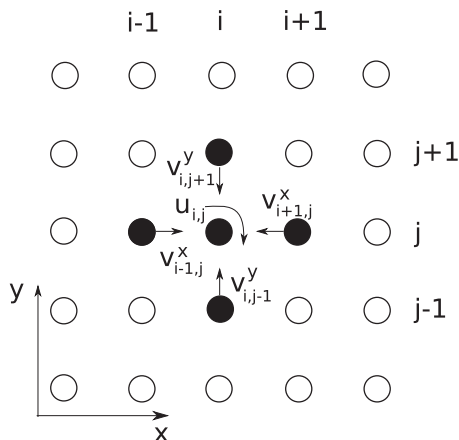


FIG. 1. Schematic representation of the two-dimensional Holstein-Peierls system.

In the semi-classical treatment adopted here we describe the phonon system by two separate harmonic oscillators, one for the intra-molecular modes and one for the inter-molecular modes

$$E_{intra} = \frac{K_1}{2} \sum_{i,j} (u_{i,j})^2 + \frac{m}{2} \sum_{i,j} (\dot{u}_{i,j})^2, \quad (4)$$

$$E_{inter} = \frac{K_2}{2} \sum_{i,j} [(v_{i+1,j}^x - v_{i,j}^x)^2 + (v_{i,j+1}^y - v_{i,j}^y)^2] + \frac{M}{2} \sum_{i,j} [(\dot{v}_{i,j}^x)^2 + (\dot{v}_{i,j}^y)^2], \quad (5)$$

where the force constants K_1 and K_2 and masses m and M refer to the intra- and inter-molecular oscillators, respectively.

The electric field, which acts as the driving force for charge transport, is in this work assumed to be static and directed along the x axis. This constant electric field is denoted by E_{0x} . With the time dependent vector potential described as $\Lambda_x(t) = -cE_{0x}t$,²⁵ the inter-molecular transfer integrals are defined as

$$J_{i+1,j;i,j}^x = J_0^x - \alpha (v_{i+1,j}^x - v_{i,j}^x) e^{i\gamma \Lambda_x(t)} \quad (6)$$

in which $\gamma \equiv ea/\hbar c$ with a as the lattice constant

$$J_{i,j+1;i,j}^y = J_0^y - \alpha (v_{i,j+1}^y - v_{i,j}^y). \quad (7)$$

Many molecular crystals are anisotropic also within the (xy-) plane. Therefore, it would have been natural to allow for this anisotropy in our studies. We find, however, that the overall polaron transport process is not dramatically affected for such relatively small anisotropies. We therefore restrict the presentation in this work to the case of isotropic values of the inter-molecular transfer integrals, i.e., $J_0^x = J_0^y$. In the same way, we could also extend the studies to simulations with the electric field pointing in a general direction in the xy-plane. This extension is also left out from this study in order to put the focus on the more fundamental aspects of polaron dynamics.

The on-site energies $\varepsilon_{i,j}$ (see Eq. (2)) correspond to the eigen-energies of the molecular orbitals involved in the charge transport process. In the case of an additional electron added to the system this will be the manifold of lowest unoccupied molecular orbitals (LUMO) of each molecule. In a perfectly ordered system these energies are identical on all sites and $\varepsilon_{i,j}$ could be set to zero. With disorder included, the on-site energies will of course vary between sites in a way that reflects the degree of disorder in the system (see below).

The dynamic of the electronic system is described by the time-dependent Schrödinger equation

$$i\hbar \dot{\psi}_{i,j}(t) = \sum_{i',j'} H_{i,j;i',j'}(t) \psi_{i',j'}(t) \quad (8)$$

in which $H_{i,j;i',j'}$ is an element in the Hamiltonian matrix and $\psi_{i,j}(t)$ is the time-dependent wavefunction of the two-dimensional system at site (i, j). The wavefunction is constructed as a linear combination of the molecular LUMOs. As initial condition ($t = 0$), it corresponds to the eigenvector of the lowest energy eigenvalue of $H(t = 0)$. Note that in our simulations, the electron dynamics is not restricted to the

time-evolution of this single eigenstate of the Hamiltonian. The methodology allows for the time-dependent wavefunction to be expressed as a linear combination of several eigenstates, i.e., a wavepacket.

The lattice dynamics is governed by the Newton's equations of motion

$$m\ddot{u}_{i,j}(t) = -K_1 u_{i,j}(t) - A\rho_{i,j;i,j}(t), \quad (9)$$

$$\begin{aligned} M\ddot{v}_{i,j}^x(t) = & -K_2(2v_{i,j}^x(t) - v_{i+1,j}^x(t) - v_{i-1,j}^x(t)) \\ & - \frac{\alpha}{M} e^{-i\gamma\Lambda_x(t)} (\rho_{i,j;i-1,j}(t) - \rho_{i+1,j;i,j}(t)) \\ & - \frac{\alpha}{M} e^{i\gamma\Lambda_x(t)} (\rho_{i-1,j;i,j}(t) - \rho_{i,j;i+1,j}(t)), \quad (10) \end{aligned}$$

$$\begin{aligned} M\ddot{v}_{i,j}^y(t) = & -K_2(2v_{i,j}^y(t) - v_{i,j+1}^y(t) - v_{i,j-1}^y(t)) \\ & - \frac{\alpha}{M} (\rho_{i,j;i,j-1}(t) - \rho_{i,j+1;i,j}(t) + \rho_{i,j-1;i,j}(t) \\ & - \rho_{i,j;i,j+1}(t)). \quad (11) \end{aligned}$$

The electron-lattice coupling shows up in the terms including the electron density matrix, $\rho_{i,j;i',j'}(t)$ given by

$$\rho_{i,j;i',j'}(t) = \psi_{i,j}(t)\psi_{i',j'}(t)^*. \quad (12)$$

The Newton's equations of motion are solved simultaneously with time dependent Schrödinger equation using the ode45 solver contained in Matlab. The underlying algorithm is based on an explicit Runge-Kutta (4,5) formula with variable step size.

The dynamical simulations presented here deal with a system containing a single charge carrier occupying the lowest eigenstate of the conduction band. With the set of parameters presented in Table I the ground state of this system contains a localized polaron. The shape of the polaron is shortly described in Sec. III A below. Since we are using periodic boundary conditions, the location of the polaron is arbitrary. The initial intra- and inter-molecular velocities can either be set to zero or we can use the values from, for instance, a previous calculation. If a simulation is started with zero velocities there is a short waiting-time before the polaron gets mobile but once the polaron is moving there is no difference in the

polaron dynamics for the two different initial conditions. As concerns the electric field, we put this to its constant value already from the start, in most calculation the field strengths is set to $E_{0x} = 2.0 \text{ meV/\AA}$.

The simulations on the two-dimensional systems are carried out on systems consisting of 20×20 sites (molecules). We have also performed simulations on larger systems to verify that there is no size dependence in the results presented here. Typically, we run the simulations over a time period 1–2 ps during which the polaron moves a distance of 10–15 molecular units which is normally enough to get a good picture of the polaron mobility in a ordered system. In the case of disordered system (see below), we have instead studied a number of different generations (usually 10) of disordered site energies to get a good picture of the behaviour of the polaron in different energy landscapes.

We use a standard set of parameters that is not specific for any particular molecule.¹⁸ Of course, our model system is very much simplified compared to any real molecular crystal, for instance, we include only one intra-molecular and one inter-molecular phonon mode. Therefore, we cannot expect a direct qualitative agreement with any real system but we have the advantage to be able to vary these parameters and study, in particular, the dynamical behaviour of the polaron within a range of parameter values. In such a way we are able to discuss different types of behaviour and their relevance for the type of systems we are interested in. The way we perform these studies is to keep all parameters but one to the values shown in Table I and when these results are discussed below, we explicitly state the value(s) of the parameter which is changed.

It is common in studies of disordered systems to account for the long-range forces that result from, for instance, charge-permanent dipole interactions with a number of different neighbours.^{26–28} The disorder that exist in such systems is not completely random but contains spatial correlations. To model spatial correlations we have used a simple averaging procedure, the energy of site (i,j), $\varepsilon_{i,j}$ (see Eq. (2)) is obtained by averaging a set of auxiliary random variables $\kappa_{i',j'}$ over a chosen number of neighbouring sites

$$\varepsilon_{i,j} = N^{-1} \sum_{i',j'} \kappa_{i',j'}. \quad (13)$$

The random variables $\kappa_{i',j'}$ are here taken from a rectangular distribution of width W . We have included four nearest neighbouring sites (see Fig. 1) in the summation. Accordingly, site energies have a considerably smoother variation in the energies between neighbouring sites than that given by a set of random numbers.

III. RESULTS

The results presented in this work are focussed on the dynamics of the Holstein-Peierls polaron in a two-dimensional system resembling a molecular crystal. As a starting point for dynamics calculations, we first present results for the optimized geometrical and electronic structure of the system without the electric field applied, followed by the results obtained for the dynamics of the system for different values

TABLE I. Holstein-Peierls parameters.

Parameter	Unit
Intermolecular transfer integral $J_0^x = 50$	(meV)
Intermolecular transfer integral $J_0^y = 50$	(meV)
Intramolecular el-ph coupling $A = 1.5$	(eV/Å)
Intermolecular el-ph coupling $\alpha = 0.5$	(eV/Å)
Intramolecular force constant $K_1 = 10$	(eV/Å ²)
Intermolecular force constant $K_2 = 1.5$	(eV/Å ²)
Intramolecular mass $m = 1.3 \times 10^9$	(eV(as/Å) ²)
Molecular mass $M = 2.6 \times 10^{10}$	(eV(as/Å) ²)
Intramolecular vibrational frequency $\omega_{intra} = \sqrt{\frac{K_1}{m}}$	(1/as)
Intermolecular vibrational frequency $\omega_{inter} = \sqrt{\frac{K_2}{M}}$	(1/as)
Lattice constant $a = 3.5$	(Å)

of the parameters presented in Table I and at different field strengths. Section III C contains the results for the disordered system.

A. Static polaron

We start by considering a system consisting of 20×20 sites (molecules). The geometry of the system is optimized using the resilient backpropagation, RPROP, algorithm.²⁹ For the standard set of parameters presented in Table I, the charge distribution corresponding to the optimized structure is shown in Fig. 2. The polaron is localized to five molecules with its main contribution ($\sim 48\%$) residing on a single central molecule. The polaron energy here defined as the gain in energy with respect to a delocalized band state, is in this case 35 meV. The geometrical distortion associated with the polaron shows a negative value of the internal coordinate $u_{i,j}$, i.e., a compression of the molecule, as well as a decrease in the intermolecular distances between the molecules associated with the polaron as a result of the positive values of α and A and the fact that both the charge density and the intermolecular bond-order are positive. More details concerning the behaviour of $u_{i,j}$, $v_{i,j}^x$, and $v_{i,j}^y$ are presented in Sec. III B below.

As discussed in our previous work,¹⁸ the polaron energy is increased by increasing the electron-phonon couplings α and A . For $\alpha = 0.6$ eV/Å (with $A = 1.5$ eV/Å), the polaron energy is 64 meV and for $\alpha = 0.7$ eV/Å, it increases to 100 meV, while for A equal to 1.7 eV/Å and 1.9 eV/Å (with $\alpha = 0.5$ eV/Å) the polaron energies are 44 meV and 58 meV, respectively. These polaron energies are well in agreement with those reported in the literature for pentacene and rubrene, which are 55 meV³⁰ and 78 meV,³¹ respectively. Even though our definition of the polaron energy is not in exact agreement with the quantity that is experimentally accessible, this justifies that we are using parameters that are relevant for the type of molecular crystals that are of interest for this work. We also notice that the polaron becomes more localized with increasing A but more delocalized with increasing inter-molecular

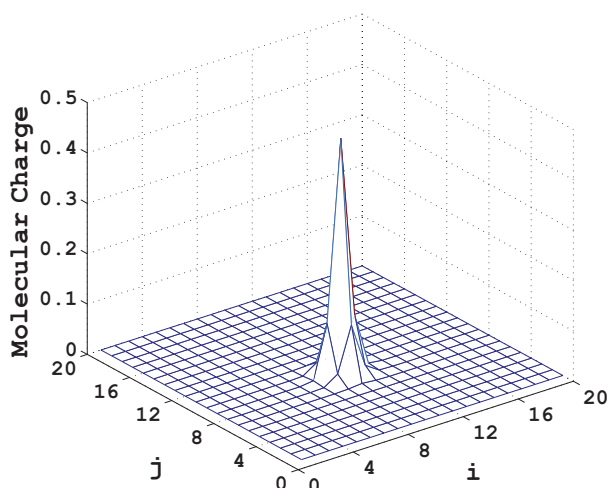


FIG. 2. A typical ground state molecular charge distribution of a Holstein-Peierls polaron in a two-dimensional 20×20 system. The parameter values used are those given in Table I.

coupling α . This will have an effect of the mobility of the polaron as will be discussed in Sec. III B below.

B. Polaron dynamics

In Fig. 3(a) is shown the time dependence of the molecular charge distribution of the 20×20 molecular lattice. The standard parameter set from Table I is used. Applying the external electric field from the start and with zero initial velocities the charge starts moving after some time (approximately 250 fs, this initial period of time is not shown in Fig. 3) and moves with a constant velocity of about 25 Å/ps.

In addition to the charge distribution, Fig. 3 also shows the intra-molecular distortions, $u_{i,j}$ (panel (b)), the intermolecular bond length distortions in the x direction, $v_{i+1,j}^x - v_{i,j}^x$ (panel (c)), and in the y direction, $v_{i,j+1}^y - v_{i,j}^y$ (panel (d)). Since we have adopted periodic boundary conditions, the polaron performs a “circular” motion, i.e., when it reaches the end of the system in the x -direction ($i = 20$) it appears on the other side of the system ($i = 1$). The moving polaron is clearly a Holstein-Peierls polaron since both the intra- and the inter-molecular motions are following the moving localized charge through the system. The intra-molecular distortions (panel (b)) correspond to a local contractions of the molecule. A part of the potential energy of the charge in the external electric field is transferred to intra-molecular vibrations, as can be seen from the oscillatory behaviour of $u_{i,j}$ after the polaron has moved away from that site. This is

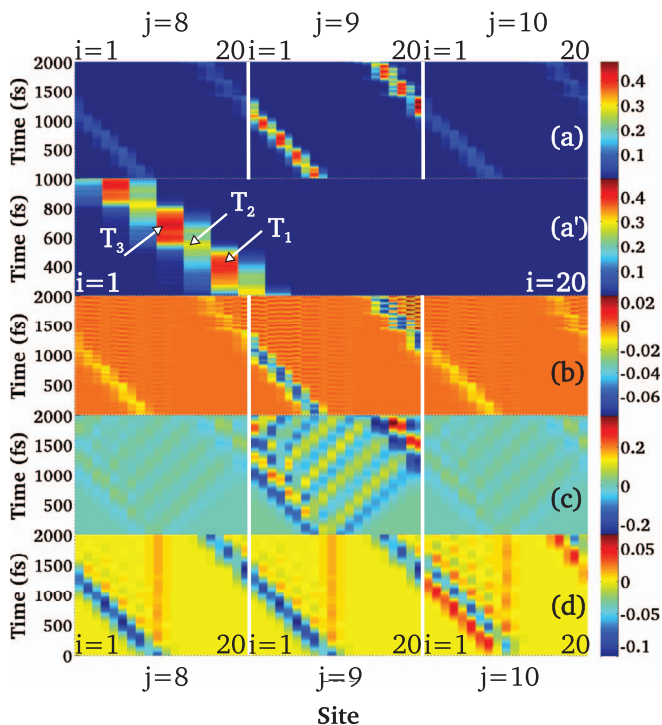


FIG. 3. Polaron dynamics in a two-dimensional system: (a) molecular charge distribution, (a') enlarged part of (a), (b) intra-molecular displacement (in Å), $u_{i,j}$, (c) inter-molecular bond length (in Å) in the x direction, $v_{i+1,j}^x - v_{i,j}^x$, and (d) inter-molecular bond length (in Å) in the y direction, $v_{i,j+1}^y - v_{i,j}^y$. The parameter values used are those given in Table I. The electric field is given by $E_{0x} = 2.0$ mV/Å.

a strictly intra-molecular motion which remains localized to a particular molecule. The frequency of this oscillation is essentially identical to the frequency of a local oscillator $\sqrt{K_1/m}$.

In contrast to the intra-molecular distortions, the inter-molecular bond-length deviations form travelling waves in the system. The deviations directly associated with the polaron correspond to a local contraction (blue color in Figs. 3(c) and 3(d)) of the lattice. This contraction is concentrated to the four inter-molecular bonds around the central molecule of the polaron as shown in Fig. 1. The recoil travelling wave of x-direction displacements ($v_{i+1,j}^x - v_{i,j}^x$, see Fig. 3(c)) that emerge from the polaron and that move in the backward direction with respect to the polaron shows an oscillatory behaviour involving both local expansions and contraction of the lattice. Note that there is no such recoil in the y-direction displacements ($v_{i,j+1}^y - v_{i,j}^y$, see Fig. 3(d)) in the backward direction since there is no external driving force acting in the y-direction. We also note that the oscillations of the individual molecules have the frequency of a classical spring-mass-spring oscillator since there is no contribution from the electrons to the equation of motion in this case. This issue is discussed in more detail below.

It is worthwhile to stress that the motion depicted in Fig. 3 is a nonadiabatic process which involves a linear combination of eigenstates to the Hamiltonian in Eq. (1). This linear combination changes with time and is during some periods of time restricted to a single eigenstate and during other periods involving a large number of eigenstates. Without going into all details of the polaron motion, we would like to point to the most crucial step, namely, the transfer of charge from one molecule to the next. As can be seen in Fig. 3, the charge density at an instant of time goes from being centered on one molecule (T1 in Fig. 3(a)) to being shared equally between two molecules (T2) and then quickly transfers to be centered on a third molecule (T3). Thus, it regains its ground state structure on every second molecule only. The intermediate state of the polaron being shared equally between two molecules has an energy close to the ground state, an energy which is overcome by the force exerted by the electric field, which in this simulation is 2.0 mV/Å.

We have performed the same simulations as shown in Fig. 3 for a large number of different parameter values. There are essentially three different types of behaviour of the dynamical system here classified according to the ground state polaron energy of the polaron at rest. At low polaron energies, the moving polaron destabilizes after some time into a delocalized state which is essentially decoupled from the lattice. In the intermediate regime of polaron energies, the behaviour is that shown in Fig. 3 but with slight variations in the polaron velocity. For large polaron energies, the polaron is immobile in our model since the barriers for moving between molecules is too large to be overcome by the potential provided by the external electric field. To observe charge transport in this regime, we have to extend the present model to include also temperature effects, i.e., the absorption of energy from the phonon system. This work is in progress and will be presented in the near future.

For practical reasons we limit the presentation of the parameter dependence of the polaron dynamics in the follow-

ing way: we fix the values of K_1 and K_2 to those shown in Table I. Furthermore, we perform studies of the polaron dynamics by varying the remaining parameters (including the electric field strength) individually while keeping the other parameters fixed to the values shown in Table I. For varying strengths of the on-site electron-phonon coupling, A , we observe a moving polaron in the parameter range from 1.2 to 1.7 eV/Å, which corresponds to ground state polaron energies, E_p , in the range from 25 up to (and including) 44 meV. For values of A above 1.7 eV/Å, the polaron becomes immobile and below 1.2 eV/Å the polaron destabilizes into a band state as a result of the non-equilibrium situation caused by the external electric field. In the same way we observe polaronic motion for α in the narrow range from 0.5 eV/Å up to (and including) 0.6 eV/Å. It is interesting to note that the polaron energies within this range of parameters vary from 35 meV up to 64 meV, i.e., slightly larger than those found in the case of varying A . This is due to the fact that by increasing α the polaron width also increases (as opposed to the creating a more localized polaron by increasing A). A polaron which is extended over more sites exhibits in general a smaller barrier for motion in the system. Finally, for varying strengths of the transfer integral, $J_0^{x,y}$, the observed range for which the polaron is dynamically stable is 40–80 meV with the corresponding values of the polaron energies 78 meV (at $J_0^{x,y} = 40$ meV) and 44 meV (at $J_0^{x,y} = 80$ meV). Below $J_0^{x,y} = 40$ meV the polaron becomes immobile and above $J_0^{x,y} = 80$ meV the polaron is not dynamically stable.

Also the strength of the external electric field has an effect on the polaron behaviour. The higher the electric field gets, the larger is the driving force on the polaron and the more excess energy is gained by the system. This excess energy acts to destabilize the polaron into a band state. For the standard set of parameters (see Table I) the polaron remains dynamically stable up to a field strength of 3.8 mV/Å, at least during the simulation time shown in Fig. 3. For higher field strengths the polaron dissociates into a band state. We note that the energy difference over the extension of the polaron (approximately 7 Å) in this case is around 27 meV which becomes comparable to the polaron energy of 35 meV.

We can conclude that the parameter range for which the polaron is stable and at the same time mobile is rather limited. The polaron velocity within this regime varies in the range from 24 Å/ps up to 26 Å/ps, i.e., is essentially constant and to a large extent determined by the frequency of the intermolecular vibrations.²⁴ The bare sound velocity $c = a\sqrt{K_2/M}$ is, with the parameters from Table I, equal to 26.7 Å/ps, i.e., very close to the polaron velocity.³³ The sound waves are observed in Fig. 3, panel (c) and are generated each time the polaron makes a transition from one molecule to the next. It is interesting to note that for every second such transition the initiated wave corresponds to an expansion of the lattice (yellow color) and that the intermolecular polaron transitions between these generate a contraction of the lattice (blue color). The change of the intermolecular distance within the polaron is, as described above, always a contraction.

The fact that the polaron velocity is constant is consistent with earlier studies of polaron motion in one-dimensional conjugated polymer chain systems.⁶ In these studies, which

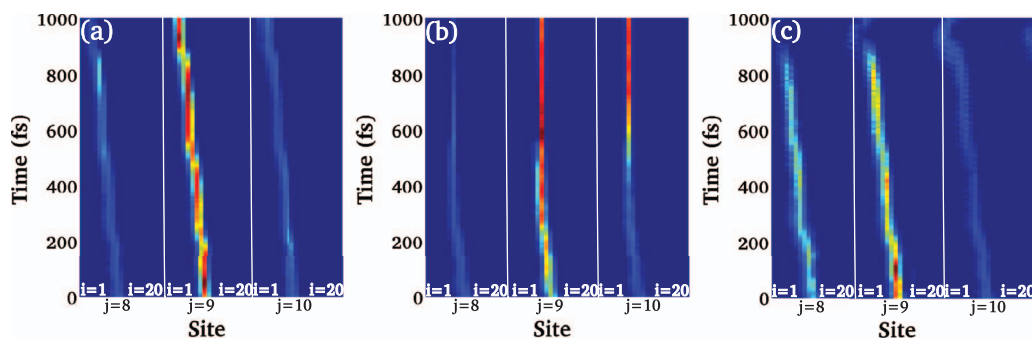


FIG. 4. Polaron dynamics in a disordered two-dimensional system: (a) moving polaron, (b) trapped polaron, and (c) disassociating polaron. The parameter values used are those given in Table I. The electric field is given by $E_{0x} = 2.0$ mV/Å.

are based on the Su-Schrieffer-Heeger (SSH) model³² there is only one degree of freedom in the phonon system. Here, we have introduced three degrees of freedom which can exchange energy with the electronic system. Despite this change, the basic feature that the polaron moves with a constant velocity in the presence of an external electric field is preserved. As noted above, in reality there will be more vibrational modes that couple to the electronic system. Even though this will change the speed of sound in the system, the effect is very small³³ and we do not expect that this will alter the conclusions presented above.

C. Disorder

Even though a very high degree of order can be achieved in molecular crystals disorder can never be completely avoided. As discussed above, there are different ways in which the disorder appears but we restrict the presentation here to the case of static on-site disorder. The disorder is not completely random but is generated in such a way that it contains a certain degree of correlation between neighbouring sites.

We have studied the polaron dynamics for different disorder strengths. In order to get an idea about how the disorder would affect the polaron transport properties in a system considerably larger than the 20×20 system used in the simulations we have generated 10 different distributions of the on-site energies. For each such distribution we characterize the behaviour of the polaronic motion with the aim to locate the critical disorder strength for which the polaron becomes immobile. In all calculations we use the same initial condition, namely, the one used in the simulation presented in Fig. 1. In this way, the polaron usually starts from a position which does not correspond to the ground state of the system and either moves more or less in the same way as shown in Fig. 3 or moves only a short distance to a position where it gets stuck in a local potential well. There is also a third possibility, that the polaron destabilizes due to a cooperative effect of the external electric field and the disorder potential, i.e., the charge carrier decouples from the lattice distortion. This is the corresponding to the band state in the completely ordered system. However, due to the limited size of the system it is difficult to make any predictions concerning the localization of the charge carrier wavefunction in this case.

Figure 4 shows the three types of behaviour discussed above. For a disorder strengths of $W = 100$ meV we observe that eight out of ten generated distributions result in an immobile polaron (Fig. 4(b)), whereas in the remaining two samples the polaron destabilizes (Fig. 4(c)). With a disorder strengths of $W = 75$ (50) meV we found five (one) samples that resulted in an immobile polaron, four (eight) samples in which the polaron was moving through the whole system (Fig. 4(a)) and one (one) sample in which the polaron destabilized. At $W = 25$ meV, however, there is no sign of polaron trapping or destabilization in any of the disorder distributions and the behaviour is typically that shown in Fig. 4(a), i.e., similar to the ideal ordered system presented in Fig. 3.

IV. SUMMARY AND CONCLUSIONS

It is clear from the results presented above that the values of parameters that describe the different types of interactions within a molecular crystal and that result in a stable mobile polaron fall into a rather limited region of the parameter space. Nevertheless, the parameters that result in such a mobile polaron agree well with the interaction strengths that we can expect in molecular crystals. It is therefore plausible that the charge transport in terms of large polaron motion occurs in molecular crystals. From the simulations we obtain detail information about the character of the moving polaron and how the dynamics of the electronic wavefunction couples to sound waves and local oscillations in the system. However, considering the rather narrow parameter range for which the polaron is dynamically stable, it is also highly likely that, depending on the type of molecular system, that there are molecular lattices (or parts of such systems) for which the band model applies and other systems which are best described by a small polaron model, i.e., systems in which the polaron can only move via a thermally activated hopping process. In particular, if there is disorder present in the system, the possibility to observe motion of the polarons is further reduced.

Clearly, further studies are needed to investigate the different possibilities for charge transport in organic crystals. The fact that the molecules contain several phonon modes that couple with different strength to the electronic system will certainly affect the quantitative behaviour of the system. Also, as mentioned above, temperature effects have to be included in order to get an understanding of the temperature

dependence of the polaron mobility. The present work should thus be regarded as a first step in obtaining a realistic dynamical model for charge transport in molecular crystals.

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