

Charge-Transport Regime of Crystalline Organic Semiconductors: Diffusion Limited by Thermal Off-Diagonal Electronic Disorder

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We propose that the electron transport in crystalline organic semiconductors at room temperature (RT) is neither polaronic nor a combination of thermally activated hopping and polaronic transport, as previously thought. Thermal molecular motions cause large fluctuations in the intermolecular transfer integrals that, in turn, localize the charge carrier. This effect destroys the translational symmetry of the electronic Hamiltonian and makes the band description inadequate for RT organic crystals. We used a one-dimensional semiclassical model to compute the (temperature dependent) charge carrier mobility in the presence of thermal fluctuations of the electronic Hamiltonian. This transport mechanism explains several contrasting experimental observations pointing sometimes to a delocalized "bandlike" transport and sometimes to the existence of strongly localized charge carriers.

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Notwithstanding the great technological interest toward organic materials for electronics [1] the charge-transport mechanism in crystalline organic semiconductors at room temperature is not well understood. Since the majority of the experimental observations [2–4] in the 100–300 K range indicate a decrease of the mobility with the increase of the temperature the transport is often described as *bandlike* [5–7], i.e., delocalized charge carrier are scattered by impurities or phonons and their mobility is ultimately determined by their effective mass and average time between collisions. The most studied crystalline semiconductors are based on large conjugated molecules like pentacene. For these, computational and spectroscopic studies in the gas phase indicate a modest nuclear reorganization energy ($\sim 800\text{ cm}^{-1}$) [8] similar or smaller than the average intermolecular transfer integral ($\sim < 1000\text{ cm}^{-1}$) [9], suggesting that charge localization, due to the formation of a small polaron with the charge localized on a single molecule, is unlikely. With such modest energy of polaron formation the theory predicts that charge carriers are delocalized over many unit cells (large polaron). The polaron bandwidth decreases with increasing temperature (T) leading to the well-known power law ($\mu \sim T^{-n}$) dependence of the mobility (μ) upon the temperature [10]. This picture, however, is inconsistent at temperatures higher than $\sim 150\text{ K}$ [7], where the analysis of the experimental data indicates a mean free path of the charge carriers of the same order of magnitude of the unit cell, a fact in clear contrast with a delocalized picture [11]. Moreover, there are spectroscopic evidences supporting the localization of the charge carrier within one or few molecules [12]. These contrasting evidences cannot be explained by an existing transport model and some peculiarity of organic crystals might be responsible for the observations. In this Letter we suggest that the softness of these materials is the cause of their anomalous charge-transport properties: room temperature molecular motions are sufficient to destroy

the translational symmetry of the electronic Hamiltonian. This observation can be incorporated in a one-dimensional model Hamiltonian that allows the computation of the charge carrier mobility. The resulting transport mechanism, as we will see, conciliates the contrasting evidences of experiments and computational studies.

Differently from an inorganic semiconductor, as silicon, the components of an organic solid are held together by weak interactions that make these materials much softer than inorganic solids. The transfer integrals among the HOMOs and LUMOs orbitals of the individual molecules are responsible of the (small) band dispersion of the highest occupied and lowest unoccupied band of the semiconductor determining the low-temperature hole and electron mobility. HOMOs and LUMOs in organic semiconductors of common use have complex shapes with several nodal planes, and, consequently, the transfer integrals between neighboring molecular orbitals is extremely sensitive to very small nuclear displacements. This sensitivity is exemplified by the great variability of the band structure of very similar polymorphs of pentacene [9,13] or by the significant crystallogromy of perylene derivatives [14]. It is therefore not surprising that the intermolecular transfer integral are very effectively modulated by thermal nuclear motions. Recent computational investigations quantified this modulation for various compounds, showing that *the fluctuation amplitude of the transfer integral is of the same order of magnitude of its average value* [15]. For example, the largest coupling between HOMOs of pentacene molecules in a crystal has an average value of 980 cm^{-1} and a fluctuation amplitude of 400 cm^{-1} at 300 K . The fluctuation of the transfer integral is due to low frequency modes with the largest contribution by modes around 40 cm^{-1} . In the presence of a transfer integral modulation of the same order of magnitude of the average transfer integral, the band description of the crystal breaks down, the k vector ceases to be a good quantum number and the charge

carriers can be localized by the (dynamic) disorder in the intermolecular coupling.

To investigate the effect of this thermal electronic disorder on the transport mechanism we built a model Hamiltonian which mimics the essential features derived by the computational studies on realistic systems. We considered a one-dimensional stack of planar conjugated molecules (see Fig. 1), with one molecular orbital per molecule (for example the HOMO in case of hole transport). Each molecule j , associated with the orbital $|j\rangle$, has mass m and can be displaced transversally by a length u_j from its equilibrium position to which it is held with a force constant K . The transfer integral τ between the consecutive orbitals $|j\rangle$ and $|j+1\rangle$ is modulated linearly by the term $\alpha(u_{j+1} - u_j)$ with α the electron-phonon coupling constant. We considered a lattice with $N = 600$ sites and periodic boundary conditions ($|N+1\rangle \equiv |1\rangle$). The semiclassical Hamiltonian for this system reads:

$$H = \sum_j [-\tau + \alpha(u_{j+1} - u_j)](|j\rangle\langle j+1| + |j+1\rangle\langle j|) + \sum_j \frac{1}{2}m\dot{u}_j^2 + \sum_j \frac{1}{2}Ku_j^2. \quad (1)$$

It can be seen as the combination of a quantum Hamiltonian for the electron, whose off-diagonal elements are modulated by the nuclear position $\{u_j\}$:

$$H^{\text{el}} = \sum_j [-\tau + \alpha(u_{j+1} - u_j)](|j\rangle\langle j+1| + |j+1\rangle\langle j|), \quad (2)$$

and a classical Hamiltonian for the nuclei, whose potential energy is determined by the electronic wave function $\psi(t)$:

$$H^{\text{nucl}} = \sum_j \frac{1}{2}m\dot{u}_j^2 + \sum_j \frac{1}{2}Ku_j^2 + \langle \psi(t) | H^{\text{el}} | \psi(t) \rangle. \quad (3)$$

The model is almost identical to the Su-Schrieffer-Heeger (SSH) model used for conductive polymers [16] but the parameters appropriate for molecular crystals are very different and the transport regime, as we will see, is not comparable with that of conductive polymers. The main parameters set used here is based on the computations of Ref. [15]. The mass m is chosen to be close to the mass of pentacene (250 amu), the elastic constant K (set to $14\,500 \text{ amu ps}^{-2}$) is such that the transverse mode energy is 40 cm^{-1} , and the distance between two consecutive sites is $L = 4 \text{ \AA}$. We used τ in the range of $150\text{--}600 \text{ cm}^{-1}$, typical of most organic molecular crystal, and the electron-phonon coupling term α (in the $700\text{--}1400 \text{ cm}^{-1}/\text{\AA}$ range) is such that, at 300 K, the standard deviation of the intermolecular coupling $-\tau + \alpha(u_{j+1} - u_j)$ is approximately 1/3 of its average value, in accordance with the computational studies. We note that, in this model, the electronic terms $[-\tau, \text{ and } \alpha(u_{j+1} - u_j)]$ are comparable with the thermal energy above $\sim 100 \text{ K}$, a condition making thermal disorder important for the charge-transport mecha-

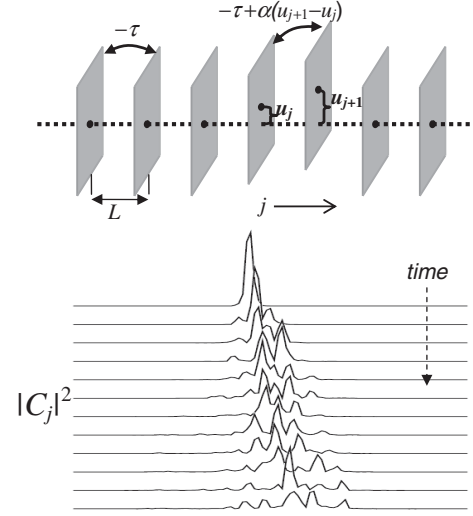


FIG. 1. (Upper panel) Scheme of the model used to describe the charge transport in organic semiconductors. (Lower panel) Example of time evolution of the probability density in the considered model ($K = 14\,500 \text{ amu ps}^{-2}$, $\tau = 300 \text{ cm}^{-1}$, $\alpha = 995 \text{ cm}^{-1}/\text{\AA}$, $m = 250 \text{ amu}$, $T = 150 \text{ K}$). The profile of the density is represented for each snapshot every 0.15 ps starting from $t = 0$ (only 100 sites are shown).

nism. Equation (1) is valid for larger conjugated molecules (like pentacene) for which the neglected nuclear reorganization energy is not sufficient to localize the charge carriers.

The numerical integration of Eq. (1) is straightforward [17]. Given the set of positions u_j , velocities \dot{u}_j , and wave function $\psi(t)$ at a given time t , and an integration time step Δt , (i) the classical accelerations are computed as

$$m\ddot{u}_j(t) = -Ku_j(t) - \frac{\partial}{\partial u_j} \langle \psi(t) | H^{\text{el}} | \psi(t) \rangle, \quad (4)$$

(ii) the wave function is updated as ($\hbar = 1$):

$$\psi(t + \Delta t) = \psi(t) - iH^{\text{el}}\psi(t)\Delta t - \frac{1}{2}i[H^{\text{el}}(t)\dot{\psi}(t) + \dot{H}^{\text{el}}(t)\psi(t)]\Delta t^2, \quad (5)$$

[where we have expanded $\psi(t + \Delta t) = \psi(t) + \dot{\psi}(t)\Delta t + \frac{1}{2}\ddot{\psi}(t)\Delta t^2$, used the Schrödinger equation $\dot{\psi}(t) = -iH^{\text{el}}(t)\psi(t)$, and $\ddot{\psi}(t) = -i(H^{\text{el}}(t)\dot{\psi}(t) + \dot{H}^{\text{el}}(t)\psi(t))$, (iii) the positions are updated with the Verlet algorithm as

$$u_j(t + \Delta t) = 2u_j(t) - u_j(t - \Delta t) + \ddot{u}_j(t)\Delta t^2. \quad (6)$$

The time derivative of the H^{el} [in Eq. (5)] is $\dot{H}^{\text{el}} = \sum_j [\alpha(\dot{u}_{j+1} - \dot{u}_j)](|j\rangle\langle j+1| + |j+1\rangle\langle j|)$, and, if we expand the wave function as $\psi(t) = \sum_j C_j(t)|j\rangle$, the derivatives in Eq. (4) can be written as $\partial/\partial u_j \langle \psi(t) | H^{\text{el}} | \psi(t) \rangle = \alpha(-C_j^* C_{j+1} - C_{j+1}^* C_j + C_{j-1}^* C_j + C_j^* C_{j-1})$. The conservation of the total energy was used to make sure that the

integration time step of 0.025 fs was sufficiently small for the length of the simulations (15 ps).

The initial nuclear positions $\{u_j(0)\}$ and velocities $\{\dot{u}_j(0)\}$ for the simulation at temperature T were randomly chosen from the Boltzmann distribution appropriate for a collection of non interacting harmonic oscillators, i.e., a Gaussian distribution of the displacements u_j with variance $k_B T/K$ and a Gaussian distribution of the velocities \dot{u}_j with variance $k_B T/m$. The initial wave function $\psi(t=0)$ was chosen in the set of eigenfunctions $\psi_n(0)$ such that $H^{\text{el}}(0)|\psi_n(0)\rangle = E_n|\psi_n(0)\rangle$ and the probability that the trajectory starts from the eigenstate $\psi_n(0)$ is $P_n = \exp(-E_n/k_B T) / \sum_{n=1}^N \exp(-E_n/k_B T)$.

With the sets of parameters used here the initial wave function is localized within very few sites. Initial localization is induced by the disorder in the off-diagonal terms of the electron Hamiltonian, while the subsequent spread of the electron density is determined by the time dependence of the transfer integrals. A typical evolution of the charge density $|C_j(t)|^2$ is depicted in Fig. 1.

For the quantitative study of the charge motion inside this system we monitored the time dependency of the temperature averaged squared displacement defined as

$$\langle r^2(t) \rangle_T - \langle r(t) \rangle_T^2 = \sum_{n=1}^N P_n [\langle \psi_n(t) | r^2 | \psi_n(t) \rangle - \langle \psi_n(t) | r | \psi_n(t) \rangle^2]. \quad (7)$$

The matrix elements of the previous equation can be computed from the relation $\langle j | r | j' \rangle = \delta_{jj'} jL$. The results presented are averaged over 125 computed trajectories with different initial $\psi_n(0)$.

The mean square displacement, after a short initial period, increases linearly with time (see Fig. 2), indicating a diffusive behavior. The diffusion coefficient can be computed as $D = \lim_{t \rightarrow +\infty} \langle r(t)^2 \rangle / 2t$. Repeating the simulation with higher (or lower) oscillator mass m , we explored the case of slower (or faster) modulation of the transfer integral and identical amount of electronic disorder (only dependent on τ , α , and K). The diffusion coefficient decreases with the decrease of the oscillator frequency. The limiting case of infinite mass oscillator corresponds to a system with *static* disorder that is insulating in one dimension regardless of the amount of disorder [18].

The temperature dependent charge mobility can be computed using the Einstein relation $\mu = De/k_B T$, and some $\mu(T)$ curves for different values of τ and α are plotted in Fig. 3. The increase of the average coupling term τ causes an increase in the mobility because it corresponds to a decrease of the effective disorder, i.e., the limiting factor for the diffusion. Analogously, the decrease of the electron-phonon coupling term α causes a decrease of the disorder and an increase of mobility. These results suggest that a viable strategy for the design of high mobility materials is to reduce the α/τ ratio [19]. If the localization is too

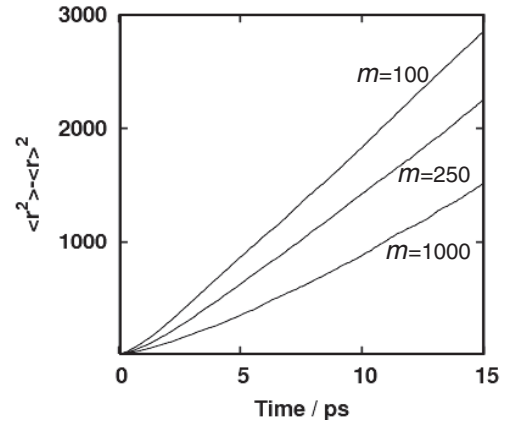


FIG. 2. Plot of the temperature averaged squared displacement [in units of L^2 , Eq. (7)] versus time, using the parameters in the caption of Fig. 1 and the oscillator mass m as indicated on the plot in amu.

modest (i.e., with values of τ much larger or values of α much smaller than the ones considered here, or in the low-temperature limit) the approach proposed in this Letter is less convenient and the usual band description of the charge carrier motion should be used instead. In a band description each charge carrier is in a delocalized state defined by the wave vector k and has a (small) chance to be scattered into a new states k' because of the (small) coupling with phonons or impurities. While in the delocalized case the dynamics should be studied in the reciprocal (k) space, with a sufficiently large amount of disorder (as in all cases of Fig. 3), the most convenient approach is the one taken here, where the wave function evolution is studied in the real space and the band description is not useful. A complete picture of the transport should also take into account the reorganization energy term neglected in Eq. (1). This can be important for smaller molecules like naphthalene, for which the localization is due to the small polaron formation and that due to dynamic localization may cooperate, affecting the global mechanism. Although it seems possible to increase the mobility reducing the oscillator mass m (see Fig. 2), in practice, much smaller molecules have larger band gap and reorganization energy making them less suitable semiconductors.

The $\mu(T)$ plots follow to a good approximation the power law dependence, often considered a fingerprint of the band transport [5]. In this case, very far for the conditions of band transport, the charge carriers are localized by the dynamic disorder of the lattice (and *not* by the formation of a small polaron). The room temperature mobilities around $\sim 3 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ found for our model system are in good agreement with the available experimental measurements ($\sim 1 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for 2D pentacene thin films). The parameters used are derived from the computational studies [15] and changing them within a physically meaningful range for organic solids does not modify this regime of transport, leading to mobilities in the

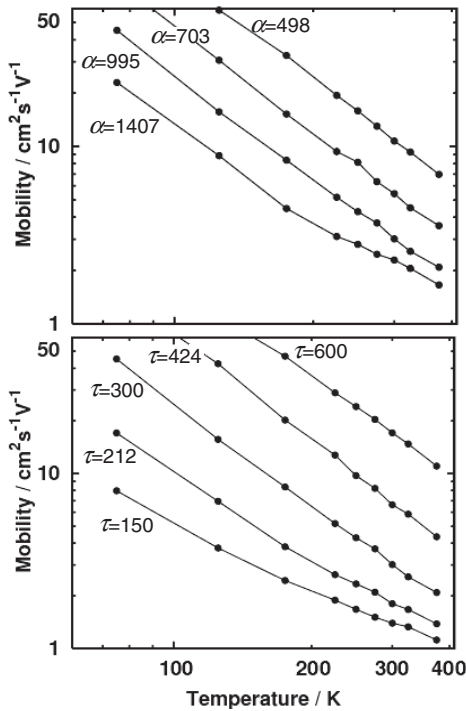


FIG. 3. Temperature dependence of the mobility for the model system. For both panels $K = 14\,500 \text{ amu ps}^{-2}$ and $m = 250 \text{ amu}$. (Upper panel) $\tau = 300 \text{ cm}^{-1}$ and α varies as indicated in $\text{cm}^{-1}/\text{\AA}$. (Lower panel) $\alpha = 995 \text{ cm}^{-1}/\text{\AA}$ and τ varies as indicated in cm^{-1} . For the system size considered here (600 sites) only mobilities below 60 cm^{-1} are guaranteed to be unaffected by the boundary conditions (for higher mobilities the carrier could interact with its image for some trajectories).

limited range of $0.1\text{--}50 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ at 300 K. If many charge carriers are trapped by impurities the measured mobility may appear thermally activated. However, our model can be always compared with Hall mobility measurements [20], which exclude the contribution of trapped electrons. Since this model predicts a characteristic localized carrier residence time of $t_R \sim 10^{-13} \text{ s}$, it follows that spectroscopic investigations with characteristic energy $E \gg \hbar/t_R$ should reveal localized carriers (as found experimentally) [12].

It is convenient to remark how similar model Hamiltonians lead to completely different phenomenology when their characteristic parameters assume values of different orders of magnitude. For example, the model used here, apparently similar to the SSH Hamiltonian, leads to a very different transport mechanism because the thermal fluctuations deeply affect the electronic structure. The SSH parameters for a typical conductive polymer are [21] $m = 13 \text{ amu}$, $K = 203\,000 \text{ amu ps}^{-2}$, $t = 20\,125 \text{ cm}^{-1}$, $\alpha = 33\,000 \text{ cm}^{-1}/\text{\AA}$, $\hbar\sqrt{K/m} = 660 \text{ cm}^{-1}$. This parameter set implies that, in conductive polymers, the electronic terms are marginally affected by the thermal

disorder [22]. Similarly, it can be verified that thermal disorder is negligible in the most common inorganic semiconductors. The different transport mechanism in ordered organic materials originates from the very weak interactions among the molecular constituents.

In conclusion, using a simple semiclassical model, suggested by several computational studies, we showed that thermal molecular motions in organic crystals are sufficient to destroy the translational symmetry of the electronic Hamiltonian, localizing “dynamically” the charge carriers. The model proposed to describe the charge dynamics in these materials is consistent both with the spectroscopic observation of localized carriers and the bandlike dependence of the charge mobility (two facts previously considered in contradiction). According to this mechanism, the most efficient way to improve the charge mobility in organic materials is to reduce the thermal electronic disorder.

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