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Impact of the Electron-Phonon Coupling Symmetry on the Polaron Stability and Mobility in Organic Molecular Semiconductors

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Abstract

The influence of the interplay between symmetric and antisymmetric inter-molecular electron-phonon (e-ph) coupling mechanisms on the polaron stability and mobility in organic semiconductors has been theoretically investigated at a molecular level. A semi-empirical Holstein-Peierls model is used which in addition to the symmetric and antisymmetric inter-molecular e-ph interactions also includes an antisymmetric intra-molecular e-ph coupling. Our results show that the symmetric e-ph coupling plays the role of destabilizing the polaron as a result of temperature induced phonons that, via the symmetric coupling, affects the charge distribution of the polaron. Considering this kind of coupling, the parameter space for which the polaron is dynamically stable is strongly temperature-dependent. For the combination of symmetric e-ph coupling strength and temperature, which results in a stable polaron, the velocity of the polaron, and therefore also the charge carrier mobility, is not affected by the symmetric e-ph coupling strength.

Keywords: Holstein–Peierls Model, Polaron, Electron–Phonon Coupling, Charge Transport, Organic Semiconductors.

The charge transport mechanism in organic molecular semiconductors is recognized as one of the most important traits to be developed in order to increase substantially the performance of organic optoelectronics devices.[1,2] Moreover, relevant efforts have been applied to enlighten the understanding of the polaron stability in these materials at atomic[3–6] and molecular[7,8] scales, in the scope of a tight–binding approach. Regarding this kind of approach, there are two different electron–phonon (e–ph) coupling mechanisms that can affect the charge transport in organic semiconductors: the Holstein-type that involves the modulation of the site (intra-molecular) energy vibrations and the Peierls-type that describes the modulation of the (inter-molecular) transfer integral triggered by phonons. In this context, the asymmetric coupling has been studied in great detail since the pioneering work of Su and colleagues.[9] However, detailed investigations considering the impact of the symmetric e–ph coupling on the polaron stability and its dynamical properties are lacking in the literature.

Very recently, Li *et al.* have shown, in the context of a tight–binding description, that the electronic and charge transport properties in organic molecular semiconductors are greatly impacted by the non–local e–ph coupling to both acoustic and optical lattice vibrations.[10,11] Their results report that, when the antisymmetric and symmetric contributions to the e–ph coupling are considered, only the antisymmetric coupling mechanism is operational in the case of acoustic vibrations. Furthermore, neglecting the quantum nature of the phonons, the effect of the e–ph interactions with acoustic and optical phonons is similar in the cases where contributions of these two e–ph mechanisms are equal. Coropceanu *et al.* have investigated the non–local e–ph interactions in a naphthalene crystal also in the framework of a tight–binding approach.[12] Their results reveal that the first nine low–energy (intermolecular) vibration modes, derived at the Γ–point, can contribute to the non–local electron–phonon and hole–phonon interactions. Also it was suggested that, along some crystal directions, the non–local interactions are not totally symmetric. From the above–mentioned researches, it is possible to note that further investigations of the symmetric–like and antisymmetric–like non–local coupling mechanisms and their impact on the polaron stability in organic molecular semiconductors and, consequently, on the charge transport in these materials, will be of major interest.

In this work, using a semi–empirical Holstein–Peierls model, a systematic numerical study is performed in order to investigate the impact of the symmetric e–ph coupling on the polaron stability and its dynamical properties when thermal effects and an external electric field are considered. An Ehrenfest Molecular Dynamics is carried out in the framework of a one–dimensional tight–binding model, which includes lattice relaxation. The investigations are performed in systems which approximately resembles a stack of molecular semiconductors such as pentacene,[13] anthracene,[14] or rubrene.[15] This work is intended to give a physical picture of the polaronic stability and mobility in organic molecular semiconductors when symmetric–like and antisymmetric–like non–local coupling mechanisms are considered and contribute to the understanding of these important processes, that may provide guidance to improve the charge transport efficiency in organic optoelectronics devices.

In our model, each molecule is represented by a site with index i having three degrees of freedom where v_i^x and v_i^y are the site displacements involved in the antisymmetric (longitudinal) and symmetric (transversal) non–local vibrational modes, respectively, and u_i is the single internal phonon mode coupled to the electronic system through of the local e–ph coupling, according represented in Figure 1. In this way, the combined Holstein–Peierls Hamiltonian is described as $H_{HP} = H_{elec} + H_{latt}$ and can assumes the following form for the first part (electronic Hamiltonian):

$$H_{elec} = \sum_i \alpha_1 u_i \hat{c}_i^\dagger \hat{c}_i + \sum_i (J_{i+1,i} \hat{c}_i^\dagger \hat{c}_{i+1} + h.c.) \tag{1}$$

where $J_{i+1,i}$ is the inter-molecular transfer integral between two neighboring sites and is defined as

$$J_{i+1,i} = J_0 - [\alpha_2^x (v_{i+1}^x - v_i^x) - \alpha_2^y |v_{i+1}^y - v_i^y|] e^{i\gamma\Lambda_x(t)}. \tag{2}$$

The operator $\hat{c}_i^\dagger$ ($\hat{c}_{i+1}$) creates (annihilates) a carrier at the i-th lattice site; J_0 is the transfer integral for a pristine lattice; $\gamma \equiv ea/\hbar c$ with e being the absolute value of the electronic charge, c is the speed of light, and a is the lattice constant; α_1, α_2^x, and α_2^y are the e–ph coupling constants for intra–molecular, antisymmetric inter–molecular, and symmetric inter–molecular vibrations, respectively. The electric field is assumed to be static and included in the model by means of the time dependent potential vector $\Lambda_x(t) = -cEt$.

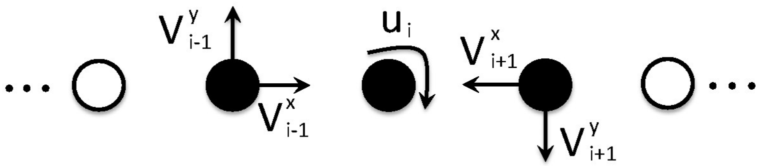

Figure 1: Schematic representation of the one–dimensional Holstein–Peierls System.

The last part in H_{HP} is the Hamiltonian of the lattice backbone ($H_{latt} = H_{latt,1} + H_{latt,2}$) which is described by the two separate harmonic oscillators, considering the intra- and inter-molecular modes:

$$H_{latt,1} = \frac{K_1}{2}\sum_i (u_i)^2 + \frac{M_1}{2}\sum_i (\dot{u}_i)^2 \tag{3}$$

and

$$H_{latt,2} = \frac{K_2}{2}\sum_i [(v_{i+1}^x - v_i^x)^2 + (v_{i+1}^y - v_i^y)^2] + \frac{M_2}{2}\sum_i [(\dot{v}_i^x)^2 + (\dot{v}_i^y)^2], \tag{4}$$

where the force constants K_1 and K_2 as well as the masses M_1 and M_2 refer to the intra– and inter–molecular oscillators, respectively. Here, we have used the following values for the above–mentioned parameters: $J_0 = 50$ meV, $\alpha_1 = 1.5$ eV/Å, $\alpha_2^x = 0.5$ eV/Å, $K_1 = 10$ eV/Å^2, $K_2 = 1.5$ eV/Å^2, $M_1 = 1.3 \times 10^9$ eV(as/Å)^2, $M_2 = 2.6 \times 10^{10}$ eV(as/Å)^2, and $a = 3.5$ Å , which are recognized as standard and have been used recently in previous simulations.[7,8,16–18] The dynamical simulations are carried out using this standard set of parameters. However, in order to obtain a good physical picture of the polaron stability and mobility in one–dimensional organic molecular semiconductors, when a symmetric coupling term is taken into account, we have performed simulations where α_2^y lies in the range [0–0.45] eV/Å.

The electronic dynamics is performed by means of the time-dependent Schrödinger equation.[8] By introducing instantaneous eigenstates, the solution at each instant of time can be expressed in the form

$$\psi(n, t + \Delta t) = \sum_l \left[\sum_m \phi_l^*(m)\,\psi(m,t)\right] \times e^{(-i\varepsilon_l \Delta t/\hbar)}\phi_l(n), \tag{5}$$

in which $\phi_l(m)$ and ε_l are the eigenfunctions and eigenvalues of H_{elec} at time t, respectively.

The equations of motion for the lattice backbone are given by the newtonian equations for the intra–molecular displacement (F_u), for the antisymmetric inter–molecular vibrations (F_{v^x}), and for the symmetric inter–molecular vibrations (F_{v^y}), similarly to reported in reference.[8] The temperature effects are included in our approach by adding thermal random forces with zero mean value $\langle\zeta(t)\rangle \equiv 0$ and variances

$$\langle R_i^{intra}(t) R_{i\prime}^{intra}(t\prime)\rangle = 2K_B T M_1 \lambda \delta_{i,i\prime}\delta(t - t\prime) \tag{6}$$

and

$$\langle R_i^{inter}(t) R_{i\prime}^{inter}(t\prime)\rangle = 2K_B T M_2 \lambda \delta_{i,i\prime} \delta(t - t\prime) \tag{7}$$

to the equation of motion for the lattice. In this way, the new equations of motion has the following form

$$F'_u = F_u - M_1 \lambda \dot{u}_i(t) + R_i^{intra}(t), \tag{8}$$

$$F'_{v^x} = F_{v^x} - M_2 \lambda \dot{v}_i^x(t) + R_{x,i}^{inter}(t), \tag{9}$$

and

$$F'_{v^y} = F_{v^y} - M_2 \lambda \dot{v}_i^y(t) + R_{y,i}^{inter}(t). \tag{10}$$

These equations can be integrated using the "half a kick" algorithm, as extensively explained in reference.[19] Both the dissipative force and the random force having the power spectral density given by the fluctuation–dissipation theorem. The fluctuations are obtained using the equation reported in reference.[20] It should be emphasized that including temperature effects by means of a Langevin formalism is widely used in the literature with a good track record.[21–27]

We have pointed out above that our model can distinguish between three degrees of freedom where the inter–site displacements are related to antisymmetric and symmetric non–local vibrational modes and the intra–site displacements are described by one single internal phonon mode. The distortions related to the polaron shows a negative value for the intra–site displacements, which denotes a compression of the molecules due to the excess of charge.[8,28] The inter–molecular distortions v^x show a contraction (negative values) for the two neighboring inter–molecular displacements of the central molecule, where the polaron is initially localized, as represented in Fig. 1. These contractions are followed by elongations (positive values) in the displacements of the other molecules. These elongations decrease with increasing numbers of molecules, in order to keep the constraint of fixed total displacements.[8] It is worth to stress that there are no distortions in v^y, considering the ground state solution for the polaron. The lattice geometry of the system is optimized using the resilient backpropagation, RPROP, algorithm.[29] For the charge distribution presented by the optimized geometry, the polaron is localized initially at three molecules with its main contribution residing on a central molecule.[8,28]

With this geometry configuration and charge localization in mind, we now turn to simulations for the dynamical stability of a polaron, in which we have varied the symmetric e–ph coupling strength and the temperature. The thermal regimes considered ranging from 0 to 300 K, with increment of 25 K. In order to characterize the polaron stability, we have used the time average value ($\overline{IPR}$) of the inverse participation ratio

$$IPR = \frac{\sum_i |\rho_i|^2}{\left(\sum_i |\rho_i|\right)^2} \tag{11}$$

with respect to the charge density. The molecular charge density is defined as $\overline{\rho_i}(t) = \sum_i \psi_i(t)\psi_{i'}(t)^*$. The dynamical simulations for the polaron stability, considering all cases, have started from a ground state solution that contains a stable polaron.[28] The time period considered for the polaron dynamics was 5 ps. In order to eliminate the ground state solution for the ($\overline{IPR}$) calculations, which is equal for all cases, the IPR is calculated ate each time step during the last 2 ps. In this way, $\overline{IPR}$ values greater than 0.4 represent a stable polaron solution, in which the charge remains coupled and localized to three molecules (named large polaron). For $\overline{IPR}$ values greater then 0.8 the polaron becomes localized almost totally to a single molecule (termed small polaron).

Figure 2 depicts the dynamical stability of the polaron with no field strength. The planar light–yellow regions correspond to the parameter space in which the interplay between the symmetric e-ph coupling strength and temperature annihilates the polaron. The value used for the fixed parameters (see above) are such that the polaron is stable at low temperatures (large polaron solution).[7] In these thermal regimes, the value of α_2^y has no effect on the polaron since the ground state solution corresponds to $v_i^y = 0$ for all sites i.

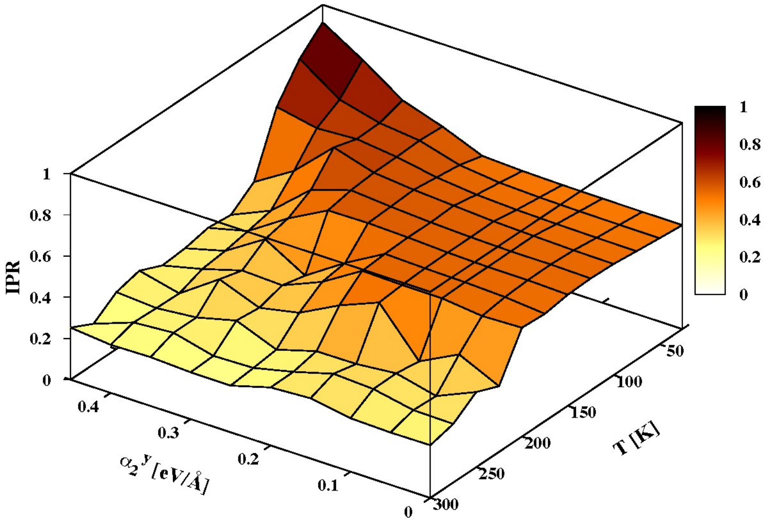

Figure 2: The average value ($\overline{IPR}$) of the inverse participation ratio (IPR) as a function of temperature and symmetric e–ph coupling strength with no field included. The remaining parameters are fixed according the standard values presented in the previous section. Concerning the data related to temperatures close to zero, it should be pointed out that these results fall outside regime in which the classical approach used in this work is fully justified.

From Figure 2 we observe a destabilization of the polaron as the temperature increases. This destabilization increases with increasing strength of the symmetric e–ph coupling. Considering α_2^y values smaller than 0.2 eV/Å, the critical temperature regime in which the polaron loses its stability is 200 K. This thermal regime for the polaron annihilation agrees with our previous calculations where the effects of the symmetric were not taken into account.[28] On the other hand, when α_2^y values higher than 0.4 eV/Å are considered, the critical temperature reduces to around 100 K. This result is the opposite to the effect of the asymmetric coupling.[7] In order to understand this we again emphasize the basic feature of the symmetric coupling, namely, that this coupling has no effect on the ground state (zero temperature) polaron solution. The only effect that can be observed is that the temperature induced phonons act on the charge associated with the polaron in such a way that it deviates from the most stable charge distribution. This is the reason for the destabilization.

In order to understand this in more detail, we observe from Figure 2 that an increase in the symmetric e–ph coupling strength at non-zero temperatures results in an increase of the IPR value, i.e., to further increase the charge localization. For α_2^y values smaller than 0.2

eV/Å, the polaron is delocalized between three molecules and remains stable until thermal regimes of 200 K. For values of α_2^y higher than 0.3 eV/Å, the polaron becomes much more localized and has the stability reduced in the sense that it is annihilated for temperature regimes higher than 100 K. Apparently, the effect the symmetric phonons have on the polaron at finite temperatures is to increase the polaron localization compared to the ground state solution. This is the reason for the lower stability of the polaron in the presence of a strong symmetric e–ph coupling.

We now turn our discussions to the polaron dynamics for a system subject to 100 K for an electric field strength of 2.0 mV/Å and $\alpha_2^y = 0.3$ eV/Å, in order to depict the impact of the symmetric e-ph coupling on the polaronic mobility. These values for the temperature and α_2^y result in a stable polaron solution (see Figure 2). The features presented by the intra– and inter–molecular distortions in a system containing a mobile polaron at zero temperature and in the absence of a symmetric e–ph coupling mechanism, were discussed detailed in our earlier works.[8,28] However, as the effects of the symmetric e–ph coupling mechanism and temperature on the stability and dynamics of a polaron in the framework of a Holstein–Peierls approach have not been reported before, we present here some basic features of the dynamics of the inter–molecular distortions $(v_{i+1}^x - v_i^x)$ and $(v_{i+1}^y - v_i^y)$, where the last are related to the presence of a symmetric e–ph coupling constant. Figure 3 displays the time evolution for (a) the molecular charge density, (b) the molecular displacements occasioned by asymmetric e–ph interactions, (c) and the molecular displacements due to symmetric e–ph interactions. For the sake of clarity, we have displayed the polaron dynamics for the lattice sites between 45–70 during the first 4 ps of the simulation.

Figure 3 (a) shows that the charge associated with the polaron is centered on a certain molecule at a given time instant (t_1). A short time after (t_2) it becomes shared between two neighboring molecules and then drifts to the center of the next molecule (t_3). Importantly, the charge transport mechanism depicted in Figure 3 (a) is an adiabatic process involving a single state of the Hamiltonian (H_{HP}, see above). Moreover, it can be seen that the temperature

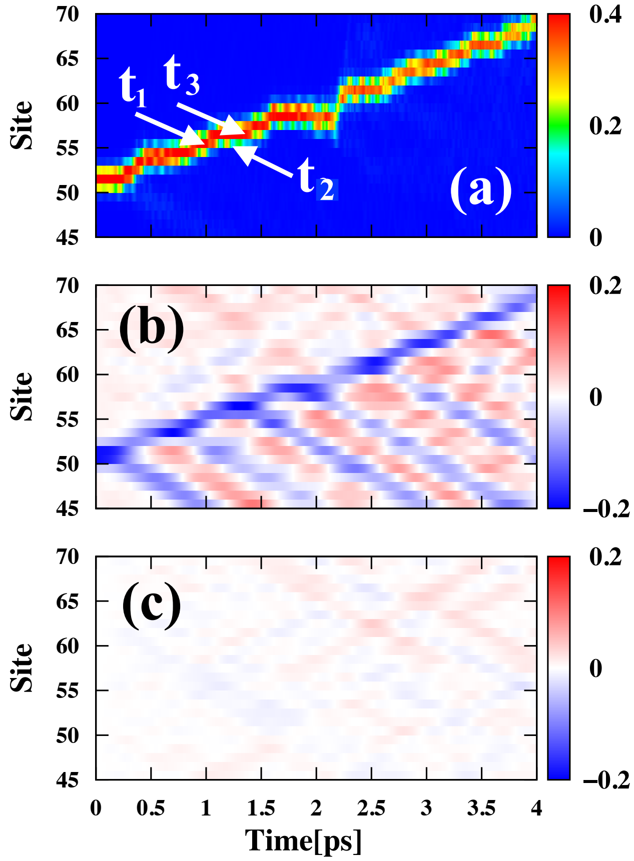

Figure 3: Time evolution of the (a) the molecular charge density, (b) the molecular displacements occasioned by asymmetric e–ph interactions, (c) and the molecular displacements due to symmetric e–ph interactions at 100 K considering an electric field strength of 2.0 mV/Å and $\alpha_2^y = 0.3$ eV/Å.

causes fluctuations in the charge density profile, but the polaron keeps its integrity until the end of the simulation in agreement with the results presented in Figure 2. From Figure 3 (b) is it clear that the inter-molecular displacements associated with the asymmetric e–ph coupling, which are lattice compressions, follow the moving charge. Another typical feature is the travelling waves moving in backward direction. These are sound waves that travel with the velocity of about 25 Å/ps.[8,30] It should be noted that the polaron velocity is about 15 Å/ps, i.e., considerably lower than the sound velocity.

The phonons emitted in the backward direction may be understood as an intrinsic scattering of the polaron, showing an oscillatory pattern which involves local expansions and contractions of the lattice. The polaron can also emit travelling waves in the forward direction, but with lower degree of deformation. Figure 3 (c) shows the symmetric v_i^y displacements. It is clear from this figure that there are no such displacements following the moving charge. Again, this is a result of the features of the ground state polaron structure which contains no v_i^ydisplacements. The main contributions to these displacements are coming from the temperature. However, the mechanism of charge transfer discussed above can also cause distortions in the molecular displacements v_i^y moving upwards and downwards the next neighboring molecules of a molecule in which the charge pass to be centered.

The temperature influence on the system is noted to take place by the oscillations presented by the v_i^x and v_i^y distortions in Figure 3(b) and (c), respectively. Since the force constants in the x– and y–directions are the same, the phonon pattern in the asymmetric and the symmetric modes are the same. However, as a consequence of the difference in the coupling to the polaron solution, there are considerable differences between the amplitudes of the two types of phonons. For the asymmetric modes tha amplitudes are of the order of 0.2 Å whereas the distortions for the symmetric vibrational mode are typically of the order of 0.05 Å.

In order to depict the influence of the symmetric e-ph coupling mechanism on the polaron mobility, we now present a comparison between the polaron trajectories for a system without and with α_2^y, as shown in Figure 4. The polaron trajectory is obtained using the polaron center positions at a given time, calculated from a cyclic mean value of the mean charge density.[28]

Considering a system without the influence of α_2^y at a temperature of 50 K and with an electric field strength of 1.5 mV/Å (as depicted in Figure 4), the final polaron velocity is about 15 Å/ps. At the same temperature and electric field regimes and now considering the influence of the symmetric e–ph coupling mechanism over the polaron trajectory (as shown in Figure 4 for $\alpha_2^y = 0.45$ eV/Å), the final polaron velocity obtained is basically the same. It should be pointed out that, in the same way as for the calculation of the IPR values, we should look at the last part of the simulation in order to avoid initial state effect and to ensure a higher degree of equilibrium.

The result shown in Figure 4 is somewhat surprising considering the increased localization of the polaron shown in Figure 2. However, except for the initial period of about 1 ps, this shape of the polaron changes somewhat and the moving polaron becomes more delocalized than the polaron at rest. In fact, the shape of the moving polaron for the two cases is essentially the same which explains also the similarities in their field induced velocities.

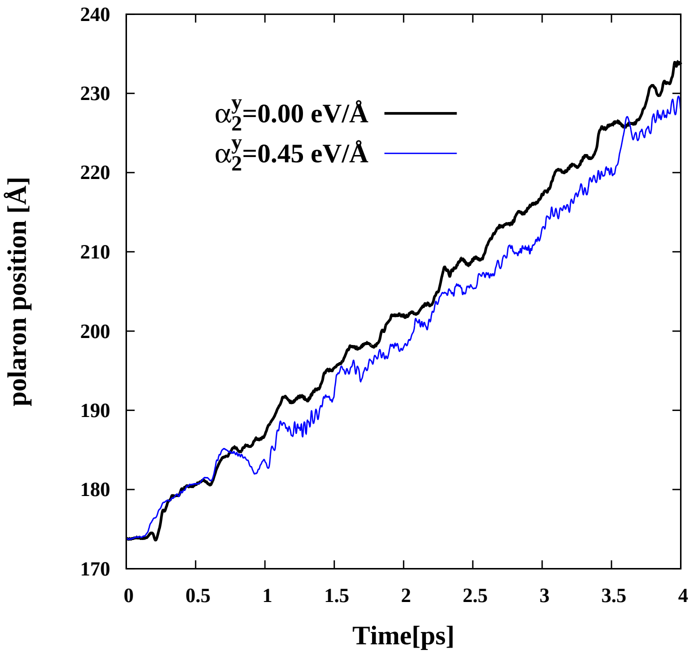

Figure 4: Polaron trajectories at 50 K considering an electric field strength of 1.5 mV/Å for $\alpha_2^y = 0.0$ eV/Å and $\alpha_2^y = 0.45$ eV/Å.

In summary, a semi-empirical Holstein-Peierls approach is used to investigate the impact of the electron-phonon (e–ph) coupling symmetry on the polaron stability in organic semiconductors at a molecular scale. Our model takes into account both intra- and inter-molecular e–ph interactions and is aimed at describing the polaron mobility when an external electric field and temperature effects are considered. Our findings shown that the symmetric e–ph coupling can play the role of alter the molecular charge distribution at finite temperature but not at zero temperature. The temperature induced symmetric lattice displacements affect the charge localization from a polaron localized to three molecules for a weak symmetric e–ph coupling to a smaller polaron primarily localized to a single molecule at e–ph coupling strengths above 0.2 eV/Å. This lowers considerably the polaron stability as a function of temperature. Considering polaron dynamics at a certain temperature and electric field strength, the equilibrium polaron velocities are essentially unaffected by the inclusion of the symmetric e–ph coupling. The reason for this is that the moving polaron becomes does not interact with the symmetric phonons in the same way as the static polaron. Our simulations show instead that the symmetric coupling becomes essentially unimportant for the polaron dynamics and therefore also for the charge carrier mobility in molecular materials.

It is worth mentioning here that a detailed knowledge regarding the influence of the inter-molecular e-ph coupling symmetry on the charge transport mechanism is not available experimentally due to the difficulty of control the contributions of each degree of freedom separately. This is precisely the goal of the present work to address this issue providing a better understanding of the impact of the nonlocal e-ph interactions on the polaron stability and mobility in organic molecular semiconductors. To the best of our knowledge, the approach we have taken has not been included in direct studies of charge transport and the results are therefore primarily of use for further theoretical and computational studies. However, also from an experimental point of view, our observations are very important. If there are ways to synthesize a material which reduces the symmetric electron-phonon coupling this should lead to an increased polaron stability and therefore have a strong impact in the transport properties.

Acknowledgement

The authors gratefully acknowledge the Swedish Research Council (VR) for financial support, the Swedish National Infrastructure for Computing (SNIC), the CENAPAD-SP for provide the computational facilities, and the financial support from the Brazilian Research Councils CAPES and FAPDF.

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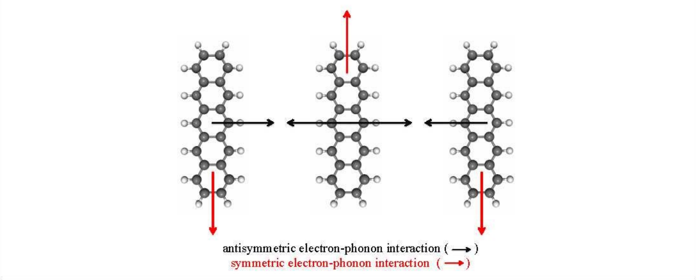
Graphical TOC Entry



Schematic representation of a pentacene stack with two inter-molecular degrees of freedom.