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# Supplemental Material for
# “Polaron Stability in Molecular Semiconductors: Theoretical Insight Into the Impact of the Temperature and the System Dimensionality”

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## I. GEOMETRY CONFIGURATION

Here, we discuss important aspects related to the lattice configuration for a two-dimensional system (molecular crystal) containing a polaron. As depicted in Figure 1 of the main text, the polaron is localized to five molecules with its main contribution (~48%) residing on a single central molecule. The geometrical distortion associated with the polaron shows a negative value of the internal coordinate $u_{i,j}$, which represents a compression of the molecules in the presence of charge, as shown in Fig 1(b). Considering the inter-molecular relative displacements, it is possible to note in Figs. 1(c) and 1(d) that there is a contraction (negative displacements) presented by the four inter-molecular displacements around the central molecule of the polaron, as represented in Fig 1. These contractions are followed by expansions (positive displacements) on the x and y directions through the row and column, respectively, of the molecular array where the central molecule is localized. The expansions are expected to decrease by a factor of $\delta/n_{x,y}$ increasing the number of molecules in both directions, where $\delta$ represents the value of the first elongation and $n_{x,y}$ the total number of molecules in x- or y-direction, in order to keep the constraint of fixed total displacement, i.e., $\sum_i v^x_{i+1,j} - v^x_{i,j} = \sum_j v^y_{i,j+1} - v^y_{i,j} = 0$. The distortion associated with the polaron along the x-direction is thus followed by successive expansions for the other regions of the row on the molecular array in the absence of charge. To realize a polaron motion, all distortions in the y-direction (the compressions associated with polaron and the resulting expansions) should be transferred from one column to another. This is the first remarkable behavior we noticed concerning the polaron dynamics in going from a one-dimensional to a two-dimensional system: an increase in the number of rows in the molecular array increases the effective mass of the polaron and results in trapping of the charge carrier.

## II. THE INCLUSION OF THE TEMPERATURE EFFECTS

The temperature effects are simulated by adding thermal gaussian random forces with zero mean value $\langle\zeta(t)\rangle \equiv 0$ and variances

$$\langle R^{intra}_{i,j}(t) R^{intra}_{i',j'}(t')\rangle = 2K_B T M_1 \lambda \delta_{i,j;i',j'} \delta(t-t') \tag{1}$$

and

$$\langle R^{inter}_{i,j}(t) R^{inter}_{i',j'}(t')\rangle = 2K_B T M_2 \lambda \delta_{i,j;i',j'} \delta(t-t') \tag{2}$$

to the equation of motion for the lattice. In order to keep the temperature constant, after a transient period (named thermalization), it is necessary to introduce a damping factor, $\lambda$. In this way, we can derive the new equations of motion from the equations 10–12 presented in the main text in the following form

$$F'_u = F_u - M_1 \lambda \dot{u}_i(t) + R^{intra}_i(t), \tag{3}$$

$$F'_{v^x} = F_{v^x} - M_2 \lambda \dot{v}^x_i(t) + R^{inter}_{x,i}(t), \tag{4}$$

and

$$F'_{v^y} = F_{v^y} - M_2 \lambda \dot{v}^y_i(t) + R^{inter}_{y,i}(t). \tag{5}$$

The modified equations $F'_u$, $F'_{v^x}$, and $F'_{v^y}$ constitute a system of stochastical differential equations (SDEs). It is then important to find a proper integrator for solving SDEs. Here, we have adopted the Brünger-Brooks-Karplus integrator (BBK) [1]. The

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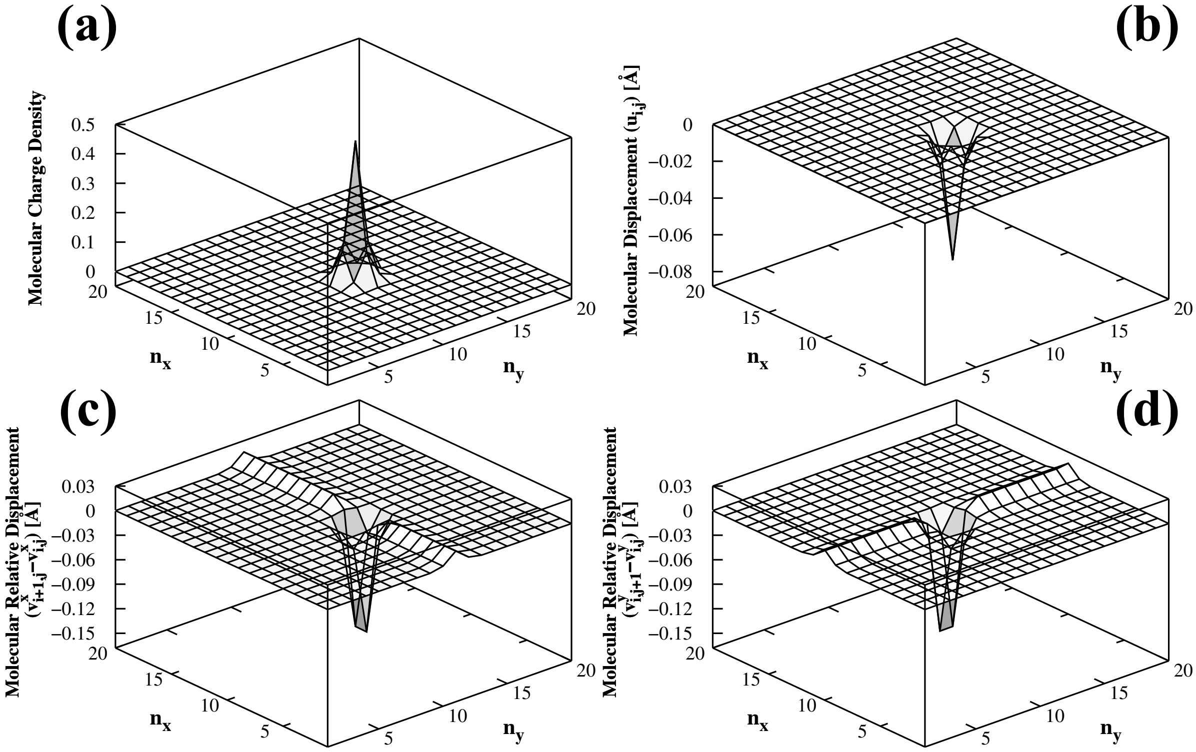

FIG. 1. A typical ground state (a) molecular charge density, (b) intra-molecular displacement $u_{i,j}$, (c) inter-molecular relative displacement in the x-direction $v^x_{i+1,j} - v^x_{i,j}$, and (d) inter-molecular relative displacement in the y-direction $v^y_{i,j+1} - v^y_{i,j}$ of a Holstein-Peierls polaron in a two-dimensional $20 \times 20$ system. The parameter values are those given in the previous subsection.

method is also called "half a kick" and the algorithm is explained in the following. In order to avoid confusions, the general letter $X$ is used for the intra-molecular, $u_i$ or the inter-molecular, $v_i^{x,y}$, displacements. Accordingly, $\dot{X}$ and $\ddot{X}$ will represent the velocities and accelerations, respectively. To simplify further, the molecule indices ($i$) are also removed and the modified forces and the random forces are labeled as $F$ and $R$, respectively. $M$ can demonstrate either of the intra- or inter-molecular masses. The half a kick algorithm is them expressed as

$$\dot{X}^{+\frac{1}{2}} = \left(1 - \frac{1}{2}\lambda\Delta t\right)\dot{X}^n + \frac{1}{2}\Delta t(F^n + R^n) \tag{6}$$

*drift*

$$\dot{X}^{n+1} = X^n + \Delta t\dot{X}^{n+\frac{1}{2}} \tag{7}$$

*half a kick*

$$\dot{X}^{n+1} = \frac{\dot{X}^{n+\frac{1}{2}} + 1/2M^{-1}\Delta t(F^{n+1} + R^{n+1})}{\left(1 + \frac{1}{2}\lambda\Delta t\right)}, \tag{8}$$

where we have introduced both the dissipative force and the gaussian random force having the power spectral density given by the fluctuation-dissipation theorem. In this way, the fluctuations can be obtained using $R_i(t) = \sqrt{(2k_BT\lambda M)/\Delta t} \times Z^n$, where $Z^n$ is a random number. It should be emphasized that this procedure of including temperature effects by means of a Langevin formalism is extensively used in the literature and is know to yield excellent qualitative results [2–12].

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