

Transient small-polaron hopping motion

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We calculate the transient motion of a well-localized charge carrier injected into a narrow-band molecular insulator. The carrier can often move with a mobility comparable to $1 \text{ cm}^2/\text{V sec}$ for a considerable time before equilibrating to form a small polaron. Thus, time-of-flight measurements on thin films may measure this mobility rather than the low, thermally activated mobility characteristic of steady-state small-polaron hopping motion.

I. INTRODUCTION

It is well known that steady-state small-polaron hopping motion at sufficiently high temperatures is characterized by a low thermally activated mobility.^{1,2} Namely, the steady-state mobility is then given by the semiclassical formula

$$\mu = (qa^2\nu/k_B T)P \exp(-E_A/k_B T), \quad (1)$$

where q is the carrier's charge, a is the distance traversed in a hop, ν is the characteristic atomic vibrational frequency, $k_B T$ is the thermal energy and E_A is the activation energy. The mobility activation energy is the minimum strain energy required to bring the electronic energy of an *equilibrated* self-trapped carrier into coincidence with the electronic energy level of an adjacent site to which it will hop. The factor P of Eq. (1) is the probability that a carrier will be able to transfer to an adjacent site within the duration of a coincidence event. For very small values of the electronic transfer energy J , hopping is "nonadiabatic" and

$$P = 2\pi J^2 / h\nu(4E_A k_B T / \pi)^{1/2}. \quad (2)$$

For larger values of J [such that P in Eq. (2) exceeds unity], the hopping is "adiabatic" and P should be replaced by unity in Eq. (1).

If we were to somehow eliminate the need to strain the system to form a coincidence, the small-polaron mobility would be given by the preexponential factor of Eq. (1). At temperatures comparable to room temperature (with $P = 1$) this yields a mobility comparable to $1 \text{ cm}^2/\text{V sec}$.

Transient experiments, such as time-of-flight measurements, are often employed to determine the carrier mobility in situations in which small-polaron hopping is suspected. However, the transient mobility of a small polaron has not been previously calculated. Rather, it has been implicitly assumed that once an injected carrier is well localized it will move with the low thermally activated mobility characteristic of steady-state small-polaron hopping motion. Here the transient motion of a well-localized injected carrier (such as is characteristic of an

electron injected in a narrow-band molecular solid) is explicitly calculated. It is shown that (except for very small values of J) immediately after injection, a well-localized carrier will typically hop to another site in a time $\sim 1/\nu$. This gives rise to a transient mobility comparable to $1 \text{ cm}^2/\text{V sec}$. Furthermore, with reasonable estimates of the vibrational dispersion, this type of rapid, activationless, small-polaron hopping can persist for a long time ($\gg 10^{-9}$ sec in molecular solids).

Prior to describing our calculations, we outline the physics of the situation we envision. Upon injection, a well-localized carrier in a narrow-band molecular solid will find itself confined to a single molecule with atoms that experience only thermal displacements from their carrier-free equilibrium positions. As illustrated in Fig. 1, the addition of the carrier causes the *equilibrium* positions of the atoms to shift to those consistent with the presence of the carrier. For atoms adjacent to the added charge, the carrier-induced atomic displacements associated with small-polaron formation are generally very much larger than the amplitudes of their thermal vibrations. As a result, the addition of the charge carrier will induce atomic vibrations whose amplitudes are comparable to the amplitudes of the shifts of their equilibrium positions. The amplitudes of such athermal vibrations are generally sufficient to generate a coincidence event. Figure 1(b) shows a coincidence event occurring after the carrier has remained at a molecular site for about a vibrational period. This will permit the carrier to hop to another site. It is only after these athermal vibrations relax sufficiently, dissipating vibrational energy to the surrounding atoms, that the carrier will truly be self-trapped [as depicted in Fig. 1(c)] and require thermal activation to move to another site. Since the amount of vibrational relaxation that can occur within a vibrational period is small, the probability of making an immediate hop can be very large (~ 1). Hence, an injected carrier may make many hops before the atoms surrounding it can equilibrate. In other terms, we may view the preequilibrated carrier as a "hot" small polaron. The equilibrium positions of the atoms are commensurate with the carrier's presence, but the amplitudes of vibrations about these equilibrium positions are athermal.

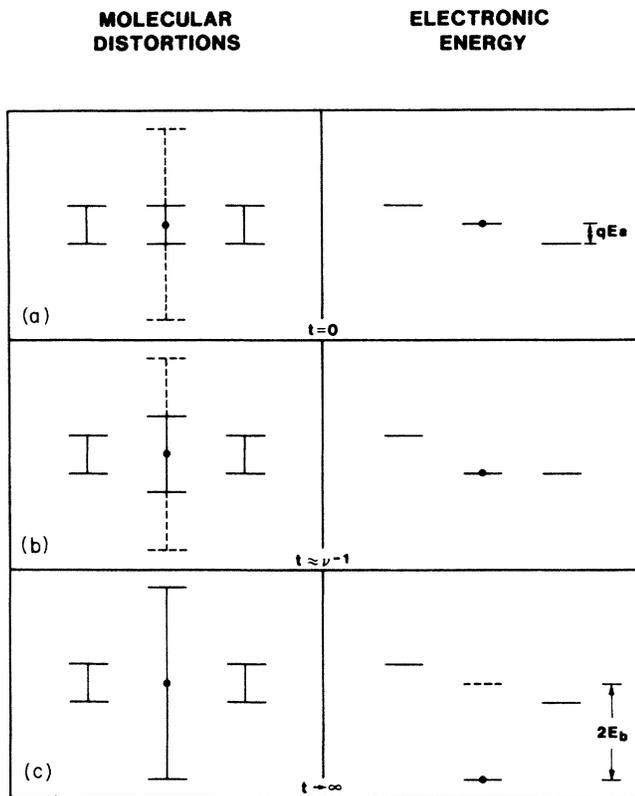


FIG. 1. A schematic representation of the configurational and energetic relaxations which follow the placing of a carrier on the central molecule of a row of three equivalent molecules at $t=0$. The left-hand side depicts the displacements of a configurational coordinate of each of the three molecules from their carrier-free equilibrium positions. The right-hand side depicts the electronic energy levels associated with each of the three molecules in the presence of an electric field of strength E . With the carrier's charge being q and the intermolecular separation being a , the potential energy difference between adjacent molecules is qEa . For simplicity, thermal fluctuations of the molecular distortions and the concomitant energy levels are ignored. (a) illustrates the situation at $t=0$. When the carrier arrives at the central molecule, the molecule is at its carrier-free equilibrium configuration. However, upon arrival of the carrier the equilibrium value of the configurational coordinate of the occupied molecule is displaced to the new value shown by the dashed line. (b) depicts the situation after about one vibrational period, $t \approx 1/\nu$. The configurational coordinate of the occupied molecule has begun to relax toward its equilibrium value. Concomitantly, its electronic energy falls. Here the electronic energy level at $t \approx 1/\nu$ is shown to be in coincidence (degenerate) with that of a neighboring molecule. Hence the carrier has an opportunity to make an activationless transfer to that molecule. (c) shows the fully relaxed (equilibrium) situation. The occupied molecule is displaced to the equilibrium configuration consistent with the presence of the carrier while its electronic energy is reduced by $2E_b$, a value twice the small-polaron binding energy E_b . The dashed energy level in (c) shows the unrelaxed electronic energy level.

More generally, this phenomenon is a manifestation of the fact that, even in the steady state, the hopping motion of a small polaron is often "correlated."³⁻⁶ That is, having made one hop, the probability of another hop before the lattice has relaxed is often very great, ~ 1 . Thus, often one should view small-polaron motion as occurring in flurries. Namely, periods of rapid small-polaron motion involving many hops are followed by dormant periods in which the carrier remains static. In equilibrium, these periods compensate one another to give rise to the average mobility described by Eq. (1). However, an injected carrier initially finds itself in a configuration suitable for rapid motion. Hence, the mobility of injected carriers is initially well above that of steady-state hopping motion. With time, as an increasing fraction of the injected carriers equilibrates, the number of injected carriers which move rapidly decreases. Thus, in a time-of-flight experiment the current of injected carriers will fall with time as the injected carriers equilibrate.

Extrinsic traps can alter this situation somewhat. Namely, traps can serve as centers at which a carrier is confined for a sufficiently long period to allow vibrational relaxation. Thus, we view an injected carrier as moving a mobility $\sim 1 \text{ cm}^2/\text{V sec}$ until it encounters a trap. It remains at the trap long enough for vibrational relaxation to occur. Subsequent release from the trap to a well-localized neighboring state is essentially a hop upwards in energy. Namely, the highest probability release event is associated with the lowest-energy coincidence event between the trap site and an adjacent host site. This is illustrated in Fig. 2. Here the released carrier finds itself on a site which is substantially displaced from its carrier-free configuration. Hence, after release the carrier moves as an equilibrated small polaron.

The bulk of this paper begins, in Sec. II, with a brief description of the molecular-crystal model. Then, in Sec. III, the (time-dependent) jump rate for subsequent hops of a carrier placed on an essentially undeformed molecule is discussed. From this expression we determine, in Sec. IV, the vibrational relaxation time associated with the motion of an injected carrier in our narrow-band molecular crystal. Section V contains a calculation of the probabilities of hops before and after vibrational relaxation has occurred. In Sec. VI these probabilities are utilized to calculate the transient drift current in a constant applied electric field. An estimate of the time characterizing the duration of the transient drift current is contained in Sec. VII. Section VIII contains a description of how carrier-induced changes of the lattice stiffness slow vibrational relaxation and extend the duration of the high-mobility transient drift current. In Sec. IX the role of extrinsic traps is considered. It is argued that, with very long times required for the intrinsic relaxation of the transient current, traps play a major role in confining the carrier for a sufficient period of time to permit vibrational relaxation. Section X provides a qualitative discussion of the transient motion of charge carriers in materials with electronic bands sufficiently wide to provide the "barrier for self-trapping." The essential results are then summarized in Sec. XI.

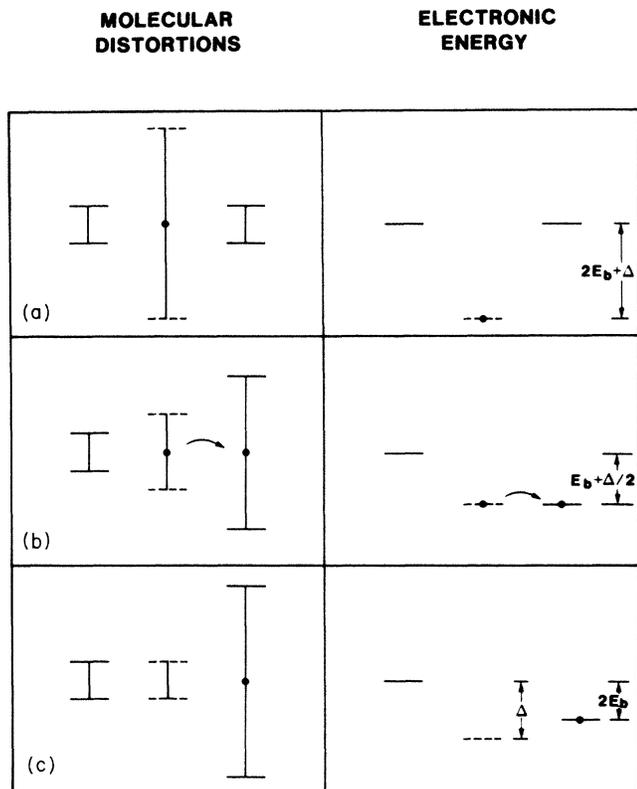


FIG. 2. A schematic illustration of the dominant process for the semiclassical release of a charge carrier from a trap which has equilibrated after capture. The left-hand side of the figure depicts the configurational coordinates of the trap molecule (the central unit of the figure parts) and two molecules of the host solid which are adjacent to it. The right-hand side of the figure shows the electronic energy levels of the trap molecule and its neighboring host molecules for three molecular configurations which sequentially illustrate the semiclassical release process. Our illustration corresponds to a simple model in which the electron-lattice coupling strengths and local stiffnesses of the trap molecule and the host molecules are equal to one another. (a) depicts the equilibrium situation with the carrier in the trap. The presence of the carrier induces an alteration of the equilibrium configuration of the occupied trap. Associated with this polaronic deformation, the electronic energy of the trapped carrier is reduced from its deformation-free value, $-\Delta$, to $-(\Delta + 2E_b)$, where E_b is the small-polaron binding energy. (b) depicts the dominant (lowest energy) coincidence event via which the carrier can be semiclassically released from the trap. Here the configurational coordinate of the trap molecule is reduced, thereby raising the electronic energy level of the trap. In addition, the configurational coordinate of a host molecule is expanded, thereby lowering the electronic energy level of the host molecule. In our model the magnitudes of the distortions of the trap and host molecules equal one another and the electronic energy of the coincidence event is $-(E_b + \Delta/2)$. (c) shows the situation after the carrier has left the trap and equilibrated at an adjacent molecule. The trap molecule returns to its distortion-free configuration with an electronic energy level at $-\Delta$. The carrier forms a small polaron at a host molecule. That host molecule is deformed and the carrier's electronic energy is reduced by $-2E_b$.

II. THE MOLECULAR CRYSTAL MODEL

For definiteness, we consider Holstein's molecular-crystal model.⁷ Using this model we envision an electron added to a regular array of harmonically vibrating molecules. Each molecule is associated with a single configurational coordinate. Namely, the molecule at the g th site is associated with the deformation coordinate x_g . The energy of the carrier-free molecular crystal is

$$E = \sum_g [M\dot{x}_g^2/2 + M\omega_0^2 x_g^2/2 + M\omega_0\omega_b x_g \sum_h \hat{x}_{g+h}], \quad (3)$$

where M and ω_0 are, respectively, the reduced mass and the angular frequency associated with the vibrations of a molecule. The final term provides coupling between the motions of adjacent molecules. As such, it gives rise to dispersion of the vibrational frequencies of the molecular solid. For the narrow band of optical-vibration frequencies considered in this paper, $\omega_b \ll \omega_0$, the eigenfrequencies associated with the k th vibrational model are

$$\omega_k = \omega_0 + (\omega_b/2) \sum_h \cos(\mathbf{k} \cdot \mathbf{h}),$$

where $-\pi \leq \mathbf{k} \cdot \mathbf{h} \leq \pi$.

In a molecular solid the narrow dispersion of the optical-vibrational bands arises because of the relatively weak interaction between the atoms of adjacent molecules. In a simple (nonmolecular) diatomic lattice, weak vibrational dispersion of the optical modes results from a large asymmetry of the atomic masses, m_{light} and m_{heavy} . Here, the relative dispersion $\Delta\omega/\omega_{\text{optical}}$ becomes $m_{\text{light}}/2m_{\text{heavy}}$ for $m_{\text{light}} \ll m_{\text{heavy}}$.

The energy of an electron localized on one of the molecules is taken to be a linear function of the configurational coordinate of that molecule: $E_g = E_g^0 - Ax_g$. Here A is the electron-lattice coupling constant. The presence of an electron on a molecule produces a displacement of the equilibrium value of that molecule's configurational coordinate to $\sim A/M\omega_0^2$.

At sufficiently high temperatures the hopping motion of a small polaron can be described semiclassically. Then a hop is always associated with a momentary equality of the electronic energies associated with adjacent sites, i.e., a coincidence event. For each such coincidence there is a finite probability of a hop between the involved sites. In Holstein's nonadiabatic theory, the probability that a carrier avails itself of the opportunity to hop when there is a coincidence between sites g and $g+h$ is

$$P_{g,g+h} = 2\pi J^2 / \hbar A |v_{g,g+h}|, \quad (4)$$

where $v_{g,g+h}$ is the relative configurational velocity $\dot{x}_g - \dot{x}_{g+h}$ evaluated at the coincidence event.

III. CONDITIONAL HOPPING RATE

We envision an electron injected into a narrow-band molecular crystal and residing on a particular site at $t=0$. We then compute the nonadiabatic rate characterizing a hop to an adjacent site at some later time t . In carrying this out in the Appendix, we follow the occurrence probability technique described in earlier work.^{4,5}

A carrier which arrives at a molecular site which possesses a configurational coordinate equal to x_0 at $t=0$ can then hop to an adjacent site. The rate characterizing a subsequent hop at a time t later is

$$R(x_0, t) = \nu P [1 - G^2(t)/2]^{-1/2} \times \exp \frac{-[4E_A + \Delta + (Ax_0 - 4E_A)G(t)]^2}{16E_A k_B T [1 - G^2(t)/2]}, \quad (5)$$

where

$$G(t) = N^{-1} \sum_{\mathbf{q}} [1 - \cos(\mathbf{q} \cdot \mathbf{h})] \cos(\omega_{\mathbf{q}} t). \quad (6)$$

Here N is the number of molecules of the molecular crystal. Δ is the distortion-independent difference of the electronic energy between initial and final sites. For a hop from site \mathbf{g} to site $\mathbf{g} + \mathbf{h}$, $\Delta = E_{\mathbf{g} + \mathbf{h}}^0 - E_{\mathbf{g}}^0$. In a regular crystal, in the absence of an applied electric field, $\Delta = 0$. In our subsequent discussion, we consider a carrier of charge q hopping between sites of a regular crystal separated by the distance a under the influence of an electric field ($|\Delta| = qEa$). We also consider the capture and release of carriers from traps, $\Delta \neq 0$.

$G(t)$ is called a "relaxation function." For a symmetric system it is independent of the nearest-neighbor position vector \mathbf{h} . The relaxation function is unity at $t=0$ and vanishes as $t \rightarrow \infty$. At long times, $t \rightarrow \infty$, where $G(t)$ vanishes, Eq. (5) reduces to the semiclassical small-polaron jump rate. Thus, regardless of the initial condition (the x_0 value), at sufficiently long times the standard jump-rate expression emerges.

The activation energy of Eq. (5) is readily interpretable at $t=0$, where $G(t=0)=1$. Namely, at $t=0$, the activation energy of Eq. (6) is $(Ax_0 + \Delta)^2 / 8E_A$. Noting that $E_A \approx A^2 / 4M\omega_0^2$ and utilizing the definition of Δ this activation energy is rewritten as

$$(M\omega_0^2/2)[(E_{\mathbf{g} + \mathbf{h}}^0 - E_{\mathbf{g}}^0)/A + x_0]^2.$$

This is the energy which is required to strain site $\mathbf{g} + \mathbf{h}$ so as to form a coincidence with site \mathbf{g} when site \mathbf{g} has a displacement of x_0 . To see this, we note that if site $\mathbf{g} + \mathbf{h}$ were undistorted at $t=0$, the difference between its electronic energy and that of site \mathbf{g} is $E_{\mathbf{g} + \mathbf{h}}^0 - (E_{\mathbf{g}}^0 - Ax_0)$. Thus, to establish coincidence at $t=0$, site $\mathbf{g} + \mathbf{h}$ must be distorted by an amount $[E_{\mathbf{g} + \mathbf{h}}^0 - (E_{\mathbf{g}}^0 - Ax_0)]/A$.

Our concern is with the transient motion of a charge carrier after its injection or creation in a narrow-band ($12J \leq h\nu$) molecular solid. In particular, we consider a

carrier moving between molecules on a time scale which is short compared to that required for significant atomic relaxation (ω_b^{-1}). In this situation, a carrier will generally arrive on a site which experiences only thermal deviations from its carrier-free equilibrium configuration. Thus, it is appropriate to average the rate of Eq. (5) over a Boltzmann distribution of *carrier-free* initial configurations to obtain

$$R(t) = \frac{\int_{-\infty}^{\infty} dx_0 \exp(-M\omega_0^2 x_0^2 / 2k_B T) R(x_0, t)}{\int_{-\infty}^{\infty} dx_0 \exp(-M\omega_0^2 x_0^2 / 2k_B T)} = \nu P \exp(-\{4E_A [1 - G(t)] + \Delta\}^2 / 16E_A k_B T). \quad (7)$$

Here we first note that in the long-time limit, where $G(t)$ vanishes, Eq. (7) reduces to the standard expression for the semiclassical small-polaron jump rate. To discuss the short-time regime, first consider the situation when $\Delta = 0$. Here the transient hopping activation energy of Eq. (7) is $E_A [1 - G(t)]^2$. At very short times, $t \rightarrow 0$, $G(t)$ approaches unity and the activation energy vanishes. This is because a carrier placed on a site which has not yet equilibrated (with the occupied site relaxing about a substantially displaced configurational coordinate) will readily establish a coincidence with a neighboring site which also has not undergone displacement. With $\Delta \neq 0$, the situation changes somewhat. The activation energy vanishes when $G(t) = 1 + \Delta/4E_A$. Thus, the activation energy is never zero for a hop to a state of higher electronic energy, $\Delta > 0$. However, for a hop to a state with lower electronic energy $\Delta < 0$, the activation energy will vanish for $t > 0$. This reflects the propensity of the carrier to hop to a site of lower energy. Indeed, as will be discussed in the following section, as the lattice relaxes there may be numerous zero-activation-energy changes for a carrier to hop downward in energy.

Finally, we note that if one presumes that the molecule upon which the carrier is placed is in the equilibrium associated with the carrier's presence, then the rate averaged over initial configurations, $R(t)$, must be the time-independent equilibrated rate. We confirm that this is so. Namely, in this circumstance, the configurational coordinate of the occupied site is distributed about its displaced value, $A/M\omega_0^2$. Then, averaging over the equilibrium distribution appropriate to an equilibrated occupied site yields the (time-independent) rate previously obtained for an equilibrated system:

$$R(t) = \frac{\int_{-\infty}^{\infty} dx_0 \exp[-M\omega_0^2(x_0 - A/M\omega_0)^2 / 2k_B T] R(x_0, t)}{\int_{-\infty}^{\infty} dx_0 \exp[-M\omega_0^2(x_0 - A/M\omega_0)^2 / 2k_B T]} = \nu P \exp[-(4E_A + \Delta)^2 / 16E_A k_B T]. \quad (8)$$

IV. VIBRATIONAL RELAXATION TIMES

It is evident from the discussion of Eq. (7) that the jump rates for the hopping motion of an injected particle fall with time to those of a small-polaron in an equilibrated system. It is the purpose of this section to determine

the characteristic times associated with these relaxations.

The time dependence of $R(t)$ of Eq. (7) arises from the time dependence of the relaxation function $G(t)$. Thus, determination of the relaxation times requires knowledge of the temporal dependence of $G(t)$. Fortunately, this function has been analyzed previously. It is simply the re-

laxation function associated with a return hop [Eq. (33) of Ref. 4] in the limit of weak vibrational dispersion. Here, we recall the essential features of this function.

The relaxation function $G(t)$ for the molecular-crystal model can generally be written as

$$G(t) = A(\omega_b t) \cos[\omega_0 t - \phi(\omega_b t)]. \quad (9)$$

This function is governed by two distinct time scales. Namely, $G(t)$ oscillates with a frequency ω_0 while its amplitude and phase vary on the time scale $1/\omega_b$. Since $\omega_0 \gg \omega_b$, the amplitude and phase of the oscillations of $G(t)$ change slowly on the scale of the oscillations themselves. The time dependence of the relaxation function amplitude, $A(\omega_b t)$, is of prime interest in our present discussion. Explicit expressions for $A(\omega_b t)$ are presented and plotted in Ref. (5). In essence, with increasing time $A(\omega_b t)$ falls from unity to zero while undergoing oscillations of diminishing amplitude. The rapidity of the decay increases with the dimensionality of the system.

Explicitly, for a vibrational system of dimensionality d ,

$$A(\omega_b t) = |J_0(\omega_b t)|^d - 1 [J_0^2(\omega_b t) + J_1^2(\omega_b t)]^{1/2}, \quad (10)$$

where $J_0(\omega_b t)$ and $J_1(\omega_b t)$ are Bessel functions. Directing our attention to the short-time limit, $\omega_b t \ll 1$, where

$$J_0(\omega_b t) = 1 - (\omega_b t/2)^2, \quad (11)$$

and

$$J_1(\omega_b t) = (\omega_b t/2), \quad (12)$$

we have

$$A(\omega_b t) = 1 - [2(d-1) + 1](\omega_b t)^2/8. \quad (13)$$

Thus, at short times, $\omega_b t \ll 1$, $A(\omega_b t) = 1 - (\omega_b t)^2/8$ for $d=1$, and $A(\omega_b t) = 1 - 5(\omega_b t)^2/8$ for $d=3$. The phase factor $\phi(\omega_b t)$ is independent of dimensionality:

$$\phi(\omega_b t) = \cos^{-1} \{ J_0(\omega_b t) / [J_0^2(\omega_b t) + J_1^2(\omega_b t)]^{1/2} \}. \quad (14)$$

At short times, $\omega_b t \ll 1$, $\phi(\omega_b t) = (\omega_b t/2)$.

To determine the relaxation times, we direct our attention to the transient jump rate, Eq. (7). The temporal dependence enters through the activation energy. In particular, the activation energy for a hop is given by

$$\epsilon_A(t) = \{ 4E_A [1 - G(t)] + \Delta \}^2 / 16E_A.$$

Incorporating the general expression for $G(t)$, Eq. (9), into the hopping activation energy yields

$$\epsilon_A(t) = (4E_A \{ 1 - A(\omega_b t) \cos[\omega_0 t - \phi(\omega_b t)] \} + \Delta)^2 / 16E_A. \quad (15)$$

Over a time scale $\sim 2\pi/\omega_0$ the time-dependent activation energy, $\epsilon_A(t)$, will assume a wide range of values. In each such time interval the activation energy has a minimum at $\cos[\omega_0 t - \phi(\omega_b t)] = 1$. This corresponds to a sharp maximum of the jump rate. Thus, over a longer time interval, $\sim 2\pi/\omega_b$, the activation energy has a series of such minima corresponding to maxima of the jump rate. The heights of these maxima of the jump rate tend to fall with time. These maxima provide the dominant contributions to the jump rate before the activation energy

achieves its fully relaxed time-independent value $(4E_A + \Delta)^2 / 16E_A$. Thus, after the placement of a carrier on an unrelaxed site, the jump rate has a series of peaks at intervals of $\sim 2\pi/\omega_0$. These peaks, corresponding to minima of the time-dependent activation energy, diminish with time as the atoms of the solid relax toward their equilibrium configuration.

We define the relaxation time for a hop to be the time at which the minimum value of the activation energy rises to a value of $k_B T$. Using our expression for $\epsilon_A(t)$, with $\cos[\omega_0 t - \phi(\omega_b t)] = 1$, the relaxation time τ is determined by the relation

$$1 - A(\omega_b \tau) = [(16E_A k_B T)^{1/2} - \Delta] / 4E_A. \quad (16)$$

We direct our attention to the common situation defined by $E_A \gg |\Delta|$ and $E_A \gg k_B T$. In these instances, the time-dependent activation energy $\epsilon_A(t)$ can only achieve values less than $k_B T$ at relatively short times, $\sim 2\pi/\omega_b$. Therefore, we adopt the short-time expression for the relaxation amplitude $A(\omega_b t)$ and write

$$A(\omega_b t) = 1 - \alpha^2 (\omega_b t)^2, \quad (17)$$

where $\alpha^2 = \frac{1}{8}$ for a one-dimensional system and $\alpha^2 = \frac{5}{8}$ for a three-dimensional system. The relaxation time is then given by the relation

$$\tau(\Delta) = (\alpha \omega_b)^{-1} (k_B T / E_A)^{1/4} \times [1 - \Delta / (16E_A k_B T)^{1/2}]^{1/2}. \quad (18)$$

It should be noted that the relaxation time depends on Δ , the electronic energy difference between sites in the absence of atomic displacements. Thus, for hops to states of larger electronic energy, $\Delta > 0$, the relaxation time is reduced. Similarly, for hops to sites of lower electronic energy, $\Delta < 0$, the relaxation time is increased.

V. PROBABILITY OF AN IMMEDIATE HOP

After injection, a carrier will generally make a series of hops involving coincidences for which the initial and final molecules are both near their carrier-free equilibrium values. The probability of making such a hop from site \mathbf{g} to site $\mathbf{g} + \mathbf{h}$ involving the electronic energy difference Δ_h before vibrational relaxation occurs is

$$P(\Delta_h) = \int_0^{\tau(\Delta_h)} dt S(t) R(\Delta_h, t). \quad (19)$$

Here $R(\Delta_h, t)$ is the time-dependent jump rate and $S(t)$ is the survival probability:

$$S(t) = \int_0^t dt' \sum_{\Delta_h} R(\Delta_h, t'). \quad (20)$$

By assuming that hops only occur to unoccupied molecules adjacent to the carrier, the summation only includes all potential near-neighbor hops of the carrier. In general, these hops are to sites with different values of Δ_h .

To evaluate these formulas we adopt a simple model which displays the essential physics. We represent the jump rate as

$$R(\Delta_h, t) = \begin{cases} (\omega_0/2\pi) P = R_0, & \text{for } t < \tau(\Delta_h) \\ R(\Delta_h, \infty) = R_\infty, & \text{for } t \geq \tau(\Delta_h). \end{cases} \quad (21a)$$

$$R(\Delta_h, \infty) = R_\infty, \quad \text{for } t \geq \tau(\Delta_h). \quad (21b)$$

For simplicity, we consider a one-dimensional molecular crystal with an applied electric field E in the easy direction. Hops encouraged by the application of the electric field are said to be in the "forward" direction with $\Delta = -qEa < 0$. The relaxation time associated with forward hops is designated as τ_f . Similarly, hops discouraged by the application of the electric field are said to be in the "backward" direction with $\Delta = qEa > 0$. The relaxation time associated with such hops is designated as τ_b . Since more vibrational relaxation must occur to preclude an "immediate" hop to a site of lower electronic energy than to preclude an immediate hop to a site of higher electronic energy, $\tau_f > \tau_b$. Thus, immediate hops in the forward direction are favored.

Utilization of Eqs. (19) and (20) along with the model described in Eqs. (21a) and (21b) and accompanying text, straightforwardly yields expressions for the probabilities of immediate backward and forward hops, P_b and P_f , respectively:

$$P_b = [1 - \exp(-2R_0\tau_b)]/2, \quad (22a)$$

$$P_f = [1 - \exp(-2R_0\tau_b)]/2 + [R_0/(R_0 + R_\infty)] \exp(-2R_0\tau_b) \times \{1 - \exp[-(R_0 + R_\infty)(\tau_f - \tau_b)]\}. \quad (22b)$$

In the limit of the applied electric field being small, $\tau_f \rightarrow \tau_b$, Eq. (22b) becomes

$$P_f = [1 - \exp(-2R_0\tau_b)]/2 + [R_0(\tau_f - \tau_b)] \exp(-2R_0\tau_b). \quad (23)$$

We also utilize the general expression for τ , Eq. (18), to find (the lowest-order nonvanishing) expressions for τ_b and $\tau_f - \tau_b$ in the limit of small electric fields, $|\Delta| \rightarrow 0$:

$$\tau_b = (\alpha\omega_b)^{-1} (k_B T / E_A)^{1/4}, \quad (24)$$

$$\tau_f - \tau_b = (4\alpha\omega_b)^{-1} [|\Delta| / 4(E_A^3 k_B T)^{1/4}]. \quad (25)$$

We can now combine these results to write the total probability of an immediate hop, $P_f + P_b$, and the difference between the probabilities of forward and backward hops, $P_f - P_b$:

$$P_f + P_b = 1 - \exp[-2(\omega_0/2\pi)(\alpha\omega_b)^{-1} P(k_B T / E_A)^{1/4}], \quad (26a)$$

$$P_f - P_b = (\omega_0/2\pi) P(4\alpha\omega_b)^{-1} [|\Delta| / 4(E_A^3 k_B T)^{1/4}] \times \exp[-2(\omega_0/2\pi)(\alpha\omega_b)^{-1} P(k_B T / E_A)^{1/4}]. \quad (26b)$$

Finally, we note that dimensionality and the associated local coordination enter into our calculation in two ways. First, vibrational relaxation depends on dimensionality through the factor α , e.g., in a simple cubic lattice $\alpha(3d)/\alpha(1d) = \sqrt{3}$. Second, the coordination affects the survival probability via the number of channels by which a carrier can hop from a site. For example, the fact that a site in a linear chain has two nearest neighbors accounts for the first factor of 2 in the argument of the exponential in Eqs. (26a) and (26b). In a system with six nearest

neighbors (e.g., a simple cubic arrangement of sites), this factor will be multiplied by three. Thus, the numerical factors in the exponential have only a weak dependence on dimensionality. Namely, passing from a one-dimensional model to a three-dimensional model only introduces a factor of $3/\sqrt{3}$ in the exponential.

VI. TRANSIENT CURRENT

In this section we calculate the transient current associated with the hopping of injected carriers in a spatially and temporally constant electric field. We consider carriers that are created in the bulk of the one-dimensional molecular-crystal model at $t=0$. There is relatively rapid motion of carriers between molecules before the occupied molecules relax to the equilibrium configurations commensurate with their occupation. Once a carrier remains on a molecule sufficiently long so that the molecule adjusts to its occupation, the intermolecular jump rate of the carrier is greatly reduced. We regard such slow-moving (equilibrated) carriers as essentially static. We ignore their contribution to the transient current.

In modeling this situation, we describe the transient motion in terms of immediate hops. Immediate hops occur sufficiently rapidly that a molecular site which becomes occupied is unable to relax significantly toward its carrier-induced equilibrium configuration before the carrier hops to another site. There are three probabilities of interest to us.

(1) P_f is the probability that a carrier placed on an undeformed site immediately hops in the forward (energetically preferred) direction to an essentially undeformed neighboring site of lower energy.

(2) P_b is the probability that a carrier placed on an undeformed site immediately hops in the "backward" (energetically unfavorable) direction to an essentially undeformed neighboring site of higher energy.

(3) The probability that a carrier placed on an undeformed site does not hop before the occupied molecule relaxes to its equilibrium configuration is $1 - P_f - P_b$.

We begin by noting that $P_f/(P_f + P_b)$ is the fraction of immediate hops which are in the forward direction. Similarly, $P_b/(P_f + P_b)$ is the fraction of immediate hops which are in the backward direction. Thus, the net average displacement after N successive immediate hops is

$$l = Na[(P_f - P_b)/(P_f + P_b)], \quad (27)$$

where a is the intermolecular separation. We now write the number of immediate hops N as the ratio of the time t to the characteristic time for an immediate hop, t_{hop} ($\sim \nu P$) $^{-1}$: $N = t/t_{\text{hop}}$. Then the velocity associated with immediate hopping motion, $v = dl/dt$, is given by

$$v = (a/t_{\text{hop}})[(P_f - P_b)/(P_f + P_b)]. \quad (28)$$

We note that the probability of making an immediate hop is $P_f + P_b$. Thus $(P_f + P_b)^N$ is the probability of making N successive immediate hops. Since there is a finite probability of an occupied site relaxing before the carrier can hop away, i.e., $P_f + P_b < 1$, there is a vanishing probability of making an infinite number of successive immediate hops: $\lim_{N \rightarrow \infty} (P_f + P_b)^N \rightarrow 0$. Reexpressing N

in terms of time divided by the mean time between immediate hops, $N = t/t_{\text{hop}}$, we find that the number of carriers which are making immediate hops falls exponentially with time, i.e., as $\exp[(t/t_{\text{hop}})\ln(P_f + P_b)]$. Thus, the transient current (the product of the number of transient carriers, their individual charge q , and their velocity) is given by

$$I(t) = n(0)q(a/t_{\text{hop}})[(P_f - P_b)/(P_f + P_b)] \times \exp[(t/t_{\text{hop}})\ln(P_f + P_b)], \quad (29)$$

where $n(0)$ is the initial density of charge carriers.

VII. NUMERICAL ESTIMATES: LONG RELAXATION TIMES

At this point it is useful to estimate the characteristic number of successive immediate hops which occur before relaxation:

$$N_{\text{relax}} = -1/\ln(P_f + P_b). \quad (30)$$

Inserting our expression for $P_f + P_b$, Eq. (26a), into Eq. (30) we obtain

$$N_{\text{relax}} = -1/\ln\{1 - \exp[-2(\omega_0 P / 2\pi\alpha\omega_b)(k_B T / E_A)^{1/4}]\}. \quad (31)$$

A molecular solid with an extremely narrow electronic bandwidth, $P \ll 1$, and a molecular solid with a wider electronic energy band, $P \approx 1$, represent two limits of Eq. (31).

In the narrow-band case Eq. (31) reduces to

$$N_{\text{relax}} = -1/\ln[2(\omega_0 P / 2\pi\alpha\omega_b)(k_B T / E_A)^{1/4}]. \quad (32)$$

Hence, as $P \rightarrow 0$, $N_{\text{relax}} \rightarrow 0$. Thus, if the intermolecule hopping motion is slow enough, a carrier will reside on a molecule for a sufficient period of time for that molecule to equilibrate about its carrier-induced deformed configuration. That is, the carrier will make no immediate hops. Writing the nonadiabaticity condition $P \ll 1$ in terms of the electronic bandwidth parameter J [via Eq. (2) with $\nu = \omega_0/2\pi$], we see that this domain typically requires extremely narrow electronic bandwidths:

$$J \ll (\hbar\omega_0/2\pi)^{1/2}(4E_A k_B T)^{1/4}. \quad (33)$$

For example, with $\hbar\omega_0 = k_B T = 2.5 \times 10^{-2}$ eV and $E_A = 0.2$ eV, the electronic bandwidth parameter J ($\frac{1}{12}$ of the electronic bandwidth of a cubic material) must be $\ll 2.4 \times 10^{-2}$ eV.

With a wide enough electronic bandwidth so that $P \approx 1$, the argument of the exponential factor of Eq. (31) is sufficiently large that Eq. (31) may be rewritten as

$$N_{\text{relax}} = \exp[(\omega_0 P / \pi\alpha\omega_b)(k_B T / E_A)^{1/4}]. \quad (34)$$

In these instances N_{relax} is generally much larger than unity. For example, taking $E_A = 0.2$ eV, $k_B T = 2.5 \times 10^{-2}$ eV, $P = 1$, recalling that $\alpha = 1/\sqrt{8}$ yields $N_{\text{relax}} \approx \exp(\omega_0/2\omega_b)$. With a narrow, yet physically reasonable, optical bandwidth ($6\omega_b$ in a cubic lattice) for a molecular solid of $\omega_0/10$, we have $N_{\text{relax}} \sim 10^{13}$. In other terms, with the characteristic time between immediate

hops being $\sim 1/\nu$, this corresponds to a relaxation time for the transient current of ~ 1 sec. Therefore, it is clear that the time associated with the intrinsic relaxation of the transient current in an ideal narrow-band molecular solid can be comparable with experimental observation times. Indeed, the long relaxation times estimated here suggest that relaxation of a transient current on a time scale comparable to observation times (10^{-12} – 10^{-3} sec) can be a general feature of a much broader range of condensed matter where the vibrational dispersion is not so small.

VIII. CARRIER-INDUCED VIBRATIONAL LOCALIZATION INCREASES RELAXATION TIMES

To this point, our discussion has ignored another physical effect which acts to further increase the relaxation time. Namely, the molecular-crystal model described in Sec. II has a carrier inducing a shift of the equilibrium configuration of an occupied model. In addition, the presence of a carrier also generally alters the stiffness of the occupied molecule. This effect corresponds to the presence of a quadratic component of the electron-lattice interaction.

The addition of a carrier to a molecule typically produces a shift of about 10% in the molecule's vibrational frequencies. Since this shift is comparable to, or greater than, the vibrational dispersion in molecular solids, the presence of the charge carrier can induce local vibrational modes. In this circumstance the vibrations of the occupied molecule tend to decouple from the remaining (unoccupied) molecules. As a result, the lattice relaxation is slowed further.

While it is not our intent to discuss this phenomenon in depth, we do want to indicate its potential importance. For this purpose, we cite the results of studying the classical dynamics of two coupled harmonic oscillators with frequencies which differ by δ .

Consider displacing one of the oscillators. With time, some fraction of the displacement is transferred to the neighboring oscillator. The fraction of the initial displacement which remains with the initially displaced oscillator depends upon the frequency mismatch relative to the vibrational dispersion parameter, ω_b . In particular, the ratio of the minimum vibrational energy which remains at the initially displaced site to the initial vibrational energy of the site is $\delta^2/(\delta^2 + \omega_b^2)$. As is well known, with no frequency mismatch ($\delta = 0$) the energy transfer is complete; the above ratio is zero. However, with a sizable energy mismatch, $\delta^2 \gg \omega_b^2$, the vibrational energy tends to remain at the initially displaced site; the ratio approaches unity.

Thus, the carrier-induced localization of vibrational energy, due to the quadratic component of the electron-lattice interaction, will significantly slow atomic relaxation at an occupied site. This will further prolong the duration of relatively rapid immediate hopping motion associated with the creation of small polarons.

IX. EXTRINSIC TRAPPING AND EQUILIBRATION

We have seen that the current relaxation times for immediate small-polaron hopping in an ideal molecular crys-

tal can be very long. Thus, in such instances, the charge carriers have ample opportunity to encounter traps of extrinsic origin before undergoing intrinsic relaxation. For example, using the standard formula for the trapping time,

$$1/t_{\text{trap}} = 4\pi DR_{\text{trap}}N_{\text{trap}}, \quad (35)$$

and associating the transient (immediate) small-polaron hopping motion with a diffusion constant of $D=va^2$, we have

$$1/t_{\text{trap}} = 4\pi va^2 R_{\text{trap}} N_{\text{trap}}, \quad (36)$$

where R_{trap} is the capture radius of the trap and N_{trap} is the density of traps. Here a density of traps of 10^{13} cm^{-3} with a trapping radius equal to a ($\sim 10^{-7} \text{ cm}$) and a vibrational frequency of $6 \times 10^{12} \text{ sec}^{-1}$ yields a trapping time $\sim 10^{-6} \text{ sec}$. This is far shorter than the intrinsic relaxation time of 1 sec calculated in Sec. VII for the transient motion of small polarons in a molecular solid. Thus, we see that since intrinsic relaxation is very slow, extrinsic trapping may play an essential role in the equilibration of injected carriers.

However, a trap can only be effective in the equilibration of an injected small polaron if (1) the carrier actually enters the trap, and (2) the carrier is not rapidly ejected from it. We now address these questions.

The initial amplitude of vibration of a molecule induced by placing a carrier on an undeformed molecule is $\sim A/M\omega_0^2$, where A is the electron-lattice coupling force. Thus, the electronic energy level of the occupied molecule samples a range of energies $\sim 2A(A/M\omega_0^2) \approx 8E_A$ immediately after the molecule is occupied. This is generally a very wide energy range since typical values of E_A , the steady-state activation energy for small-polaron hopping, lie between 0.1 and 1.0 eV. Thus, after occupying a molecule adjacent to a trap level, one expects a coincidence event between the occupied molecule and a trap level. Given such a coincidence, it is reasonable to expect easy capture.

With a carrier well localized on a trap, the equilibrium positions of the atoms at and surrounding the trap will adjust to the carrier's presence. In direct analogy with our considerations of vibrational relaxation on a newly occupied molecule, occupation of a trap by a carrier initially places the trap in a vibrationally agitated state. An immediate escape from the trap will correspond to an immediate small-polaron hop to a site of higher energy. However, as shown by Eq. (18), the relaxation time for a hop depends upon whether the hop is to a state of higher or lower electronic energy (e.g., whether Δ is positive or negative). Namely, the relaxation time for a hop, $\tau(\Delta)$, is reduced as the final-state energy is increased. As a result, the probability of an immediate release diminishes as the trap depth increases. For example, if the values of Δ associated with hopping out of a trap are greater than $(16E_A k_B T)^{1/2}$, [c.f. Eq. (18)] the relaxation time for these hops will vanish. Then, the probability of an immediate release from the trap, as defined in our model (Sec. V), vanishes.

Thus, these considerations imply that extrinsic trap sites will play an essential role in the relaxation of the rel-

atively rapid transient hopping motion of small polarons in materials with narrow electronic energy bands. Namely, an injected carrier will typically diffuse via a succession of immediate (nearly activationless) hops between adjacent sites until it encounters a trap. Upon occupying the site, the carrier will remain there long enough for lattice relaxation to occur. As described in Sec. I surrounding Fig. 2, release corresponds to a thermally activated hop to a higher-energy electronic state. Here the carrier hops to a deformed site rather than the basically undeformed site characteristic of one from which an immediate hop is possible. Thus, the subsequent motion of the carrier will be via thermally activated hopping. Its hopping may be correlated, wherein hops will occur in flurries followed by dormant periods. Nonetheless, on average the jump rate of a carrier will be the thermally activated jump rate that characterizes the hopping motion of an equilibrated small polaron, Eq. (1).

X. DELAYED LOCALIZATION: WIDE-BAND MATERIALS

In materials with sufficiently wide electronic energy bands, a carrier which finds it energetically favorable to self-trap to form a small polaron can exist metastably in a delocalized state.⁸⁻¹¹ Then, since extreme localization is at the expense of increasing the carrier's kinetic energy, there is an "energy barrier to self-trapping." In particular, an adiabatic treatment of an excess electron in a three dimensional deformable continuum yields a barrier height proportional to J^3/E_A^2 .¹⁰ Thus, in wide-band materials with self-trapping, an injected carrier will be delocalized and move itinerantly until the barrier is negotiated. This involves an appropriate confluence of atomic displacements providing a suitable center at which to localize. The time that characterizes the localization of the carrier is called the "time delay for self-trapping."¹¹ Analogously, the severe localization of an itinerant charge carrier at a point defect or impurity in a wide-band material is associated with negotiating an energy barrier to trapping. This provides a time delay for its capture.^{10,12}

For semiclassical capture or self-trapping in these instances, the lattice must assume a deformed configuration in order to create a "coincidence" configuration. The slow relaxation of the lattice from this deformed configuration can provide opportunities for a carrier to be "immediately" released from the time-varying wells associated with either self-trapping or capture at an extrinsic trap. Namely, following the coincidence associated with the capture, there will be a series of residual coincidences or near coincidences which provide opportunities for release. Here immediate release is analogous to the immediate hopping we have been addressing in this paper.

In particular, semiclassical self-trapping or trapping at a deep (noncoulombic) center in a wide-band material can be understood as proceeding via a series of steps. For definiteness, we consider the self-trapping scenario. An injected carrier will remain quasifree until there is a sufficient deformation about some site so that the electronic energy level associated with the concomitant localized state is coincident with the electronic energy of the itinerant carrier. Then, there is some probability (analo-

gous to P) of the itinerant carrier transferring to the localized state. Once such a transfer occurs, the atoms surrounding the self-trapping site will relax toward the equilibrium configuration consistent with the presence of the self-trapped carrier. However, there is a tendency for a coincidence event to repeat itself before full relaxation occurs. These repeated coincidences (or near coincidences) provide opportunities for the nonactivated immediate escape of the carrier.

The probability of a carrier availing itself of the opportunity to escape, P , is essentially equal to the probability factor which enters into its capture. If it is sufficiently large, capture will often be followed by release. That is, self-trapping will be inefficient. Then an injected carrier will suffer many such near-self-trapping events before actual self-trapping occurs. The motion of such a carrier will be itinerant modified by occasional brief "near-capturing" events which last about $1/\nu$. Thus, a transient measurement at short enough times will find the carrier to be itinerant.

If P is sufficiently small, the probability of a carrier availing itself of the coincidence event and being captured is relatively small. Concomitantly, the probability of immediate release is small. That is, for a given rate of forming coincidence configurations, capture and release are relatively rare. Thus, this regime is analogous to the rapid-relaxation regime $P \ll 1$ of our narrow-band results.

Thus, we see that the basic physical ingredients of our treatment of the immediate hopping of a carrier injected into a narrow-band molecular solid also apply to self-trapping (and trapping by a defect or impurity) in a wide-band solid. In these instances, rather than executing immediate hops before relaxation, the carrier leaves its self-trapping (or trapping) site and executes itinerant motion. The fundamental mechanism for the immediate hopping of a carrier in a narrow-band molecular solid is the same as that for immediate release from a self-trapping (or trapping) site. Namely, before relaxation is completed, the coincidence configuration associated with the carrier's self-trapping (or trapping) tends to repeat. This provides athermal opportunities for the release of the carrier from the confining site. Thus, the physical phenomenon is a general one which is only inoperative when the capture and release probabilities are very small, $P \ll 1$, or the lattice relaxation is rapid.

XI. SUMMARY

We have considered the transient motion of a charge carrier injected into a narrow-band molecular solid in which it is energetically favorable for the carrier to self-trap to form a small polaron. Due to the solid's narrow electronic band, an injected carrier finds itself localized at a particular molecular site. Associated with the carrier being confined to a single molecule, the equilibrium positions of the atoms of the occupied molecule are altered. The shifting of the equilibrium positions of a molecule's atoms with its occupation provides an impulse to the vibrations of the occupied molecule. That is, immediately upon placement of a carrier upon it, the molecule is vibrationally agitated. These carrier-induced athermal vibra-

tions generate opportunities for immediate nonactivated motion to adjacent molecules. With a jump time of the order of a vibrational period, the mobility associated with such motion is $qva^2/k_B T$, $\sim 1 \text{ cm}^{-2}/\text{V sec}$ near room temperature. However, once the carrier remains at a site long enough for the vibrational motion of the occupied molecule to equilibrate, the mobility will garner an additional thermally activated factor. This factor reflects the necessity of the molecules involved in a hop accumulating sufficient vibrational energy from the thermal bath of the system's vibrations so as to establish a coincidence event.

We determine the duration of the intrinsic nonactivated transient motion in an ideal narrow-band molecular solid with one intramolecular vibrational mode, Holstein's molecular crystal model. (The situation of multiple intramolecular vibrational modes is to be addressed in another paper.) We find that the initial relatively rapid nonactivated hopping can persist for times which are even longer than typical observational times. However, we observe that a carrier at a trap has a larger probability of equilibrating than a carrier at an intrinsic site in a perfect lattice. Thus, equilibration in real systems may frequently be governed by capture at extrinsic centers.

Finally, we note that similar situations can occur in systems with wider electronic energy bands. Then, a carrier which finds itself in the vibrationally excited environment which characterizes self-trapping or capture by a deep trap can be expelled from the localized center. This occurs when the conditions associated with its localization are essentially duplicated before vibrational relaxation takes place. In other words, after encountering a trapping center, a carrier has a high probability of escape before lattice relaxation occurs. Thus, the transient motion of injected charge carriers is characterized by the persistence of the itinerant motion characteristic of injected carriers which are neither trapped nor self-trapped.

The pivotal physical element of the phenomenon we discuss is the slow relaxation of localized regions of vibrationally excited atoms. In particular, we are concerned with circumstances in which there is little dispersal of vibrational energy over times of the order of a vibrational period. With the very weak vibrational dispersion characteristic of their intramolecular vibrational modes, intramolecular vibrational excitations in molecular solids are the epitome of this circumstance.

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APPENDIX: OCCURRENCE PROBABILITY CALCULATIONS

We envision an electron being placed on the g th molecule of a narrow-band molecular crystal at $t=0$. We then compute the nonadiabatic rate characterizing a hop to an

adjacent molecule located at $\mathbf{g} + \mathbf{h}$ at some later time t .

(1) To do this, we first compute the probability of a coincidence between site \mathbf{g} and an adjacent site, $\mathbf{g} + \mathbf{h}$, occurring with a relative configurational coordinate velo-

city between $v_{\mathbf{g},\mathbf{g}+\mathbf{h}}$ and $v_{\mathbf{g},\mathbf{g}+\mathbf{h}} + dv_{\mathbf{g},\mathbf{g}+\mathbf{h}}$ between times t and $t + dt$ when the configurational coordinate of the \mathbf{g} th site assumes a value of x_0 with a configurational velocity between v_0 and $v_0 + dv_0$ between times 0 and dt_0 :

$$P(x_0, v_0; v_{\mathbf{g},\mathbf{g}+\mathbf{h}}, t) dt dv_{\mathbf{g},\mathbf{g}+\mathbf{h}} dt_0 dv_0 = Z^{-1} \int \cdots dx_{\mathbf{g}'} \cdots \times \int \cdots dv_{\mathbf{g}'} \cdots \int e^{-E/k_B T} \times \delta(x_{\mathbf{g}}(t) - x_{\mathbf{g}+\mathbf{h}}(t) + \Delta/A) |v_{\mathbf{g},\mathbf{g}+\mathbf{h}}| dt \times \delta(v_{\mathbf{g}}(t) - v_{\mathbf{g}+\mathbf{h}}(t) - v_{\mathbf{g},\mathbf{g}+\mathbf{h}}) dv_{\mathbf{g},\mathbf{g}+\mathbf{h}} \times \delta(x_{\mathbf{g}}(0) - x_0) |v_0| dt_0 \delta(v_{\mathbf{g}}(0) - v_0) dv_0. \quad (\text{A1})$$

Here $\Delta = E_{\mathbf{g}+\mathbf{h}}^0 - E_{\mathbf{g}}^0$ (the distortion-independent difference of the electronic energy between molecules at sites \mathbf{g} and $\mathbf{g} + \mathbf{h}$); Z is the partition function

$$Z = \int \cdots dx_{\mathbf{g}'} \cdots \int \cdots dv_{\mathbf{g}'} \cdots \int e^{-E/k_B T}, \quad (\text{A2})$$

and, as described in Sec. II, E is the energy of the system when the carrier is localized on site \mathbf{g} with $E_{\mathbf{g}}^0 = 0$:

$$E = \sum_{\mathbf{g}'} [Mv_{\mathbf{g}'}^2/2 + M\omega_0^2/2 + M\omega_0\omega_b x_{\mathbf{g}'} \sum_{\mathbf{h}} x_{\mathbf{g}'+\mathbf{h}}] - Ax_{\mathbf{g}}. \quad (\text{A3})$$

It is useful to employ the Fourier-integral formula for the δ functions:

$$\delta(z) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\alpha \exp(-i\alpha z). \quad (\text{A4})$$

Then

$$P(x_0, v_0; v_{\mathbf{g},\mathbf{g}+\mathbf{h}}, t) = (2\pi)^{-4} Z^{-1} |v_{\mathbf{g},\mathbf{g}+\mathbf{h}}| |v_0| \int_{-\infty}^{\infty} d\alpha \int_{-\infty}^{\infty} d\beta \int_{-\infty}^{\infty} d\gamma \int_{-\infty}^{\infty} d\delta \int \cdots dx_{\mathbf{g}'} \cdots \int \cdots dv_{\mathbf{g}'} \cdots \times \int e^{-E/k_B T} \exp(-i\{\alpha[x_{\mathbf{g}}(t) - x_{\mathbf{g}+\mathbf{h}}(t) + \Delta/A] + \beta[v_{\mathbf{g}}(t) - v_{\mathbf{g}+\mathbf{h}}(t) - v_{\mathbf{g},\mathbf{g}+\mathbf{h}}] + \gamma[x_{\mathbf{g}}(0) - x_0] + \delta[v_{\mathbf{g}}(0) - v_0]\}). \quad (\text{A5})$$

At this point we introduce the normal coordinates for the vibrational motion via the transformation:

$$x_{\mathbf{g}}(t) = (2/N)^{1/2} \sum_{\mathbf{k}} [q'_{\mathbf{k}} + Q_{\mathbf{k}} \cos(\omega_{\mathbf{k}} t + \delta_{\mathbf{k}})] \sin(\mathbf{k} \cdot \mathbf{g} + \pi/4), \quad (\text{A6})$$

where \mathbf{k} is the phonon wave vector and the carrier-induced displacement of the \mathbf{k} th vibrational mode is

$$q'_{\mathbf{k}} = (2/N)^{1/2} (A/M\omega_{\mathbf{k}}^2) \sin(\mathbf{k} \cdot \mathbf{g} + \pi/4). \quad (\text{A7})$$

In terms of the normal coordinates the system's energy is given by

$$E = \sum_{\mathbf{k}} M\omega_{\mathbf{k}}^2 Q_{\mathbf{k}}^2/2 - E_b, \quad (\text{A8})$$

where the small-polaron binding energy is given by

$$E_b = (1/N) \sum_{\mathbf{k}} A^2/2M\omega_{\mathbf{k}}^2, \quad (\text{A9})$$

and the phonon dispersion relation in the weak-dispersion limit ($\omega_b \ll \omega_0$) is (cf. Sec. II)

$$\omega_{\mathbf{k}} = \omega_0 + (\omega_b/2) \sum_{\mathbf{h}} \cos \mathbf{k} \cdot \mathbf{h}. \quad (\text{A10})$$

We then have

$$P(x_0, v_0; v_{\mathbf{g},\mathbf{g}+\mathbf{h}}, t) = (2\pi)^{-4} |v_{\mathbf{g},\mathbf{g}+\mathbf{h}}| |v_0| \int_{-\infty}^{\infty} d\alpha \int_{-\infty}^{\infty} d\beta \int_{-\infty}^{\infty} d\gamma \int_{-\infty}^{\infty} d\delta \exp[i(-\alpha\Delta/A + \beta v_{\mathbf{g},\mathbf{g}+\mathbf{h}} + \gamma x_0 + \delta v_0)] \times \prod_{\mathbf{k}} (M\omega_{\mathbf{k}}^2 Q_{\mathbf{k}}/k_B T) \int_0^{\infty} dQ_{\mathbf{k}} \exp(-M\omega_{\mathbf{k}}^2 Q_{\mathbf{k}}^2/2k_B T) (2\pi)^{-1} \int_0^{2\pi} d\delta_{\mathbf{k}} \times \exp\{-i\alpha[q'_{\mathbf{k}} + Q_{\mathbf{k}} \cos(\omega_{\mathbf{k}} t + \delta_{\mathbf{k}})] G_{\mathbf{k}}^{\mathbf{g},\mathbf{g}+\mathbf{h}}\} \exp\{-i\beta[-\omega_{\mathbf{k}} Q_{\mathbf{k}} \sin(\omega_{\mathbf{k}} t + \delta_{\mathbf{k}})] G_{\mathbf{k}}^{\mathbf{g},\mathbf{g}+\mathbf{h}}\} \times \exp\{-i\gamma[q'_{\mathbf{k}} + Q_{\mathbf{k}} \cos(\delta_{\mathbf{k}})] (2/N)^{1/2} \sin(\mathbf{k} \cdot \mathbf{g} + \pi/4)\} \times \exp\{-i\delta[-\omega_{\mathbf{k}} Q_{\mathbf{k}} \sin(\delta_{\mathbf{k}})] (2/N)^{1/2} \sin(\mathbf{k} \cdot \mathbf{g} + \pi/4)\}, \quad (\text{A11})$$

where the partition function has been explicitly calculated and

$$G_{\mathbf{k}}^{\mathbf{g}, \mathbf{g}+\mathbf{h}} = (2/N)^{1/2} \{ \sin(\mathbf{k} \cdot \mathbf{g} + \pi/4) - \sin[\mathbf{k} \cdot (\mathbf{g} + \mathbf{h}) + \pi/4] \}. \quad (\text{A12})$$

Noting that $q_{\mathbf{k}}'$ is proportional to $N^{-1/2}$, we expand the exponentials keeping terms up to order $1/N$. Higher-order terms are inconsequential since they vanish in the limit of an infinite volume, $N \rightarrow \infty$. The integrals over the $\delta_{\mathbf{k}}$'s and $Q_{\mathbf{k}}$'s are then elementary. Carrying out these integrations yields

$$P(x_0, v_0; v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}, t) = (2\pi)^{-4} |v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}| |v_0| \times \int_{-\infty}^{\infty} d\alpha \int_{-\infty}^{\infty} d\beta \int_{-\infty}^{\infty} d\gamma \int_{-\infty}^{\infty} d\delta \exp(-i\alpha c_1 - i\gamma c_2 - \alpha^2 c_3 - \beta^2 c_4 - \gamma^2 c_5 - \delta^2 c_6 - \alpha\gamma a - \alpha\delta b + \beta\gamma b - \beta\delta c), \quad (\text{A13})$$

where, after some elementary manipulations of the trigonometric functions, one has

$$c_1 = (1/N) \sum_{\mathbf{k}} (A/M\omega_{\mathbf{k}}^2) [1 - \cos(\mathbf{k} \cdot \mathbf{h})] = 4E_A/A, \quad (\text{A14})$$

$$c_2 = 2E_b/A, \quad (\text{A15})$$

$$c_3 = (k_B T/A) c_1, \quad (\text{A16})$$

$$c_4 = k_B T/M, \quad (\text{A17})$$

$$c_5 = (k_B T/2A) c_2, \quad (\text{A18})$$

$$c_6 = k_B T/2M, \quad (\text{A19})$$

$$a = (k_B T/NM) \sum_{\mathbf{k}} \omega_{\mathbf{k}}^{-2} [1 - \cos(\mathbf{k} \cdot \mathbf{h})] \cos(\omega_{\mathbf{k}} t), \quad (\text{A20})$$

$$b = (k_B T/NM) \sum_{\mathbf{k}} \omega_{\mathbf{k}}^{-1} [1 - \cos(\mathbf{k} \cdot \mathbf{h})] \sin(\omega_{\mathbf{k}} t), \quad (\text{A21})$$

$$c = (k_B T/NM) \sum_{\mathbf{k}} [1 - \cos(\mathbf{k} \cdot \mathbf{h})] \cos(\omega_{\mathbf{k}} t). \quad (\text{A22})$$

In the limit of weak vibrational dispersion these expressions can be simplified by replacing $\omega_{\mathbf{k}}$ by ω_0 in algebraic factors while retaining $\omega_{\mathbf{k}}$ in the time-dependent factors. Then $c_1 = c_2 = 4E_A/A$, $a = c/\omega_0^2 = (k_B T/M\omega_0^2)G(t)$ and $b = (k_B T/M\omega_0)F(t)$, where

$$G(t) = (1/N) \sum_{\mathbf{k}} [1 - \cos(\mathbf{k} \cdot \mathbf{h})] \cos(\omega_{\mathbf{k}} t), \quad (\text{A23})$$

and

$$F(t) = (1/N) \sum_{\mathbf{k}} [1 - \cos(\mathbf{k} \cdot \mathbf{h})] \sin(\omega_{\mathbf{k}} t). \quad (\text{A24})$$

Evaluating the α , β , γ , and δ integrals (which are all Gaussian integrals) and passing to the weak-dispersion limit, we obtain

$$P(x_0, v_0; v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}, t) = |v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}| |v_0| (4\pi)^{-2} [c_3 c_4 (c_5 - a^2/4c_3 - b^2/4c_4)(c_6 - b^2/4c_3 - c^2/4c_4)]^{-1/2} \times \exp\{-v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}^2/4c_4 - (c_1 + \Delta/A)^2/4c_3 - [a(c_1 + \Delta/A)^2/2c_3 + bv_{\mathbf{g}, \mathbf{g}+\mathbf{h}}/2c_4 + (x_0 - c_2)]^2/4(c_5 - a^2/4c_3 - b^2/4c_4) - [v_0 + b(c_1 + \Delta/A)/2c_3 - cv_{\mathbf{g}, \mathbf{g}+\mathbf{h}}/2c_4]^2/4(c_6 - b^2/4c_3 - c^2/4c_4)\}. \quad (\text{A25})$$

(2) We now compute the probability that the configurational coordinate of the molecular at site \mathbf{g} , $x_{\mathbf{g}}$, assumes the value x_0 with a configurational velocity between v_0 and $v_0 + dv_0$ between times 0 and dt_0 :

$$P_0(x_0, v_0) dv_0 dt_0 = Z^{-1} \int \cdots dx_{\mathbf{g}} \cdots \int \cdots dv_{\mathbf{g}} \cdots \int e^{-E/k_B T} \delta(x_{\mathbf{g}} - x_0) |v_0| dt_0 \delta(v_{\mathbf{g}}(0) - v_0) dv_0. \quad (\text{A26})$$

This calculation is simpler, yet completely analogous, to our previous occurrence probability calculation. We obtain

$$P_0(x_0, v_0) = |v_0| (4\pi)^{-1} (c_5 c_6)^{-1/2} \exp[-v_0^2/4c_6 - (c_2 - x_0)^2/4c_5]. \quad (\text{A27})$$

(3) Dividing $P(x_0, v_0; v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}, t) dt dv_{\mathbf{g}, \mathbf{g}+\mathbf{h}} dt_0 dv_0$ by $P_0(x_0, v_0) dv_0 dt_0$, we obtain the probability of a coincidence between sites \mathbf{g} and $\mathbf{g} + \mathbf{h}$ occurring between times t and $t + dt$ with relative configurational velocity between $v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}$ and $v_{\mathbf{g}, \mathbf{g}+\mathbf{h}} + dv_{\mathbf{g}, \mathbf{g}+\mathbf{h}}$ if $x_{\mathbf{g}} = x_0$ and $v_{\mathbf{g}} = v_0$ at $t = 0$:

$$\hat{P}(x_0, v_0; v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}, t) dt dv_{\mathbf{g}, \mathbf{g}+\mathbf{h}} = |v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}| (4\pi)^{-1} \times [c_3 c_4 (1 - a^2/4c_3 c_5 - b^2/4c_4 c_5)(1 - b^2/4c_3 c_6 - c^2/4c_4 c_6)]^{-1/2} \times \exp\{v_0^2/4c_6 - v_{\mathbf{g}, \mathbf{g}+\mathbf{h}}^2/4c_4 - (c_1 + \Delta/A)^2/4c_3 + (c_2 - x_0)^2/4c_5 - [a(c_1 + \Delta/A)^2/2c_3 + bv_{\mathbf{g}, \mathbf{g}+\mathbf{h}}/2c_4 + (x_0 - c_2)]^2/4(c_5 - a^2/4c_3 - b^2/4c_4) - [v_0 + b(c_1 + \Delta/A)/2c_3 - cv_{\mathbf{g}, \mathbf{g}+\mathbf{h}}/2c_4]^2/4(c_6 - b^2/4c_3 - c^2/4c_4)\}. \quad (\text{A28})$$

(4) Since a carrier arriving on a molecule will encounter a thermal distribution of configurational velocities, we perform an average with a Boltzmann distribution of the initial velocities, $\exp(-Mv_0^2/2k_B T)$. This yields the probability of

a coincidence between sites \mathbf{g} and $\mathbf{g}+\mathbf{h}$ with a relative configurational velocity between $v_{\mathbf{g},\mathbf{g}+\mathbf{h}}$ and $v_{\mathbf{g},\mathbf{g}+\mathbf{h}}+dv_{\mathbf{g},\mathbf{g}+\mathbf{h}}$ occurring between times t and $t+dt$ given a value of $x_{\mathbf{g}}=x_0$ at $t=0$: $P(x_0;v_{\mathbf{g},\mathbf{g}+\mathbf{h}},t)dv_{\mathbf{g},\mathbf{g}+\mathbf{h}}dt$. Explicitly,

$$P(x_0;v_{\mathbf{g},\mathbf{g}+\mathbf{h}},t) = |v_{\mathbf{g},\mathbf{g}+\mathbf{h}}| (4\pi)^{-1} (M\omega_0/k_B T) (1 - a^2/4c_3c_5 - b^2/4c_4c_5)^{-1/2} \\ \times \exp\{-v_{\mathbf{g},\mathbf{g}+\mathbf{h}}^2/4c_4 - (c_1 + \Delta/A)^2/4c_3 + (c_2 - x_0)^2/4c_5 \\ - [a(c_1 + \Delta/A)^2/2c_3 + bv_{\mathbf{g},\mathbf{g}+\mathbf{h}}/2c_4 + (x_0 - c_2)]^2/4(c_5 - a^2/4c_3 - b^2/4c_4)\} . \quad (\text{A29})$$

(5) Finally, we determine the rate characterizing a nonadiabatic hop from site \mathbf{g} to $\mathbf{g}+\mathbf{h}$ at time t given that the configurational coordinate of the initially occupied site $x_{\mathbf{g}}$ equals x_0 at $t=0$: $R(x_0,t)$. To accomplish this, we multiply $P(x_0;v_{\mathbf{g},\mathbf{g}+\mathbf{h}},t)$ by $P_{\mathbf{g},\mathbf{g}+\mathbf{h}}$, the probability of making a nonadiabatic hop given a coincidence between electronic energy levels at sites \mathbf{g} and $\mathbf{g}+\mathbf{h}$ [given by Eq. (4)], integrate over $v_{\mathbf{g},\mathbf{g}+\mathbf{h}}$, and divide by dt , yielding $R(x_0,t)$. After replacing the coefficients (the c_i 's and a , b , and c) by the physical quantities they represent [cf. Eqs. (A14)–(A23) and surrounding text], we obtain

$$R(x_0,t) = (\omega_0/2\pi) P [1 - G^2(t)/2]^{-1/2} \exp\{-[(4E_A + \Delta) + (Ax_0 - 4E_A)G(t)]^2/16E_A k_B T [1 - G^2(t)/2]\} . \quad (\text{A30})$$

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