Theoretical study of electron-vibration coupling on carrier transfer in molecular bridges

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Electron transport through molecular bridges connecting nano-scale electrodes is investigated theoretically with the coupling effect of an electron with molecular vibrations in the bridge. The ground state of the bridge molecule changes from a polaron state to an undressed state with the increase of the transfer integral. The electronic excited states in the bridge are also determined. Transition probabilities between these states are estimated by the golden rule including the excitation of molecular vibrations. By solving the master equation with these transition probabilities, we simulate the electron transfer process in the molecular bridge. [DOI: 10.1380/ejssnt.2006.311]

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I. INTRODUCTION

Recently, various kinds of organic devices have attracted much interest. For example, organic FET and organic light emitting devices have been actively investigated aiming at the technological applications [1–3]. Besides these devices made up of layers of organic molecules, molecular bridge structures have attracted much attention, because of their possibility to reveal novel functionalities as a nano-scale switch, memory, FET, or light emitting devices [4, 5]. To clarify the properties of molecular bridges and explore their novel potentiality, it is crucial to understand the coupling of a carrier (electron or hole) with molecular vibrations, because when carriers are injected in molecules from electrodes, the structure of the molecule changes for most of the cases, which causes rather strong coupling between the carrier and the vibration.

If the linkage between a molecule and an electrode is strong enough and the bottleneck of the carrier transition through the linkage is weak, one might expect rather coherent electron transport through the molecular bridge. However the coherence tends to be broken due to the coupling with vibration modes of molecules. If the coupling is significant, the carrier transport over different segments of the molecule is dominantly caused by the dissipative hopping, and various single electron effects are expected. To analyze general realistic systems that are situated between the two different regimes, it is necessary to construct a theory which can deal with the coherent electron transport as well as the dissipative hopping transport due to a strong coupling with the vibration in a unified framework.

So far, several theoretical studies have been carried out on the coupling of the electron with the molecular vibration. Nonequilibrium Green’s function (NEGF) method was used by several researchers [6–9], but these work treat only the case of the weak couplings and does not go into the regime of the polaron. The reduced density matrix theory was used by Petrov, et al. [10]. They discussed the competition between the direct transition from the donor site to the acceptor site (superexchange process) and the transition between neighboring bridge sites (sequential hopping processes) in the molecular bridges. But the model is rather limited to a special case.

In real molecular bridges, with the decrease of the transfer integral between the neighboring molecules or molecular segments, the electronic states change from extended states to localized states due to the polaron formation. By considering the transition between the two, the carrier transfer in molecular bridges can be properly analyzed. The first purpose of this paper is to propose a unified method to treat extended and polaron like localized states coupled with molecular vibrations. The second purpose is to clarify carrier transport processes based on transition rates between coupled electronic states with vibrational modes. The case study is made for a one-dimensional molecular bridge made of the thiophene molecules.

In Section 2, we propose a model to study a carrier transport in a molecular bridge. After that, in Section 3, we present how to determine electronic states which couple with the molecular vibration in the molecular bridge. Finally, in Section 4, transition between these states is analyzed, and the carrier transport process is analyzed using the master equation.

II. MODEL

In Fig. 1, the model we treat in this paper is shown schematically. This model contains two electrodes and bridging molecules between them. The bridging molecules are arranged in a linear chain as a whole. If the interaction between the molecules is considerably large, the molecules as a whole form a single large molecule, i.e., an oligomer.
of the smaller ones. We consider a system in which one additional electron or hole exists in the otherwise neutral molecules as a whole. Only one state, i.e. HOMO (Highest Occupied Molecular Orbital) or LUMO (Lowest Unoccupied Molecular Orbital) is considered as the electronic state on each molecular unit. Hamiltonian of the total system is given as

$$H_{total} = H_{MB} + H_E + H_{MB-E},$$

(1)

where the first two terms describe the molecular bridge and electrodes, respectively, and the last term describes their coupling. Each term of the above is written as

$$H_{MB} = \sum_{n=1}^{N} E_n a_n^+ a_n + \sum_{n=1}^{N-1} V(a_n^+ a_{n+1} + a_{n+1}^+ a_n) + \sum_{\lambda} \hbar \omega_{\lambda} b_{\lambda}^+ b_{\lambda} + \sum_{n=1}^{N} \sum_{\lambda} \gamma_{\lambda}^{(n)} \hbar \omega_{\lambda} a_n^+ a_n (b_{\lambda}^+ + b_{\lambda}),$$

(2a)

$$H_E = E_0 a_0^+ a_0 + E_{N+1} a_{N+1}^+ a_{N+1},$$

(2b)

$$H_{MB-E} = V_{B1} (a_1^+ a_1 + a_{N+1}^+ a_{N+1}) + V_{B2} (a_N^+ a_{N+1} + a_{N+1}^+ a_N).$$

(2c)

Here $a_n^+ (a_n)$ creates (annihilates) a carrier (electron or hole) in the $n$-th molecular site or one of the electrodes with energy $E_n$. Here the index $n = 0 (n = N + 1)$ corresponds to the electronic state of the left (right) electrode. As mentioned above, the number of carrier in this system is assumed to one, $\sum_{n=0}^{N+1} a_n^+ a_n = 1$. Energy levels of right sites are assumed to be lower than those of the left sites, because of the applied external electric field. Transfer integrals between neighboring molecular sites in the bridge are given by $V$. The transfer integral between the left-edge (right-edge) molecular site and the left (right) electrode is given by $V_{B1} (V_{B2})$.

At each molecular site, molecular vibration modes exist. $b_{\lambda}^+ (b_{\lambda})$ creates (annihilates) a vibration quantum in mode $\lambda$ with energy $\hbar \omega_{\lambda}$. The carrier (electron or hole) is assumed to couple to the vibration modes of the molecular unit on which it locates. The labeling of $\lambda$ takes into account of the particular molecular site. The electron (carrier)-vibration coupling between the carrier at $n$-th molecular site and $\lambda$-th vibration mode is given by a parameter $\gamma_{\lambda}^{(n)}$. As shown in Appendix, the carrier-vibration coupling parameter is given by

$$\gamma_{\lambda}^{(n)} = -\sqrt{\frac{m_{\lambda} \omega_{\lambda}}{2\hbar}} \Delta \vec{d} \cdot \vec{e}_{\lambda}.$$  

(3)

Here $\Delta \vec{d}$ is the multi-dimensional displacement vector from the neutral state to the ionic state. The dimension of this vector is $3N_{\text{atom}}$ with $N_{\text{atom}}$ the number of atoms in the molecule.
FIG. 2: (a) Vibration modes in thiophene molecule. The bonds in the molecule is shown by blue lines. Red arrows show the direction of the vibration on each atom in the plane of the thiophene ring. (b) Magnitude of the hole-vibration coupling for the thiophene molecule. Inset of this figure shows the relaxation vector originated from the positive ionization by green arrows and the 16-th vibration mode by red arrows.

They are also estimated by ab initio molecular orbital method [11]. Examples of the estimated values of the transfer integral of the HOMOs of thiophene molecules are shown in Fig. 3. Later we analyze the carrier transport process in the case of (b) $|V| = 0.7 \text{ eV}$.

III. ELECTRONIC STRUCTURES IN THE MOLECULAR BRIDGE

A. Simulation methods

Next we discuss electronic structures in the molecular bridge region. Here we start from considering two extreme cases.

At first, if the transfer integral equals to 0, each site can be treated separately. The exact wavefunctions in this case are given by

$$\phi^{(m_\lambda)}_n = \prod_{\lambda} \exp\{-\gamma^{(n)}_\lambda (b^{\dagger}_\lambda - b_\lambda)\} |\{m_\lambda\}\rangle \Phi^{(n)}.$$  

Here $|\{m_\lambda\}\rangle = |m_{\lambda_1}, m_{\lambda_2}, ..., m_\lambda, ...\rangle$ is the eigenstate of the molecular vibration part: $H = \sum_\lambda \hbar \omega_\lambda b^{\dagger}_\lambda b_\lambda$. ($m_\lambda$ is the number of the excited vibration quanta of the $\lambda$-th mode.) On the other hand, $\Phi^{(n)} = a^{\dagger}_n |0_\text{el}\rangle$ is the electronic state at site $n$. ($|0_\text{el}\rangle$ is the electronic vacuum state.) The states given by Eq. (4) are generally called 'the polaron states'.

Second, if carrier-vibration coupling equals to 0, the carrier and the vibration can be treated separately. The eigenstates can be written as

$$\chi^{(m_\lambda)}_m = \left\{ \sum_{\lambda=1}^N f_\lambda^{(n)} \Phi^{(n)} \right\} |\{m_\lambda\}\rangle.$$  

Transfer integral takes a different value, depending on the relative geometry between the neighboring molecules.
Here $\sum_{n=1}^{N} f_n^m \Phi^{(n)}$ is the $m$-th eigenstate of the purely electronic part in Eq. (2a): $H = \sum_{n=1}^{N} E_n a_n^a a_n + \sum_{n=1}^{N-1} V (a_n^a a_{n+1} + a_{n+1}^a a_n) \ (f_n^m$ is the coefficient of the eigenstate.). We call the states given by Eq. (5) 'the undressed states'.

For the general case of the molecular bridge, we assumed the wavefunction is given by

$$\psi^{(a)}_n = \sum_{m=1}^{N} A^a_n \Phi^{(m)}_n + \sum_{m=1}^{N} B^a_n \chi_m^{(m)}.$$  \hspace{1cm} (6)

Here $A^a_n$ and $B^a_n$ are determined by the variational approach for the systems without the free standing phonons [12], but with the phonons contributing polarons ($m^a_\lambda = 0$):

$$\psi^{(a)(0)}_n = \sum_{m=1}^{N} A^a_n \Phi^{(m)(0)} + \sum_{m=1}^{N} B^a_n \chi_m^{(m)(0)}$$

$$= \sum_{n=1}^{N} \left[ A^a_n \prod_{\lambda} \exp \left( -\gamma^{(n)}_\lambda (b_\lambda^a - b_\lambda) \right) + C^a_n \right] \Phi^{(n)} | 0_{ph} \rangle.$$  \hspace{1cm} (7)

Here we set $C^a_n = \sum_{m=1}^{N} f_n^m B^a_m$, and $| 0_{ph} \rangle$ means the phonon vacuum state.

In detail, after defining $F = \langle \psi^{(a)(0)}_n | H_{MB} | \psi^{(0)}_n \rangle - \varepsilon^a_\lambda \langle \psi^{(a)(0)}_n | \psi^{(a)(0)}_n \rangle$ with the Lagrange multiplier $\varepsilon_\lambda$, we solved the equations of $\partial F / \partial A^a_n = \partial F / \partial C^a_n = 0$ ($n = 1, 2, ... , N$), and obtained the states: ($A^a_n$, $C^a_n$, $\varepsilon_\lambda$), ($a = 1, 2, ... , 2N$) [13].

### B. Results and discussion

Next we show numerical results of the electronic states in the molecular bridge formed of thiophene molecules. For the sake of simplicity, we take an example of 5 sites model. The energy difference between neighboring sites is set to 0.04 eV, because we assumed the distance of the neighboring sites is about 4 Å and the applied electric field is 1 MV/cm, which is a typical value used in the organic devices. Only one vibration mode, i.e., the 16-th mode in each site is taken into account to simplify the calculation, and the magnitude of the coupling is set to 1.6. This is twice of the previously mentioned thiopehene case [14].

Figure 4 shows the energies of the electronic states in the molecular bridge as a function of the transfer integral, $| V |$. Since the number of sites in the molecular bridge is 5, and two types of bases (polaron and undressed states) are considered, so there are totally 10 states in the molecular bridge. We can see there are two kinds of branches in this figure. In one group, the energy is almost constant as a function of $| V |$ and in the other group the energy changes linearly with the transfer integral.

In Fig. 5, coefficients of the wavefunction are shown in the case of (a) $| V | = 0.1$ eV and (b) $| V | = 0.7$ eV, respectively. In the case of (a) $| V | = 0.1$ eV, we can see the lower and upper five states are the polaron states and the undressed states, respectively. On the other hand, in the case of (b) $| V | = 0.7$ eV, from third to seventh states are the polaron states. And the other lower two and upper three states are the undressed ones. Therefore we can see that the nearly constant energy branches in Fig. 4 are originated from polaron states and the linearly changing branches with $| V |$ are originated from undressed states. The ground states are polaron for lower $| V |$. When $| V |$ increases, the ground state becomes undressed state. In this calculation we can determine not only the ground state but also the excited states of the carrier coupled with the vibration degrees of freedom. By considering transitions between these states, we discuss carrier transport process in the next session.

### IV. CARRIER TRANSPORT PROCESS

#### A. Simulation methods

In this section, carrier transport process through the molecular bridge will be analyzed. Electronic states coupled with the molecular vibration are expressed in the form of Eq. (6). The electronic states in the electrodes are similarly expressed as,

$$\psi^{(a)}_n = \Phi^{(0)} | \{ m^a \} \rangle \text{ (for left electrode)},$$  \hspace{1cm} (8a)

$$\psi^{(b)}_n = \Phi^{(N+1)} | \{ m^b \} \rangle \text{ (for right electrode)}. \hspace{1cm} (8b)$$

Transition rates from the state 'a' to the state 'b' are generally calculated by use of Fermi’s golden rule as

$$W_{a \rightarrow b} = \frac{2 \pi}{\hbar} \sum_{\{ m^a \}} \left| \langle H_{ab} \rangle \right|^2 \delta (E_a - E_b) | \{ m^a \} \rangle.$$  \hspace{1cm} (9)

Here the state 'a' or 'b' is the state given by Eq. (6) or (8a) or (8b). The energy of the state 'a': $E_a$ and the matrix element $H_{ab}$ are obtained as follows:

$$E_a = \langle \psi^{(a)}_n | H_{total} | \psi^{(a)}_n \rangle,$$  \hspace{1cm} (10)

$$H_{ab} = \langle \psi^{(a)}_n | H_{total} | \psi^{(b)}_n \rangle.$$  \hspace{1cm} (11)
In Eq. (9), \( \langle \ldots \rangle \) means the thermal average with the vibration states of 'a'. Here we assumed the transition process is slower than the relaxation process of vibration excitation after any of the individual transition event. Therefore the vibration state before the transition is in the thermal equilibrium. This might be a reasonable assumption for many practical cases. In this work, temperature is set to 0 Kelvin. Calculation for the finite temperature case is also possible and will be reported in a forthcoming article. For the numerical calculation, \( \delta \)-function in Eq. (9) was approximated by a Gaussian function with the width 0.05 eV. We also assumed no backflow from molecular bridge to the left electrode and from the right electrode to the molecular bridge. In order to avoid injection limit and outflow limit cases, we controlled \( V_{B1} \), \( V_{B2} \) (transfer integral between the molecular bridge and the electrodes) [15].

After calculating all the values of the transition rates, we solved the master equation numerically,

\[
\frac{dP_a(t)}{dt} = \sum_b W_{b \rightarrow a} P_b(t) - \sum_b W_{a \rightarrow b} P_a(t). \tag{12}
\]

Here \( P_a(t) \) means the population of the state 'a'.

### B. Results and discussion

In this section the transient carrier transport property will be analyzed based on the calculated results of the master equation (12) [16]. Figures 6(a) and (b) show the time-dependent population of each site and state in color scale, respectively. The site 0 in Fig. 6 (a) and the state that is numbered 11 in Fig. 6(b) are the left electrode state/shale. Similarly the site 6 in Fig. 6 (a) and the state that is numbered 0 in Fig. 6 (b) are the right electrode state/shale. The energy level at the left electrode (\( E_0 \)) is set to 0.04 eV above that at the first site (\( E_1 \)). On the other hand, the energy level at the right electrode (\( E_{N+1} \)) is set to 0.04 eV below that of the ground state in the molecular bridge region.

Before the initial time=0, the carrier is assumed to be in the left electrode. At the time=0, we started to solve the master equation of Eq. (12). In other words, the injection from the left electrode to the molecular bridge started at the time=0. When time goes by, the population at the left electrode rapidly decreases, and the population at the sites 1,2,4,5 increases as shown in Fig. 6(a). After 0.1 psec, the population of the site 6, i.e., at the right electrode increases and finally becomes '1'.

Next we analyze the time-dependent population of each state in Fig. 6(b). At first, the state 8 is occupied and next the states 7,5 and 2 are occupied sequentially with some overlap. After this transient process the state 0, i.e., the state of the right electrode is finally completely occupied. These processes are more clearly understood by looking the features of the wavefunctions and the energy levels. The wavefunctions in the molecular bridge are shown in Fig. 6(c). The energy levels of the states in the molecular bridge as well as the electrodes are shown in Fig. 6(d). From Fig. 6(c) and (d), the state 8 has large amplitude at the site 1 and its energy is near the level of the left electrode. So it is easy to understand why the state 8 is occupied at the earliest stage.

In Fig. 7, we show the transition rates from the state \( i \) to \( k \), \( W_{i \rightarrow k} \). From this figure, the most probable path is starting from the state 11 and followed as 11(Left) \( \rightarrow 8 \rightarrow 7 \rightarrow 5 \rightarrow 2 \rightarrow 1 \rightarrow 0 \) (Right), arriving to the state 0.
right electrode state. This is consistent with the result of Fig. 6. We can see $W_{2 \rightarrow 1}$ has the smallest value in the main transition path and this is a rate-limiting step. This is considered to be originated from (i) smaller overlap between the state 1 and 2, which is expected from Fig. 6(c), and (ii) the large energy difference between these states as shown in Fig. 6(d). Transition between states with a large energy difference needs a large number of phonon states to be excited. This is also consistent with carrier’s staying for a somewhat long time at the state 2, which has a node at the site 3. From these results, the transport through the undressed extended states is found to be dominant at 0 Kelvin [17].

In Fig. 8, the time-dependent central position of the carrier and its velocity are shown. The dip structure in the time-dependent velocity in this figure is originated from the rate-limiting step mentioned above. For bulk organic materials, time-of-flight (TOF) experiments are frequently used to estimate the carrier mobility [18]. The current profile of TOF is originated from the transient carrier velocity, which can be obtained in Fig. 8. It is generally considered that performing TOF experiment in molecular bridges is difficult, and there is no work as far as we know. On the other hand, it is possible to simulate TOF experiment in molecular bridges by the calculation mentioned in this paper. Therefore our method will be applicable to the design of the electrical properties of the molecular bridges.

V. CONCLUSIONS

The carrier transfer process in a one-dimensional molecular bridge of thiophene chain is theoretically analyzed with a special attention to the effect of the carrier-vibration coupling. At first, by using the linear combination of both polaron and undressed bases, the electronic ground state and excited states were determined. For smaller transfer integrals, the ground state is found to be dominated by the polaron state. When the transfer integrals become larger, the undressed states emerge as a ground and lower excited states.
FIG. 7: Transition rate: $W_{i \rightarrow k}$. For $W_{i \rightarrow k} > W_B$, the radius of the circle is set as $r_{i \rightarrow k} = r_0 \times (\log W_{i \rightarrow k} - \log W_B)/(\log W_A - \log W_B)$, ($W_A = 10^4$ psec$^{-1}$, $W_B = 10^{-2}$ psec$^{-1}$, $r_0 = 0.6$). Blue arrows show the main transition path of the carrier.

FIG. 8: Time-dependent central position of the carrier and its velocity.

The simulation of the carrier transport process in the molecular bridge has been performed. The transition rates between different states are estimated by the Fermi’s golden rule and the master equation is numerically solved with these values of transition rates. In the thiophene molecular bridge treated in this work, the transport through the undressed states is found to be dominant at 0 Kelvin, though significant contribution comes from the polaron like states.

The theoretical method proposed in this work can be used for a marginal regime of the carrier transport in a molecular bridge, i.e., the transport with the both character of the coherent molecular orbital type and the polaron like hopping type. Application of this method toward an exploration of novel properties of the molecular devices belongs to a future target.

APPENDIX

In this appendix, we derive the carrier (electron or hole)-vibration coupling parameter as shown in Eq. (3). Hamiltonian of the vibration of molecule is given by

$$H_0^{(n)} = \sum_{\lambda(n)} \frac{1}{2} m_{\lambda} (q_{\lambda}^2 + \omega_{\lambda}^2 q_{\lambda}^2). \tag{A1}$$

with the normal vibration coordinate $q_{\lambda}$ of the neutral molecule. $\omega_{\lambda}$, $m_{\lambda}$ are its frequency and reduced mass, respectively. The normal vibration coordinate $q_{\lambda}(= \vec{q}_{\lambda})$ can be expressed by the boson operators $b_{\lambda}$, $b_{\lambda}^+$ as follows:

$$\vec{q}_{\lambda} = \sqrt{\frac{\hbar}{2m_{\lambda}\omega_{\lambda}}} (b_{\lambda} + b_{\lambda}^+) \vec{e}_{\lambda}. \tag{A2}$$

with the normal vibration coordinate vector $\vec{e}_{\lambda}$. Then the Hamiltonian in Eq. (A1) can be written as:

$$H_0^{(n)} = \sum_{\lambda(n)} \hbar \omega_{\lambda} \left( b_{\lambda}^+ b_{\lambda} + \frac{1}{2} \right). \tag{A3}$$

Similarly Hamiltonian for the ionic (positive or negative) molecule is given by

$$H_1^{(n)} = \sum_{\lambda(n)} \frac{1}{2} M_{\lambda} \left( Q_{\lambda}^2 + \Omega_{\lambda}^2 Q_{\lambda}^2 + \Delta E \right). \tag{A4}$$

Here $Q_{\lambda}$ is the normal vibration coordinate of the ionic molecule. $\Omega_{\lambda}$, $M_{\lambda}$ are its frequency and reduced mass, respectively. $\Delta E$ is the energy difference between the neutral and ionic molecules. The relation between the two coordinate systems is shown in Fig. 9, with $\vec{d}_0$, $\vec{d}_1$,
which are the atomic positions of the neutral and ionic molecules, respectively. To exclude the translational and rotational contributions, we chose the origin of the coordinate fixed on the center of mass and the plane of the thiophen ring defines the $xy$-plane. The relaxation vector due to the ionization is given by $\delta \vec{d} = \vec{d}_1 - \vec{d}_0$. The atomic positions of each molecule is given by $\vec{r} = \vec{d}_0 + \vec{q} = \vec{d}_1 + \vec{Q}$. Therefore $\vec{Q} = \vec{q} - \Delta \vec{d}$ is obtained.

In this work, we discuss the carrier-vibration coupling within the linear approximation which enables the relation, $\Omega_\lambda = \omega_\lambda$ and $M_\lambda = m_\lambda$.

By using these equations, Hamiltonian in Eq. (A4) can be expressed as follows:

$$H_1^{(\alpha)} = \sum_{\lambda (\alpha)} \frac{1}{2} m_\lambda (\omega_\lambda^2 + \omega^2_{\lambda} \vec{q}_\lambda^2) - \sum_{\lambda (\alpha)} m_\lambda \omega_\lambda^2 \vec{q}_\lambda \cdot \Delta \vec{d} + \Delta E'.$$

(A5)

Here $\Delta E' = \sum_{\lambda (\alpha)} \frac{1}{2} m_\lambda \omega_\lambda^2 \mid \Delta \vec{d} \mid^2 + \Delta E$ is used. Eq. (A5) can be transformed as

$$H_1^{(\alpha)} = \sum_{\lambda (\alpha)} h_\omega_\lambda \left( b^\dagger_\lambda b_\lambda + \frac{1}{2} \right) + \sum_{\lambda (\alpha)} \gamma_\lambda a^\dagger_\lambda \gamma_\lambda (b^\dagger_\lambda + b_\lambda) + \Delta E'.

(A6)

In this Hamiltonian, the carrier-vibration coupling parameter is defined by

$$\gamma_\lambda^{(\alpha)} = - \sqrt{\frac{m_\lambda \omega_\lambda}{2\hbar}} \Delta \vec{d} \cdot \vec{e}_\lambda.$$

When a carrier exists in the molecule $n$, $a^+_n a_n = 1$, and Hamiltonian is given by $H_1^{(\alpha)}$. When it is absent, $a^+_n a_n = 0$, and Hamiltonian is given by $H_0^{(\alpha)}$. In both cases, Hamiltonian can be generally given by

$$H^{(\alpha)} = \sum_{\lambda (\alpha)} h_\omega_\lambda \left( b^\dagger_\lambda b_\lambda + \frac{1}{2} \right) + \sum_{\lambda (\alpha)} \gamma_\lambda^{(\alpha)} h_\omega_\lambda (b^\dagger_\lambda + b_\lambda) + \Delta E'.

(A8)

$\Delta E'$ term is constant, and can be incorporated in the level of the orbital $E_n$ in Eq. (2a). By considering the vibration and the carrier-vibration coupling terms at all sites as well as the purely electronic terms, Hamiltonian $H_{MB}$ in Eq. (2a) can be obtained.

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[12] Here a phonon is used to describe a vibration quantum in each molecule.
[13] By using these parameters, $(A^+_n, C_n^2)$, $\langle \psi_0^{(0)} \mid \psi_0^{(0)} \rangle = 1$ is satisfied. However, for excited phonon states given by Eq. (6), $\langle \psi_n^{(m)} \mid \psi_n^{(m)} \rangle = 1$ is not generally satisfied. So an additional normalization is considered.
[14] To discuss the general trend of the parameter dependence in our model, we chose parameters which cause the separation of the branches originated from the polaron and those from the undressed states. When $\gamma = 0.8$ is used, $\Delta E_p$ (the stabilized energy originated from the formation of polaron) = 0.115 eV.)
[15] In detail, we set $TR_{max} = IR_{max} = OR_{max}$ by controlling $V_{21}$ and $V_{22}$. Here $TR_{max}$ =’maximum transition rate in the bridge’, $IR_{max}$ =’maximum injection rate from the left electrode to the bridge’, and $OR_{max}$ =’outflow rate from the bridge to the right electrode’.
[16] The number of carrier in molecular bridge is considered to be not so much and each carrier can be treated separately in this case. So we analyzed the transient carrier transport of each carrier to investigate the electric properties of the molecular bridge.
[17] We also investigated the carrier transport for lower transfer integral case. In this case, the states in the bridge are given like Fig. 5(a). When the carrier is trapped in one of the polaron states whose energies are lower than those of the undressed states, the carrier stays there for a long time because of small transition probability originated from the small effective transfer integral between neighboring polaron states. So we understand that the hopping between polaron states is not so important at 0 Kelvin.
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