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Bridge mediated ultrafast heterogeneous electron transfer

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Abstract

Bridge mediated photoinduced ultrafast heterogeneous electron transfer (ET) from a molecularly anchored chromophore to a semiconductor surface is modelled theoretically. The continuum levels of the semiconductor substrate are taken into account in the numerical calculations via a polynomial expansion. Electron transfer for the direct injection case in the strong coupling limit is studied and compared with cases where intermediate bridging states are successively introduced to weaken the effective electronic coupling. The role of vibronic coherences in the strong electronic coupling limit as well as in off-resonant bridge mediated electron transfer is also discussed. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Photoinduced electron transfer (ET) from a molecularly anchored chromophore to the empty conduction band levels of the semiconductor substrate is a topic of current research interest [1–3]. Recent studies have included optical pump–probe techniques, and for various molecule–substrate interfaces injection times in the range of a few tens to several hundreds of femtoseconds have been reported [3–7]. The injection times are known to depend on the relevant substrate density of states that is determined by the position of the injection level [8], the strength of the electronic coupling between the molecular orbital and semiconductor

levels and reorganization of the molecule due to the formation of the cationic state [9]. As the electronic coupling strength is sensitive to the effective distance between the donor molecule and the surface it is determined by the orientation and the length of the spacer groups used to anchor the chromophore to the surface. Recently, experimental groups have inserted different spacer groups to vary the electronic coupling and to study its influence on the electron injection rate [4,10]. Although a general trend of slowing down of injection rate with an increase in the length of the spacer groups has been found, it is not clear whether the ET is through space, as the flexible spacer groups can assume different tilt angles towards the surface [10], or through bond as in a bridge mediated ET proceeding via a superexchange mechanism [11], or possibly a combination of several such pathways [12].

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Bridge-assisted ET has been an active area of interest spanning diverse bridging systems such as proteins, DNA and organic spacers between donor acceptor pairs or between electrodes as in the field of molecular electronics (see [13] and references therein). Usually in such systems the emphasis has been on long-range thermalized electron transfer, facilitated by the presence of the bridge, wherein the rate of transfer as a function of bridge length has been extensively studied. In the case of photoinduced electron injection, as the bridging units are much shorter, the timescales are in the ultrafast limit and such studies offer one the scope of examining the role of bridge-assisted transfer where coherence effects are important. Also, one can examine the bridge length dependence on electron transfer rates for the case of short bridges.

In this Letter the problem of ultrafast bridge mediated ET from a molecular donor to a continuum of final electronic levels either directly or via bridging units is addressed numerically using a simple model which excludes dissipative effects. A very strong electronic coupling leading to direct transfer times of a few femtoseconds is utilized to investigate how addition of successive bridging elements slows down the rate of electron injection. As vibronic coherences have been shown to accompany [6] and even modulate ET [7] at ultrafast timescales, the effect of vibrational wavepackets on bridge mediated as well as on direct ET in the strong coupling limit is also studied. While exploring bridge mediated ultrafast ET the continuum of semiconductor conduction band states is taken into account by an expansion in orthogonal polynomials [14], unlike in the earlier approaches [9,15] where the continuum was modelled as a quasicontinuum [16].

2. Hamiltonian and basic equations of motion

The electronic Hamiltonian consists of the molecular excited state $|\varphi_e\rangle$ that is coupled to a *uniform* electronic continuum of the band states $|\varphi_k\rangle$ of the semiconductor either directly or via a set of N nearest neighbour coupled bridge states $|\varphi_j\rangle$, where $j = 1, 2, \dots, N$. The general form is thus

$$H = H_e(Q)|\varphi_e\rangle\langle\varphi_e| + \sum_{j=1}^N H_j(Q)|\varphi_j\rangle\langle\varphi_j| + \sum_k H_k(Q)|\varphi_k\rangle\langle\varphi_k| + \left(V_{e1}|\varphi_e\rangle\langle\varphi_1| + \sum_{j=1}^{N-1} V_{j,j+1}|\varphi_j\rangle\langle\varphi_{j+1}| + \sum_k V_k|\varphi_N\rangle\langle\varphi_k| + \text{h.c.} \right). \quad (1)$$

The vibrational part of the Hamiltonian in terms of a harmonic oscillator model, for a single mode of vibrational frequency ω_0 , has the usual form

$$H_a = T + U_a^{(0)} + \frac{\hbar\omega_0}{4}(Q - Q^{(a)})^2, \quad (2)$$

where in the above a represents the electronic states e the various j 's and k 's. The nuclear kinetic energy operator is given by T . The displacement term $Q^{(k)}$ is assumed to be the same for all the ionized PES. The eigenvalues of H_a are written as

$$\varepsilon_{av} = \varepsilon_a + v\hbar\omega_0, \quad (3)$$

where the first term reads

$$\varepsilon_a = U_a^{(0)} + \frac{1}{2}\hbar\omega_0. \quad (4)$$

It is given by the minimum of the respective PES plus the total zero-point energy of the vibrational mode.

As vibrational relaxation is not crucial to the issues addressed in this Letter, a time-dependent Schrödinger equation is utilized to obtain the rise of probability signifying the formation of the molecular cationic product state upon ultrafast electron injection into the continuum levels of the semiconductor. The electron vibrational wavefunction $|\Psi(t)\rangle$ is given as

$$|\Psi(t)\rangle = \sum_{av} A_{av}(t)|\chi_{av}\rangle|\varphi_a\rangle + \sum_{k\mu} A_{k\mu}(t)|\chi_{k\mu}\rangle|\varphi_k\rangle, \quad (5)$$

where $|\chi_{av}\rangle$ and $|\chi_{k\mu}\rangle$ are the vibrational eigenfunctions of the discrete and continuum electronic states, respectively. The uniform continuum of ε_k states has been handled previously [9,15] in the context of heterogeneous ET by a quasicontinuum

representation. One can also adopt a method of representing the continuum of states by expanding the energy-dependent coefficients $A_{k\mu}(t) \equiv A_{\mu}(\varepsilon, t)$ in terms of orthogonal polynomials [14] (note the incorporation of the density of states when changing to the continuous energy variable). This results in a smaller number of coupled differential equations to be solved in order to obtain the time-dependent electron vibrational wavefunction when compared to the quasicontinuum method and hence computationally more efficient. Expanding in an orthogonal polynomial basis

$$A_{\mu}(\varepsilon, t) = \sum_s \mathcal{A}_{\mu s}(t) u_s(\varepsilon), \quad (6)$$

where $u_s(\varepsilon)$ are polynomials defined such that they are orthonormal over the width of the conduction band, i.e., in the interval $[0, \varepsilon_{\max}]$, where ε_{\max} corresponds to the state at the top of the conduction band. These are related to the Legendre polynomials $P_s[x]$ via the relation

$$u_s(\varepsilon) = \sqrt{\frac{2s+1}{\varepsilon_{\max}}} P_s[x(\varepsilon)], \quad (7)$$

where

$$x(\varepsilon) = \left(\frac{2}{\varepsilon_{\max}} \right) \varepsilon - 1 \quad (8)$$

and

$$\int_0^{\varepsilon_{\max}} d\varepsilon u_s(\varepsilon) u_{\bar{s}}(\varepsilon) = \delta_{s\bar{s}}. \quad (9)$$

The following recursion relation is satisfied by these polynomials:

$$a_{s+1} u_{s+1}(\varepsilon) = \left(\varepsilon - \frac{1}{2} \varepsilon_{\max} \right) u_s(\varepsilon) - a_s u_{s-1}(\varepsilon), \quad (10)$$

where

$$a_s = \frac{\varepsilon_{\max}}{2} \frac{s}{\sqrt{4s^2 - 1}} \quad (s = 1, 2, 3, \dots). \quad (11)$$

For the simplest case of substrate–molecule interaction, assuming a uniform density of states for the continuum and a constant electronic coupling between the N th bridging level and the continuum, one can set

$$V(\varepsilon) = \tilde{V} \sqrt{\varepsilon_{\max}} u_0(\varepsilon). \quad (12)$$

The time-dependent Schrödinger equation yields a *discrete* set of coupled differential equations for the expansion coefficients after making use of the polynomial expansion (Eq. (6)), orthonormality relation (Eq. (9)) and the recurrence relations (Eq. (10)).

$$\frac{\partial}{\partial t} A_{ev}(t) = -\frac{i}{\hbar} \left\{ \varepsilon_{ev} A_{ev}(t) + \sum_{\bar{v}} V_{e1} \langle \chi_{ev} | \chi_{1\bar{v}} \rangle A_{1\bar{v}}(t) \right\}, \quad (13)$$

$$\frac{\partial}{\partial t} A_{jv}(t) = -\frac{i}{\hbar} \left\{ \varepsilon_{jv} A_{jv}(t) + \sum_{\bar{v}} V_{j,j+1} \langle \chi_{jv} | \chi_{j+1\bar{v}} \rangle A_{j+1\bar{v}}(t) + \sum_{\bar{v}} V_{j,j-1} \langle \chi_{jv} | \chi_{j-1\bar{v}} \rangle A_{j-1\bar{v}}(t) \right\}, \quad (14)$$

$$\frac{\partial}{\partial t} A_{Nv}(t) = -\frac{i}{\hbar} \left\{ \varepsilon_{Nv} A_{Nv}(t) + \sum_{\bar{v}} V_{N,N-1} \langle \chi_{Nv} | \chi_{N-1\bar{v}} \rangle A_{N-1\bar{v}}(t) + \sum_{\mu} \tilde{V} \sqrt{\varepsilon_{\max}} \langle \chi_{Nv} | \chi_{\mu} \rangle \mathcal{A}_{\mu 0}(t) \right\}, \quad (15)$$

$$\frac{\partial}{\partial t} \mathcal{A}_{\mu 0}(t) = -\frac{i}{\hbar} \left\{ \left(\hbar \omega_{\mu} + \frac{\varepsilon_{\max}}{2} \right) a_1 \mathcal{A}_{\mu 1}(t) + \sum_{\bar{v}} \tilde{V} \sqrt{\varepsilon_{\max}} \langle \chi_{\mu} | \chi_{N\bar{v}} \rangle A_{N\bar{v}}(t) \right\}, \quad (16)$$

$$\frac{\partial}{\partial t} \mathcal{A}_{\mu s}(t) = -\frac{i}{\hbar} \left\{ \mathcal{A}_{\mu s+1}(t) a_{s+1} + \mathcal{A}_{\mu s-1}(t) a_{s-1} + \frac{\varepsilon_{\max}}{2} \mathcal{A}_{\mu s}(t) \right\} \quad (s = 1, 2, \dots). \quad (17)$$

One needs only a finite number of coefficients $\mathcal{A}_{\mu s}$ to numerically calculate the electron-vibrational wavefunction and also the populations in the various electronic levels. The expressions for the time-dependent rise of the ionic product state $P_I(t)$, the population in the various bridge states P_j and among the levels of the continuum states P_k can all

be appropriately defined in terms of the electron-vibrational wavefunction. Accordingly,

$$P_I(t) = \sum_{\mu s} |\mathcal{A}_{\mu s}(t)|^2, \quad (18)$$

$$P_j(t) = \sum_v |A_{jv}(t)|^2, \quad (19)$$

$$P_k(t) = \sum_{\mu} |A_{\mu}(\varepsilon, t)|^2. \quad (20)$$

In Section 3, for all calculations, a continuum band width of 2 eV, and two positions for the excited donor state, namely, 1.0 and 0.3 eV above the lower edge of the band has been assumed. Bridging levels when inserted are always positioned 0.6 eV above the level of excited donor state irrespective of its position relative to the band edge. For the electronic coupling strengths the following have been used namely, $V_{e,j=1} = V_{j,j+1} = 0.2$ eV and $\tilde{V} = 0.3$ eV throughout the calculations. In a superexchange process the effective electronic coupling between the donor and the final acceptor states decays exponentially with increase in the number 'n' of bridging units i.e., $V_{\text{eff}} \propto e^{-\beta n}$. The constant of proportionality β depends only on the ratio between the off-resonance energy factor of 0.6 eV and the inter-bridge electronic coupling of 0.2 eV [13]. For these values, each bridging state closely corresponds to insertion of two CH₂ units as $\beta = 2.197$ [4]. Also, the single mode of vibrational energy $\hbar\omega_0 = 0.1$ eV is assumed alongwith a reorganization energy of $\lambda = 0.225$ eV (where $\lambda = \hbar\omega_0(Q^{(k)} - Q^{(e)})^2/4$) for the case of direct injection. Subsequent increases to $\lambda = 0.27$ and 0.3 eV with the introduction of successive bridging units, respectively, follows the prescription given by the local dielectric continuum model [17]. However, such increases in the reorganization energy are clearly underestimated [17], since the intention here is to obtain trends while restricting calculations to times less than a picosecond. The initial state is either the ground vibrational level or a vibrational wavepacket in the excited donor state [9].

3. Results and discussion

Direct injection from a molecular orbital that is strongly coupled to the substrate can be of the

order of a few femtoseconds [18] and Fig. 1a,b, illustrate such a case, when the electronic coupling between the molecular level and the substrate is of the value $\tilde{V} = 0.3$ eV. In the past, similar problems wherein a molecular resonance is coupled to a continuum of electronic states has been addressed in a more general fashion [19–21]. The electronic coupling's dependence on energy [20,21] and on the nuclear coordinate has been explicitly taken into account [20]. Moreover, the effect of a thermal bath on the population transfer to the electronic continuum for various temperatures has also been investigated using a path-integral method [21]. Unlike in the above case of collisional occupancy of the molecular state [19], optically populating the excited donor state when its lifetime is so short compared to what is achievable even via the shortest possible optical pulses is quite artificial. Even so this theoretical exercise enables one to understand the contribution and the role played by higher orders of electronic coupling, and also that of reorganization energy in slowing down the transfer process, in this strong coupling regime. When the injecting level is positioned high over the conduction band edge (1.0 eV above band edge), the rise of the ionized product state (or equivalently the decay of the injecting state) is a near exponential function, as seen from the corresponding curve in Fig. 1a. Fermi's Golden rule formulation wherein the rate is given purely in terms of the second-order in electronic coupling namely, $K = (2\pi/\hbar)\tilde{V}$, seems to describe the situation reasonably as seen from the corresponding curve in Fig. 1a. It is well known from the purely electronic Fano–Anderson models [22,23], that a discrete electronic level coupled to a wide uniform continuum of states undergoes a Lorentzian broadening and its lifetime (given by the Fourier transform) corresponds to Fermi's Golden rule. Thus higher orders in electronic coupling play virtually no role in determining the lifetime of the excited state. Reorganization effects are also seen to be negligible for this case, once again confirming that one is close to the wide band limit.

For the same coupling strength however, when the position of the injecting level is closer to the conduction band edge (0.3 eV above band edge), one obtains a relatively slower rise which is

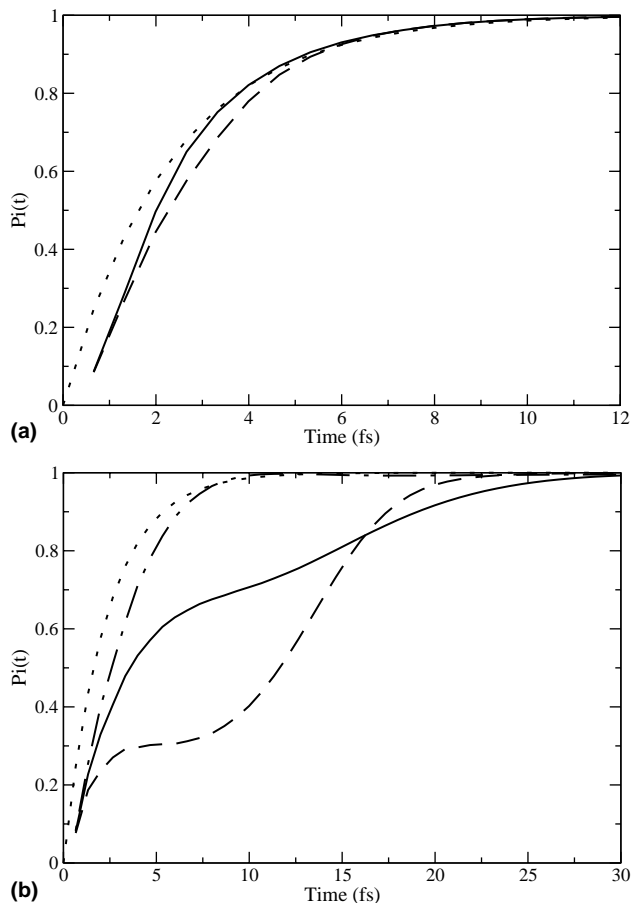


Fig. 1. Total rise of probability among continuum levels, $P_i(t)$ versus time for direct ET from excited donor to the continuum. Two initial conditions, namely, (1) IC(1): only ground vibrational level is populated, and (2) IC(2): vibrational wavepacket due to impulsive excitation as explained in Ref. [9] are considered. (a) For injection position $I_p(1) = 1.0$ eV. Fastest rise denoted by dotted line is an exponential function with a rate given by K (Fermi's Golden rule) as in text. Solid line corresponds to IC(1) and dashed line to IC(2). (b) $I_p(2) = 0.3$ eV. Same as above. The dash-dotted line shown here corresponds to the case of no reorganization.

markedly non-exponential. Similar structures such as plateaus followed by rapid population transfer have been previously observed, in short-lived resonances coupled to a continuum of electronic states, and ascribed to electron-vibrational coupling [20]. From the case of no reorganization shown in Fig. 1b (the dash-dotted curve), one can estimate the relative contributions of higher orders in electronic coupling strength and Franck-Condon factors in slowing down electron transfer when injected from the lower position. It is clear that the slower rise is mainly due to finite reorganization energy which manifests in the rate via

Franck-Condon overlap factors. Interestingly, for a given electronic coupling strength, the curve from Fermi's Golden rule in Fig. 1 seems to be the upper limit for injection time as in the case of a weaker coupling strength [9].

Instead of populating only the ground vibrational level of the excited state initially, if a set of levels is coherently populated (a vibrational wavepacket), there is not much of a difference between the rise times when the electron is injected from the aforementioned higher level relative to the band edge as in Fig. 1a. However, for injection from the level positioned relatively nearer to the

band edge, vibronic coherences seem to drastically modify the overall rise, as seen in Fig. 1b. The reason is obviously due to the Franck–Condon factors playing an important role in the transfer process and hence should not be neglected even in the very strong electronic coupling limit [24].

As stated earlier, there is currently much interest stemming from the recent experimental results [3,4], to understand how the injection rate falls off if successive non-resonant bridging electronic states are present to weaken an initial strong direct electronic coupling that could be the order of a few femtoseconds. Compared to the direct injection

case, for the higher position of injection, there is roughly a factor of around 14 increases in the transfer times in the absence of vibronic coherence. In fact, the rise of probability in the continuum levels for this case is close to the single bridge superexchange rate (dotted line in Fig. 2a) between a molecular donor and acceptor pair given by Bixon and Jortner [25]. The decay of the excited state shows an early electronic recurrence that is reciprocated by the bridge population, though its signature is not seen in the rise of the final state. Vibronic coherences mildly modify transfer times close to the wide band limit, whereas from the

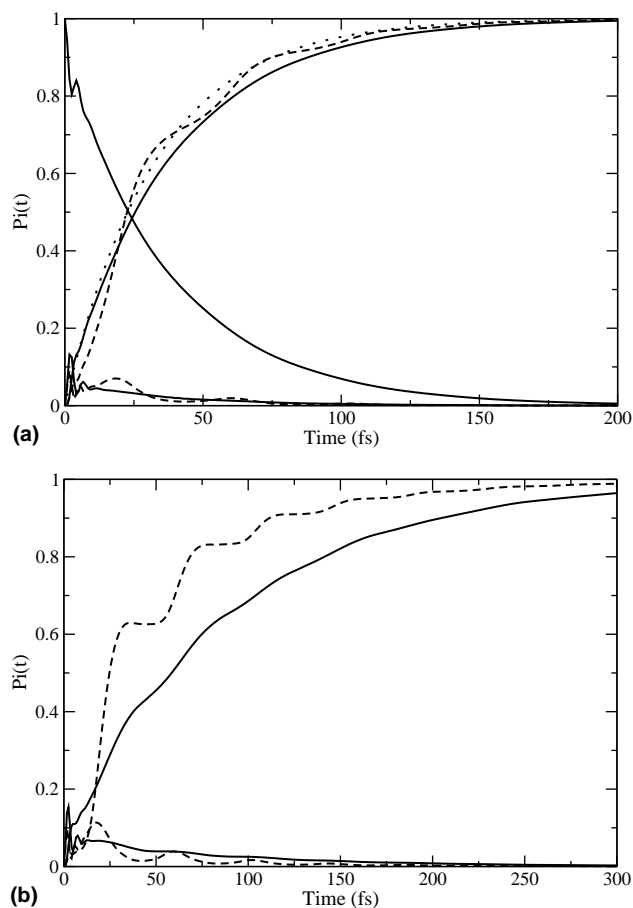


Fig. 2. Population dynamics for ET via a single off-resonant bridge. Initial conditions as in caption for Fig. 1. (a) $I_p(1) = 1$ eV. Decaying solid line: donor state population. Rising solid line corresponds to IC(1) and dashed line to IC(2). Rising dotted line: fit for superexchange rate from [25]. Solid decaying line and dashed oscillatory lines at bottom shows $P_{b_i}(t)$ for conditions IC(1) and IC(2), respectively. (b) $I_p(2) = 0.3$ eV. Same as in above except that decay of donor state and fit for the superexchange rate is absent here.

lower position of injection (see Fig. 2b), the modulation in the transfer of probability is seen to be much stronger and more importantly, the transfer is much more rapid than in the absence of vibronic coherences. Clearly, the presence of vibronic coherences and reorganization in the bridge states allow for the possibility to reduce the energetic off-resonance between donor and successive bridge states via the Franck–Condon transitions, leading to a much faster transfer process than what is possible in the absence of vibrational wavepackets. The low magnitude of the bridge population seen in Fig. 2 is indicative of the predominance of the superexchange pathway of

transfer [25]. A vibrational wavepacket leads to characteristic decaying oscillations in the bridge population (Fig. 2).

With a second bridging element there is a further slowing down of transfer times by a factor of about 20 compared to the first bridge case for the higher position of injection as is seen in Fig. 3a in the absence of vibronic coherence. For the lower injection position the rise is extremely slow (no coherences) but what is remarkable is the enormous decrease in transfer time (by several hundreds of femtoseconds) in the presence of vibrational coherence (see Fig. 3b). Again one sees that the effect of vibrational wavepackets speeds

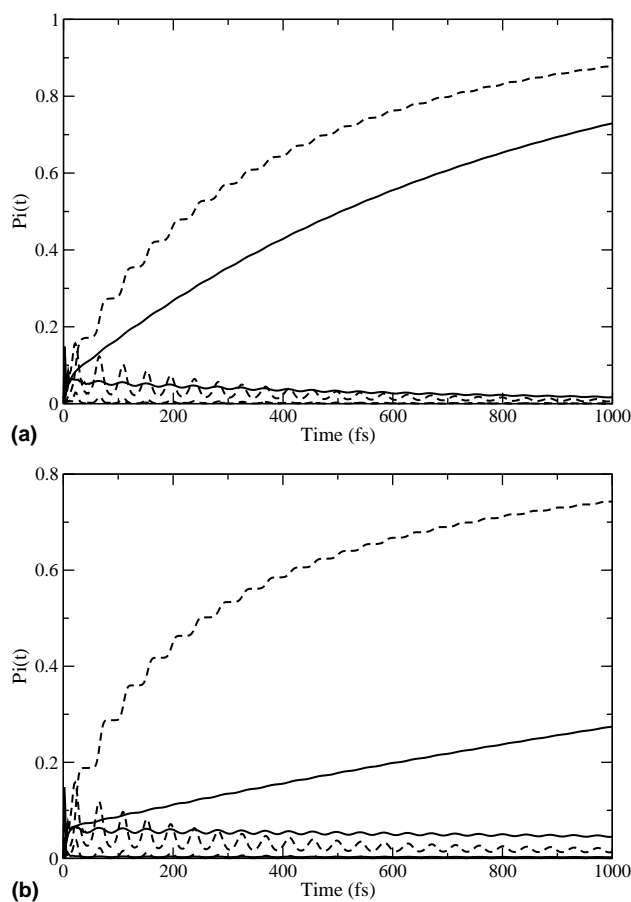


Fig. 3. Population dynamics for ET via a two off-resonant bridging electronic states. Initial conditions as in caption for Fig. 1. (a) $I_p(1) = 1$ eV. Solid line corresponds to IC(1) and dashed line to IC(2). Decaying and oscillatory solid and dashed lines at bottom shows $P_{b_i}(t)$ for conditions IC(1) and IC(2), respectively. Similarly, closest to the time axis, the decaying and oscillatory solid and dashed lines represent conditions IC(1) and IC(2), respectively. (b) $I_p(2) = 0.3$ eV. Legend similar to case (a).

up the transfer process due to the reduction of energetic off-resonance factor in the superexchange mechanism. The electronic quantum beats in the bridge population are enhanced by the presence of vibronic coherences and the bridge that is coupled to the continuum has a much lower population when compared to the one which is coupled to the excited state.

When no reorganization is assumed in the problem, calculations show that for both injecting positions, one gets a constant factor of around nine as predicted by conventional superexchange theory [11], since for the parameters considered $e^{\beta} = 9$. Therefore the larger slowing down in the transfer rates as seen from the above results, arises due to bridge length dependent reorganization which gets further enhanced by locating the injecting level closer to the band edge. As the bridge length is further increased the total reorganization energy approaches a constant value as per the model assumed here [17]. Under these conditions one can expect a constant factor for the exponential fall in transfer rate as predicted by the superexchange model [11] and experimentally observed for long chain spacers on semiconductor electrodes [26]. In fact when the reorganization was held constant while inserting the second bridging level, the factor of slow down decreased to around 12 from the value of 20 seen in Fig. 3a. In order to progress further in modelling ET of the type considered here, ab initio calculations [12,27] are necessary to determine all the relevant ET pathways between the donor and the electrode and to verify whether a nearest neighbour coupled superexchange pathway indeed dominates over all other possible pathways.

4. Conclusions

Electron-vibrational dynamics in ultrafast heterogeneous ET, including bridge mediated cases, has been addressed here via a polynomial expansion approach used previously only for calculating photoionizing signals [14]. This method is computationally more efficient than the quasicontinuum method as the runtime is about 15 times faster.

The strong electronic coupling limit leading to direct transfer in less than 10 fs has been briefly explored. It has been shown that for a given strength of electronic coupling, Fermi's Golden rule gives the fastest rate of electron injection into an electrode. From a position of injection closer to band edge, reorganization is shown to be more important than higher orders in electronic coupling in determining the rate of transfer. Vibronic coherences tend to slow down ET as in the case of weak coupling studied recently [9].

When ET was mediated via non-resonant short bridging units, the rate of injection in the femto-second domain was determined by bridge length dependent reorganization and consequent band edge effects, rather than by higher orders of the strong electronic coupling between bridge and substrate. Most interestingly, it was found that vibronic coherences in contrast to the direct injection case lead to significant speeding up of the superexchange transfer process, by allowing for decrease in the off-resonant energetic factor via multiple Franck–Condon transitions.

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