

Theory of ultrafast photoinduced heterogeneous electron transfer: Decay of vibrational coherence into a finite electronic–vibrational quasicontinuum

S. Ramakrishna^{a)} and F. Willig

Hahn-Meitner-Institut, Glienickerstrasse 100, 14109 Berlin, Germany

V. May

Institut für Physik, Humboldt-Universität, Hausvogteiplatz 5-7, 10117 Berlin, Germany

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Photo-induced electron transfer from a surface attached dye molecule to the band levels of a semiconductor is modeled via an electronic–vibronic quasicontinuum. The description enables one to obtain a fairly accurate expression for the decay of the excited molecular state, including initial vibronic coherences. The model accounts for (a) the effect of a finite band width, (b) variations in reorganization energy and electronic coupling, (c) various energetic positions for the injecting level, (d) different initial vibrational wave packets in the excited state, and (e) two vibrational modes participating in the electron transfer process. Most cases are studied numerically and can be reasonably well understood from the obtained decay expression. © 2001 American Institute of Physics. [DOI: 10.1063/1.1386433]

I. INTRODUCTION

Photo-induced heterogeneous electron transfer (ET) is a fundamental process in fields of practical importance such as AgBr-photography¹ and dye sensitized solar cells.² ET from an excited molecular donor state into a continuum of empty electronic states also occurs in more complicated surface reactions such as photodesorption.³ The simplest experimental method for studying photo-induced ET is the measurement of a stationary photocurrent.^{4,5} Ever since the advent of femtosecond laser systems and high surface area electrodes of semiconductors like TiO₂ or ZrO₂,² a growing number of experimental groups have started utilizing optical femtosecond pump–probe techniques for time resolved studies of photo-induced heterogeneous ET reactions.^{6–12}

Probe absorption can be tuned to study (i) the time dependent decay of the excited state,⁷ and (ii) the rise of the formation of the ionized product state.^{7,9,10} For a number of different chromophores as well as anchor-cum spacer groups that have been investigated, a host of electron injection times ranging from a few tens to several hundreds of femtoseconds have been measured.^{6–12} Recent experiments carried out in the experimental group of Willig and co-workers with 20 fs laser pulses have shown oscillatory behavior in the absorption of the ionized chromophore.¹² The vibrational wave packet that is initially formed in the first excited singlet state of the chromophore perylene, thus persists during the course of ET. The observed vibrational wave packet is composed of well-known normal modes of the chromophore perylene having energies 44 and 52 meV. These experiments show that electron injection in this system occurs prior to full vibrational relaxation and dephasing. Similar results have been reported earlier, for the case of ET reactions involving

donor–acceptor pairs in a solvent environment.¹³

Several theoretical studies have emerged in the last decade to address issues related to electron transfer occurring in the presence of molecular quantum beats,^{14–18} in donor–acceptor complexes. In contrast, the available theoretical descriptions of photo-induced interfacial ET have all assumed electron injection to be slower than the intramolecular redistribution of excess vibrational energy that is generated via the absorption of a photon in the chromophore,^{19–21} Recently, theory has been advanced for obtaining pump–probe signals of the donor state, using a density matrix approach ($\chi^{(3)}$ -theory), wherein the electron is injected into a continuum of band states.²² In this first theoretical treatment of ultrafast heterogeneous ET which incorporates vibrational coherences in the transfer process, the issue of reorganization and its influence on electron transfer had not been addressed since they were ignored under the assumption of a wide band limit.²² When the energetic distance of the injecting electronic level from the lower band edge is much larger than the reorganization energy, the condition of wide band limit is roughly fulfilled. A recent attempt to estimate the injection time of the electron transfer from an excited electronic state of a dye molecule to a semiconducting surface also completely ignores the effects of reorganization.²³

This article focuses on how the reorganization energy and the energetic position of the injecting level influence via the finiteness of the conduction band the decay of a vibronic coherence that is initially prepared by an ultrashort laser pulse in the excited state of the molecule. The charge transfer system of the surface–molecule complex modeled uniquely as a finite electronic–vibronic quasicontinuum (QC) will be explained in the following section. The dynamics of the injection process from the excited state to the electronic–vibronic QC is studied using a time-dependent Schrödinger equation approach. In Sec. III, results obtained earlier on the

^{a)}Electronic mail: ramakrishna@hmi.de

injection into a pure electronic QC are recapitulated since this well studied limiting case,^{24–28} provides the right context to investigate the time behavior of its extension, namely the electronic–vibronic QC. Thereafter in Sec. IV, the dynamics of the electronic–vibronic QC are studied and its properties are contrasted with the limiting case of a pure electronic QC. An approximate analytical form for the decay of vibronic coherences is obtained for the finite electronic–vibronic QC. In the sections following this expression acts as a pivotal analytical tool to clarify the results of the numerical calculations. For instance, it enables one to understand the effects of varying parameters and experimental conditions while describing the decay of the excited state.

II. HAMILTONIAN AND BASIC EQUATIONS OF MOTION

In order to describe the photoinduced injection process it suffices to characterize the molecule by two electronic states namely the ground and an excited state. A laser excitation leads to a transfer of population from the ground to the excited state. Assuming the excitation to be impulsive i.e., a delta pulse, one can ignore the ground state from all further consideration of the electron transfer problem. The initial state is thus the excited molecular state with a specific population coherently prepared (a vibrational wave packet) among its vibronic levels. The electron is transferred to the QC of uniformly spaced electronic states representing the conduction band levels of the semiconductor and to each electronic level in this QC one assigns a corresponding set of vibronic levels to represent the vibrational state of the product namely, that of the ionized molecule. Thus the final state consists of an electronic–vibronic quasicontinuum (cf. Fig. 1).

The Hamiltonian of the problem can be cast as

$$H = \sum_{a=e,k} H_a(Q) |\varphi_a\rangle \langle \varphi_a| + \sum_k (V_{ke}(Q) |\varphi_k\rangle \langle \varphi_e| + h.c.). \quad (1)$$

The electronic states considered herein, are namely the excited state $|\varphi_e\rangle$ and the levels of the electronic QC $|\varphi_k\rangle$. The Hamiltonian H_a contains the vibrational degrees of freedom for which a harmonic oscillator model will be chosen for the present problem

$$H_a = T + U_a^{(0)} + \sum_{\xi} \frac{\hbar \omega_{\xi}}{4} (Q_{\xi} - Q_{\xi}^{(a)})^2. \quad (2)$$

Here T is the nuclear kinetic-energy operator. The potential energy surface (PES) in the above is given as a sum over the various normal modes with frequency ω_{ξ} , dimensionless coordinate Q_{ξ} and displacement $Q_{\xi}^{(a)}$. The latter is usually related to a more convenient parameter $g_{a\xi} = -Q_{\xi}^{(a)}/2$. The dimensionless displacement term $Q_{\xi}^{(k)}$ is assumed to be the same for all the ionized potential energy surfaces resulting in $g_{i\xi}$.

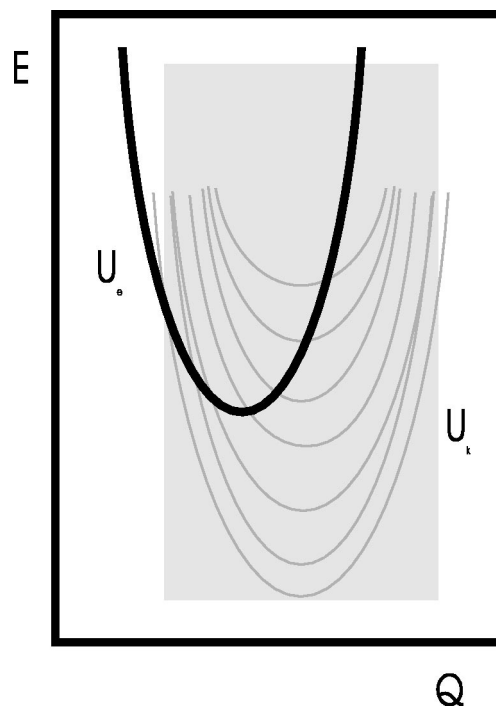


FIG. 1. Scheme of PES for the excited molecular level with PES U_e coupled to the continuum of PES U_k corresponding to the conduction band states of a semiconductor. (The gray shading represents the continuum of PES where only a selected few PES have been explicitly depicted.)

Accordingly a reorganization energy for the formation of the molecular cation can be defined

$$\lambda = \sum_{\xi} \hbar \omega_{\xi} (g_{e\xi} - g_{i\xi})^2. \quad (3)$$

For the following it is useful to introduce the *eigenvalues* and *eigenenergies* of H_a . The *eigenenergies* are written as

$$\hbar \varepsilon_{av} = \hbar \varepsilon_a + \hbar \omega_v, \quad (4)$$

where the first term reads

$$\hbar \varepsilon_a = U_a^{(0)} + \frac{1}{2} \sum_{\xi} \hbar \omega_{\xi}. \quad (5)$$

It is given by the minimum of the respective PES plus the total zero-point energy of all modes. In the case of the band continuum we will write

$$\varepsilon_k = \varepsilon_c + \Delta \varepsilon_k, \quad (6)$$

where ε_c is the reference conduction band energy (for example, the energy of the lower or upper band edge). In the case of a band continuum one usually introduces a density of state written here as

$$\rho(\omega) = \sum_k \delta(\omega - \Delta \varepsilon_k). \quad (7)$$

The second term on the right-hand side of Eq. (4) comprises the complete vibrational energy

$$\hbar \omega_v = \sum_{\xi} v_{\xi} \hbar \omega_{\xi}, \quad (8)$$

with $v \equiv \{v_\xi\}$ denoting the set of vibrational quantum numbers corresponding to the set of normal modes.

The vibrational *eigenfunctions* of H_a , Eq. (2) can be written as a product with respect to functions defined for a single normal-mode

$$|\chi_{av}\rangle = \prod_{\xi} |\chi_{av\xi}\rangle. \quad (9)$$

Since all band levels are characterized by a single type of PES, the associated vibrational states will be denoted $|\chi_{iv}\rangle$ in the following. The interstate coupling term V_{ke} may depend on the molecule to surface distance, too. However, it is assumed here that the normal mode oscillations of the molecule do not substantially modify the molecule surface distance and hence V_{ke} is set independent of Q . This is reasonable in view of the rigid anchor group chosen to attach the chromophore to the surface.⁶

As the decay of excited state can be within 100 fs it will be assumed in the present description that vibrational relaxation is not crucial. In the above experimental system injected hot electrons have been found to relax in about 150 fs²⁹ and the vibrational wave packet in the excited state of the chromophore lasts at least 1 ps.¹² Hence a time-dependent Schrödinger equation is justified to obtain the electron–vibrational wave function. It is expanded according to

$$|\Psi(t)\rangle = \sum_{av} A_{av}(t) \exp(i\varepsilon_{av}t) |\chi_{av}\rangle |\varphi_a\rangle. \quad (10)$$

To simplify the notation, oscillatory factors given by the *eigenenergies* of the various states have been split off. The initial state arising from an impulsive excitation process (at $t=0$) is given as

$$|\Psi(0)\rangle = |\chi_{g0}\rangle |\varphi_e\rangle, \quad (11)$$

where $|\chi_{g0}\rangle$ denotes the vibrational ground-state $v=0$ of the electronic ground-state ($a=g$). If expanded with respect to the excited-state vibrational wave functions, one obtains the initial conditions for the expansion coefficients

$$A_{av}(0) = \delta_{a,e} \langle \chi_{ev} | \chi_{g0} \rangle. \quad (12)$$

Thus the initial state is a coherent superposition of vibronic levels and constitutes a vibrational wave packet on the excited-state PES. The relative contributions from the various excited-state vibrational wave functions to the initial wave packet follows a Poisson distribution that is determined by the parameter g_p where

$$\langle \chi_{e0} | \chi_{g0} \rangle = \exp(-g_p^2/2). \quad (13)$$

Since g_p is related to the dimensionless displacement between the ground- and excited-state PES, as one increases the value of g_p the mean value of the Poisson distribution shifts to higher vibrational levels.

Usage of the time-dependent Schrödinger equation yields a set of coupled differential equations for the expansion coefficients

$$\begin{aligned} \frac{\partial}{\partial t} A_{ev}(t) &= -\frac{i}{\hbar} \sum_k \sum_{\mu} V_{ek} \langle \chi_{ev} | \chi_{i\mu} \rangle \exp i(\varepsilon_{ev} - \varepsilon_{k\mu}) t A_{k\mu}(t), \end{aligned} \quad (14)$$

and

$$\frac{\partial}{\partial t} A_{k\mu}(t) = -\frac{i}{\hbar} \sum_{\bar{v}} V_{ke} \langle \chi_{i\mu} | \chi_{e\bar{v}} \rangle \exp i(\varepsilon_{k\mu} - \varepsilon_{e\bar{v}}) t A_{e\bar{v}}(t). \quad (15)$$

The dynamical quantity of interest that will be calculated numerically as well as analytically in this work is the time-dependent occupation probability of the excited state of the molecule which is given by

$$P_e(t) = \sum_v |A_{ev}(t)|^2. \quad (16)$$

Time-dependent rise of the electronic distributions in the QC as well as among the vibrational states of the ionized molecule can be similarly obtained from the solutions to the above equations of motion. Interesting results have been reported on the injected population dynamics among the QC levels that can be influenced by the initial vibrational wave packet prepared in the excited state by a suitable laser pulse.³⁰

In order to obtain an analytical expression, the equation of motion for the excited state can be recast as

$$\frac{\partial}{\partial t} A_{ev}(t) = -\sum_{\bar{v}} \int_0^t d\tau M_{v\bar{v}}(t, \tau) A_{e\bar{v}}(t - \tau). \quad (17)$$

The integral kernel in Eq. (17) reads (note the introduction of transition frequencies, e.g., $\varepsilon_{ec} = \varepsilon_e - \varepsilon_c$)

$$M_{v\bar{v}}(t, \tau) = \exp(i\omega_{v\bar{v}}t) \exp(i\varepsilon_{ec}\tau) J_{ec}(\tau) \mathcal{P}_{e\bar{v}v}(\tau). \quad (18)$$

It contains vibrational and pure electronic contributions. $J_{ec}(\tau)$ is the Fourier transform of

$$\begin{aligned} J_{ec}(\omega) &= \frac{2\pi}{\hbar^2} \sum_k |V_{ek}|^2 \delta(\omega - \Delta\varepsilon_k) \\ &\equiv \frac{2\pi}{\hbar^2} |V_e(\omega)|^2 \rho(\omega). \end{aligned} \quad (19)$$

In the second part of this expression, the density of states of the electronic levels, namely Eq. (7), has been introduced. Furthermore one has set $V_{ek} = V_e(\Delta\varepsilon_k)$. Since the quantity $J_{ec}(\omega)$ [Eq. (19)], is given as a coupling weighted density of states it has to be understood as a spectral density (as it is common in dissipative quantum dynamics). The vibrational part of Eq. (18) reads

$$\mathcal{P}_{e\bar{v}v}(\tau) = \sum_{\mu} \langle \chi_{ev} | \chi_{i\mu} \rangle \langle \chi_{i\mu} | \chi_{e\bar{v}} \rangle \exp(-i\omega_{\mu\bar{v}}\tau). \quad (20)$$

A rearrangement of the state vectors shows that $\mathcal{P}_{e\bar{v}v}(\tau)$ can be interpreted as a time-dependent expectation value of the flip operator $|\chi_{e\bar{v}}\rangle \langle \chi_{ev}|$.

III. DYNAMICS OF DECAY INTO A PURE ELECTRONIC QUASICONTINUUM

It will be pertinent at this point to revisit the dynamics of a pure electronic QC. As it is a well studied problem and the electronic–vibronic QC being a further generalization, it is worthwhile to initially discuss the electronic QC dynamics before proceeding to understand how the effect of introducing vibrational transitions alters the time behavior of the QC. One expects constructive and destructive interferences to occur in the overall population dynamics due to the interaction of the discrete state with the levels of the QC. Initially the discrete state population decays continuously, however, later on rather bizarre re-population (recurrence effects) of the discrete level takes place. This is due to the presence of a finite energy spacing between successive levels.²⁵ These, however, manifest only after a certain initial period of time, the so-called recurrence time τ_r , whose magnitude is inversely proportional to the QC energy spacing $\hbar\Delta$ ²⁸

$$\tau_r = \frac{2\pi}{\Delta}. \quad (21)$$

Therefore when the QC becomes a true continuum (with $\Delta \rightarrow 0$), recurrences can occur only after an infinite period of time which effectively eliminates such effects from dynamical behavior. The excited state then decays irreversibly into the continuum in a manner that is well known from the solutions of the Wigner–Weisskopf³¹ or the Fano–Anderson model.³² All this can be seen from the analytical solution for the discrete state population obtained for the case of a uniformly spaced ($\hbar\Delta$) infinite level QC where the coupling of the discrete state to the QC is a constant²⁵ (see Appendix B).

For early times, i.e., for $t < \tau_r$, the QC behaves like a continuum as the time development is a monotonic exponential decay. The recurrence properties of the QC is an interesting study by itself but the intention here, is to utilize the continuum aspect of the QC by restricting oneself to $t < \tau_r$. This enables one to justify the modeling of a continuum of semiconductor levels via a QC approach. Thus by an appropriate choice of the QC spacing Δ , the duration of the time region of exponential decay can be tuned such that all recurrences arising from the discreteness of the QC are suppressed.

For a finite band, in the time domain $t < \tau_r$, the excited state decays in an exact exponential fashion²⁴ according to Fermi's Golden Rule (see Appendixes A and B) provided the electronic coupling is not so strong that the life time broadening extends to the band edges. It is interesting to note that fulfilling the above requirement with as few as 25 levels (for the coupling strength and QC spacing adopted in this work) it is possible to obtain results similar to the infinite QC case. The effect of positioning the injecting level close to the band edge of a continuum of band levels, results in slower and nonexponential decay that has been investigated in a previous work.²² Similar results can also be shown for the decay into a finite QC. However, the finite nature of the QC that is studied in this work, as one shall see in the next section, arises not from a consideration of transitions into a pure electronic QC but rather from that of vibrational transitions. In

other words, in the coming sections, as far as electronic transitions are concerned only the infinite band limit which is described by the Fermi's Golden Rule will be considered.

IV. DYNAMICS OF DECAY INTO AN ELECTRONIC–VIBRATIONAL QUASICONTINUUM

A. Properties of the electronic–vibronic quasicontinuum

The dynamics of the QC can become more complicated by the association of a set of vibronic levels with each electronic level, due to the presence of the Franck–Condon matrix elements in the transition between the vibronic levels of the excited state and that of the QC. Proceeding along similar lines as in the case of an electronic QC one can now obtain expressions for the more general case of the decay from a set of vibrational levels into a QC that is governed by both electronic and vibronic transitions. As in the pure electronic case, a constant coupling and an infinite electronic QC is employed. Utilizing the closure relation $\sum_{\mu\xi} |\chi_{i\mu\xi}\rangle\langle\chi_{i\mu\xi}| = \hat{I}$ to obtain $\mathcal{P}_{ev\bar{v}}(0) = \delta_{v,\bar{v}}$ one notes that the simplified expression shown in Appendix C indicates clearly that its dynamics is exactly identical to that of the pure electronic QC when $t < \tau_r$. Moreover, setting $\omega_\xi/\Delta = s_\xi$ and if s_ξ happens to be an integer then it is shown in Appendix C that the time behavior of the infinite electronic–vibronic QC for all times, becomes exactly identical to that of the pure electronic QC case.

Thus when one has a truly infinite electronic–vibronic QC for $t < \tau_r$, which is the time domain of physical interest, its dynamics has nothing new to offer when compared with the pure electronic QC case. However, since one is modeling the finite width of the conduction band levels of a semiconductor via such a QC approach one has to determine the applicability and relevance of infinite band results for the finite case. As seen in the last section, the solution obtained for the infinite case applies equally well to the finite case, provided the life-time broadening of the injecting level can be accommodated within such a finite span. The question is whether a similar criteria can be evolved for the finite electronic–vibrational QC and if so, how to characterize the energy span needed to ensure infinity results for such a finite band. In order to explore the above issues further, one can rewrite Eq. (C1) by restricting oneself to $t < \tau_r$ and to a single mode of energy $\hbar\omega_o$ as

$$\frac{\partial}{\partial t} A_{ev}(t) = -\kappa \sum_{\bar{v}} \mathcal{P}_{ev\bar{v}}(0) A_{ev}(t). \quad (22)$$

Expanding which one obtains

$$\begin{aligned} \frac{dA_{ev}(t)}{dt} = & -\kappa \sum_{\mu} |\langle\chi_{ev}|\chi_{i\mu}\rangle|^2 A_{ev}(t) \\ & - \kappa \sum_{\bar{v} \neq v} \sum_{\mu} \langle\chi_{i\mu}|\chi_{ev}\rangle \langle\chi_{ev}|\chi_{i\mu}\rangle \\ & \times \exp(-i\{\epsilon_{e\bar{v}} - \epsilon_{ev}\}t) A_{e\bar{v}}(t). \end{aligned} \quad (23)$$

Although one has started with the solution for the infinite band case, it will be shown below that the finite nature of the

electronic QC will impose restrictions on the summation over vibrational transitions and hence it will not necessarily lead to the trivial result, $\mathcal{P}_{ev\bar{v}}(0) = \delta_{v,\bar{v}}$. In the above equation each term $|\langle\chi_{ev}|\chi_{i\mu}\rangle|^2$ corresponds to a vibrational transition whereby the ionized molecule gains a vibrational energy of $(\mu-v)\hbar\omega_o$ (for $\mu>v$) and the electron loses an equal amount of energy to be injected into a level which is $(\mu-v)\hbar\omega_o$ below the excited electronic state. In other words energy conservation dictates that the following:

$$\varepsilon_k = \varepsilon_e + (v - \mu)\hbar\omega_o, \quad (24)$$

should be obeyed. However, the presence of the lower edge of the finite band of QC levels restricts further vibrational transitions as it specifies the maximum electron energy loss possible in the injection process (for each initial excited vibronic level), as no further QC electronic levels are available thereafter. Thus the summation over the vibrational transitions in Eq. (23) becomes finite and one can denote the maximum value of μ attained as μ' . Although one needs the entire set of orthonormal vibrational eigenstates to formally ensure closure and orthonormality properties [i.e., $\mathcal{P}_{ev\bar{v}}(0) = \delta_{v,\bar{v}}$], it is still possible to obtain even with a restricted summation, denoted by $\bar{\mu}$, the relations $\sum_{\bar{\mu}} |\langle\chi_{ev}|\chi_{i\bar{\mu}}\rangle|^2 \approx 1$ and $\sum_{\bar{v} \neq v} \sum_{\bar{\mu}} \langle\chi_{i\bar{\mu}}|\chi_{ev}\rangle \langle\chi_{ev}|\chi_{i\bar{\mu}}\rangle \approx 0$. This is because the value of Franck–Condon overlap terms become exceedingly small after a certain value of μ , say μ_c , and subsequent terms in the summation hardly contribute to the summed up value. This critical value depends on the dimensionless displacement parameter $g_{ei\xi} = (g_{e\xi} - g_{i\xi})$ between the excited and the ionized state. Therefore, the condition for attaining the wide-band limit even with a finite electronic vibronic QC is that $\mu_c \leq \mu'$. In such a case the vibrational transitions disappear from Eq. (23) and one obtains Fermi's Golden Rule as its solution. However, when $\mu_c > \mu'$, one obtains an interesting result as the Franck–Condon transitions are now retained in Eq. (23), although they now appear within a restricted summation that is indicative of a finite electronic QC. Now, if there are sufficient electronic levels to accommodate the life-time broadening for each vibrational transition, electronic transitions continue to see an infinite QC band while the vibrational transitions sense its finite nature.

Of course, in the above case it has been assumed that $\omega_\xi > \Delta$ since for $\omega_\xi < \Delta$ one is already in the infinity limit for electronic–vibrational transitions even prior to attaining the infinity limit for a pure electronic transition. The subsequent sections would deal mainly with the physically relevant as well as interesting case of having $\omega_\xi > \Delta$ since for the other case the dynamics is no different from that of the infinite electronic QC case but strictly only for times $t < \tau_r$ as is shown in Appendix C.

One can now derive an approximate expression for the decay of the excited state for the case when $t < \tau_r$, which is the focus of physical interest here. One utilizes Eq. (23) and solves the differential equation by assuming an exponential decay for the term

$$A_{ev\bar{v}}(t) \approx A_{ev\bar{v}}(t=0) \exp(-k_{v\bar{v}}t/2), \quad (25)$$

as a zeroth-order solution. The dominant terms of the decay can be expressed as

$$\begin{aligned} P_e(t) \approx & \sum_v |A_{ev}(t=0)|^2 \exp(-k_v t) \\ & - \sum_{v,\bar{v}} \sum_{\bar{\mu}} A_{ev}(t=0) A_{e\bar{v}}(t=0) \\ & \times \exp(-[k_v + k_{\bar{v}}]t/2) \frac{2\kappa}{\varepsilon_{ev} - \varepsilon_{e\bar{v}}} \langle\chi_{i\bar{\mu}}|\chi_{ev}\rangle \langle\chi_{e\bar{v}}|\chi_{i\bar{\mu}}\rangle \\ & \times \sin(\varepsilon_{ev} - \varepsilon_{e\bar{v}})t, \end{aligned} \quad (26)$$

where

$$k_v = 2\kappa \sum_{\bar{\mu}} |\langle\chi_{ev}|\chi_{i\bar{\mu}}\rangle|^2. \quad (27)$$

In Appendix D it is shown that the basic form of Eq. (26) can be obtained in an elegant fashion by neglecting retardation effects in the basic equation of motion given in Eq. (17). The finite nature of the QC is reflected in the restricted summation over μ which is indicated by $\bar{\mu}$. The first summation in the above expression indicates the decay of the diagonal elements and the second summation represents the coherence effects arising from the interferences between the various off-diagonal elements. Such coherent effects lead to modulation of the population in the excited state in the course of its decay. The oscillations which arise from the interference die out in the time scale of electron transfer due to the presence of the exponentially decaying functions. It should be noted that the above expression can also describe decay of the excited state when one has initially a thermal population. In this case the off-diagonal coherences in the second summation has to be ignored and for the first summation the initial probabilities need to be appropriately defined. Therefore, Eq. (26) represents a general expression for heterogeneous ET into empty levels of a semiconductor substrate.

Bixon and Jortner¹⁸ have derived a similar expression for coherent decay from a set of vibronic states into an infinite intramolecular vibrational QC. However, unlike in Ref. 18, Eq. (26) deals with a finite electronic–vibronic QC of final states wherein all allowed Franck–Condon factors are exactly included. With no restrictions on the summation, Eq. (26) goes over to the infinite (wide-band) QC limit and this is equivalent to the decay into a pure electronic QC or the constant coupling limit as it is described in Ref. 18. Herein the diagonal terms of Eq. (26) become identical with that of Fermi's Golden Rule. Also the summation over the off-diagonal terms goes to zero. The decay rate becoming independent of Franck–Condon factors in the wide band limit is a characteristic feature of heterogeneous ET has been noted in Ref. 5.

In the wide band limit, since each excited vibrational level decays at the same rate given by Fermi's Golden Rule, temperature variations do not influence the overall time dependence of the decay. However, when one is not in the wide band limit each excited vibrational level “ v ,” decays at its own specific exponential rate “ k_v ” that is weighted by its initial occupancy. Since the initial occupancies can be modified by variations in temperature, the overall decay

determined by the sum over the diagonal and the off-diagonal terms, in such a case, will acquire a temperature dependence. Although in the present treatment temperature effects cannot be explicitly included, the effect of varying initial occupancies on the decay of the excited state will be addressed in this work. One can thereby infer the effects of temperature on the decay of the excited state.

In the coming sections exact calculations will be carried out in order to study the effect of both system parameters as well as experimental parameters on the time scale and nature of the decay. In most of the cases Eq. (26) will be plotted alongside exact calculations to show its accuracy. However, for cases when ϵ_k as determined by Eq. (24) falls exactly at the band edges, Eq. (26) does not give accurate fits. The reason being that at the band edge the lifetime broadening spills over the band edge and this causes the assumption of an infinite band being available for the pure electronic transition to become invalid. One has to then make appropriate corrections to include such edge effects.

For the various numerical calculations an electronic QC of width 1.4 eV with a spacing of $\hbar\Delta = 0.01$ eV will be chosen. A single mode of vibrational spacing of $\hbar\omega_o = 0.2$ eV will be used with 11 vibronic levels in the initial excited-state manifold and 21 vibrational states for every electronic level in the QC. The electronic–vibronic QC thus consists of 2940 levels. The purely electronic lifetime of the excited state or equivalently its lifetime in the wide-band limit is determined by the value of $(2\kappa)^{-1}$ which is always around 80 fs, a value that is close to experimental results.⁶ Unless specified in the calculations, usually $g_p = 1$.

B. Effect of changing the reorganization energy

The reorganization energy λ for the formation of the molecular cation has been given in Eq. (3). If this quantity vanishes one easily realizes that Eq. (17) does not couple different vibrational states [$M_{v\bar{v}}$, Eq. (18) becomes diagonal since for $\lambda = 0$ the quantity $\mathcal{P}_{e\bar{v}\bar{v}}$, Eq. (20) equals $\delta_{v,\bar{v}}$]. As a result, all vibrational levels decay with the same rate. Once again the decay into a pure electronic QC is obtained in a manner similar to the wide-band limit. However, in this case even for $t > \tau_r$, the two QC have identical time behavior irrespective of whether $\omega_{\text{vib}}/\Delta$ is an integer or not. In a previous work when excited state decay into a continuum ($\tau_r \rightarrow \infty$) was studied,²² it was argued that $\lambda = 0$ is the same as the wide-band limit. The above reasoning seems to vindicate that assumption for the continuum limit. However, as one shall see later this is true only for a constant electronic coupling.

The decay of an initial vibrational wave packet into a finite electronic–vibronic QC for different reorganization energies is examined in Fig. 2. Here and in the following λ is varied via the change of the mutual displacement of the two PES referring to the excited molecule and to the cationic state of the molecule. One notes that the decay is fastest for $\lambda = 0$ which is also equivalent to the wide band limit. For finite values of λ , the Franck–Condon factors contribute to the population decay and their effect is essentially to slow down the rate of decay since the restricted summation is always less than unity [cf. Eq. (27)]. The finite width of the

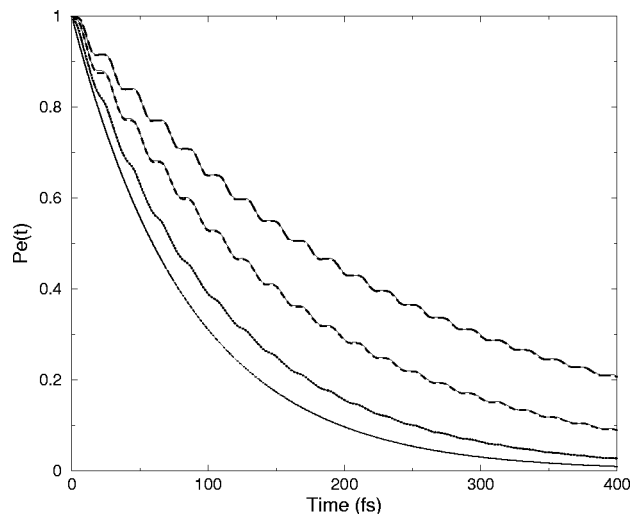


FIG. 2. Excited-state decay from an energetic position of 0.5 eV from bottom of a 1.4 eV wide QC for various reorganization energies λ . Solid line: $\lambda = 0$, dotted line: $\lambda = 0.2$ eV, dashed line: $\lambda = 0.45$ eV, long-dashed line (corresponds to the slowest decay): $\lambda = 0.8$ eV. The slender solid line represents fit for the corresponding calculations from Eq. (26).

QC results in the restricted summation over the Franck–Condon terms and more importantly leads to off-diagonal coherences.

Steplike oscillations are seen in the decay (Fig. 2) which are essentially modulations in the ET rate as the wave packet moves towards and away from the curve crossing of the initial and final (QC) of potential energy surfaces. When the wave packet is in the vicinity of the curve crossing the excited-state decays more rapidly than when it moves away (compare also Fig. 1). As a result oscillations occur in the effective ET rate as seen in Fig. 2. This is characteristic of two level systems and has been studied extensively both theoretically (see, for example, Ref. 17) as well as experimentally.¹³ Clearly an increase in the reorganization energy accentuates the finite nature of the QC as evidenced by slower and modulated oscillatory ET. Conversely for smaller values of reorganization, even though one has a vibrational wave packet in the excited state, only a smooth and rapid monotonic decay of the excited state is obtained.

By varying the reorganization energy one is essentially varying the total number of significant Franck–Condon terms that is being summed up within the restrictions imposed by the finite nature of the QC. For instance when $\lambda \leq \hbar\omega_{\text{vib}}$ the first few terms are sufficient to obtain a sum to unity leading to a wide band limit or a pure electronic QC behavior. However, if $\lambda > \hbar\omega_{\text{vib}}$ a number of terms are needed for a sum to unity and this may not be possible because of the restriction on the summation. Hence this would lead to slower and modulated decays.

C. Effect of varying the position of the injecting level

The position of the injecting level like the reorganization energy is an important system parameter. Its role in determining the dynamics of decay into the electronic–vibronic QC can be understood from Eq. (26) wherein, it determines the minimum and maximum value of $\bar{\mu}$ via the energy con-

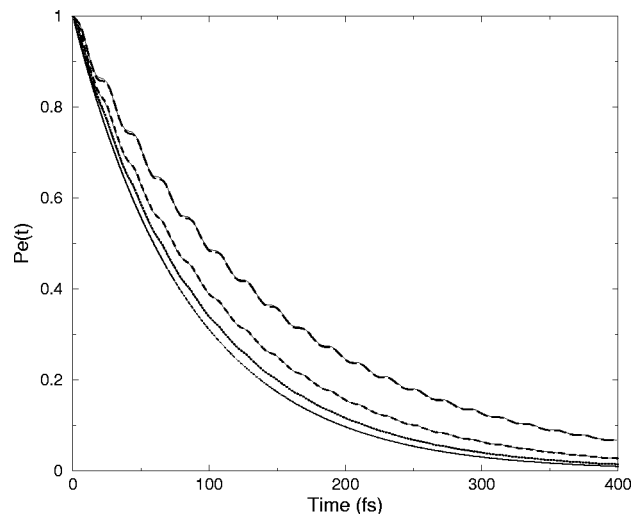


FIG. 3. Excited-state decay for a reorganization energy $\lambda=0.2$ eV and for various energetic positions ε_e from the bottom of a 1.4 eV wide band. Solid line: wide-band limit, dotted line: 0.7 eV from the bottom, dashed line: 0.5 eV from the bottom, and long-dashed line: 0.3 eV from the bottom. The slender solid line represents fit for the corresponding calculations from Eq. (26).

ervation condition of Eq. (24). When the vibronic levels of the excited state are in the middle of a sufficiently wide band one obtains a large range of allowed $\bar{\mu}$ values such that all relevant Franck–Condon factors can be summed to unity thereby obtaining the wide band limit. On the other hand when the excited state is close to either the top of the QC band or to its bottom then Eq. (24) allows for only a limited range of $\bar{\mu}$ values and one usually obtains from such a restriction, slower and oscillatory decays. This behavior is reflected in Fig. 3 which shows the effect of varying the position of the injecting level on the excited-state population decay. For a given value of reorganization energy, the decay becomes slower and more oscillatory as the injected level is shifted closer towards the lower band edge. It is interesting to note that when the excited electronic state is close to the bottom of the band, the steplike oscillations indicate ET occurs rapidly when the wave packet is moving towards the equilibrium value of the ionized state PES but levelling off when it is moving away. However, the exact opposite behavior is noted from Fig. 4 when the excited electronic state is close to the top of the QC band.

One can understand this via simple curve crossing arguments as drawn in Fig. 5. If the QC is wide enough with respect to the position of the injecting level then all intersections (curve crossings) between the excited-state PES and that of the ionized state QC is realizable. In that case electron transfer to the QC occurs at every point in the course of the trajectory of the vibrational wave packet in its co-ordinate space, and consequently the decay is monotonic and one is *de facto* in the wide band limit. When the injecting level is close to the lower band edge, there are sufficient curve crossings with the QC of the ionized state PES when the wave packet is moving towards the equilibrium value of the ionized state. Hence, ET will occur when the wave packet is moving towards the equilibrium point. On the other hand due to the lower band edge, when levels are not available for

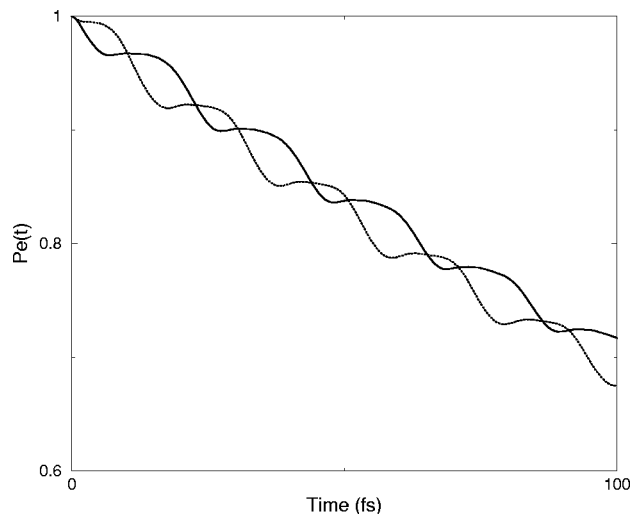


FIG. 4. Phase change occurring in the excited-state decay between two different energetic positions (reorganization energy $\lambda=0.2$ eV). Dotted line: ε_e at the bottom of the QC band, solid line: $\hbar\varepsilon_e$ positioned 0.4 eV above the top of the 1.4 eV wide QC band.

curve crossings at the farther end of the excited state PES, ET levels off when the wave packet is travelling in this vicinity. This is also the situation that is encountered in two-level problems as well as in the variation of the reorganization energy discussed previously. However, a unique situation occurs when the excited state is close to the top of the QC. Now, it can happen that sufficient curve crossings (between the excited state PES and that of the ionized QC) exist when the vibrational wave packet is moving away from the equilibrium of the ionized state PES whereas levels are not available for ET closer to the equilibrium point. In this case the excited state decays when the wave packet is away from the equilibrium point of the ionized state but levels off when it moves towards it. Thus a phase change occurs in the oscillatory decay between positions, when the injecting level is close either to the top or to the bottom of the band as is seen from Fig. 4.

D. Effect of varying the initial vibrational wave packet

In an experiment the initial vibrational wave packet (population profile among the vibronic levels of the excited state) can be varied simply by changing the pulse width and/or the wavelength of the exciting laser pulse. Since the excitation is assumed to be impulsive in this work, the initial state is varied by varying the position of the of the initial wave packet χ_{g0} . This is achieved in varying g_p , thereby achieving vibronic wave packets of corresponding higher or lower average energies. The related Poisson distribution of probabilities among the vibronic levels implies that only a finite number of them have a numerically significant initial occupancy. If each of them individually satisfy the the wide band limit, i.e., all of them have the same time decay, one obtains the decay pertaining to the pure electronic decay. For a different Poisson distribution of initial occupancies one can obtain a similar result if one is far from the band edges.

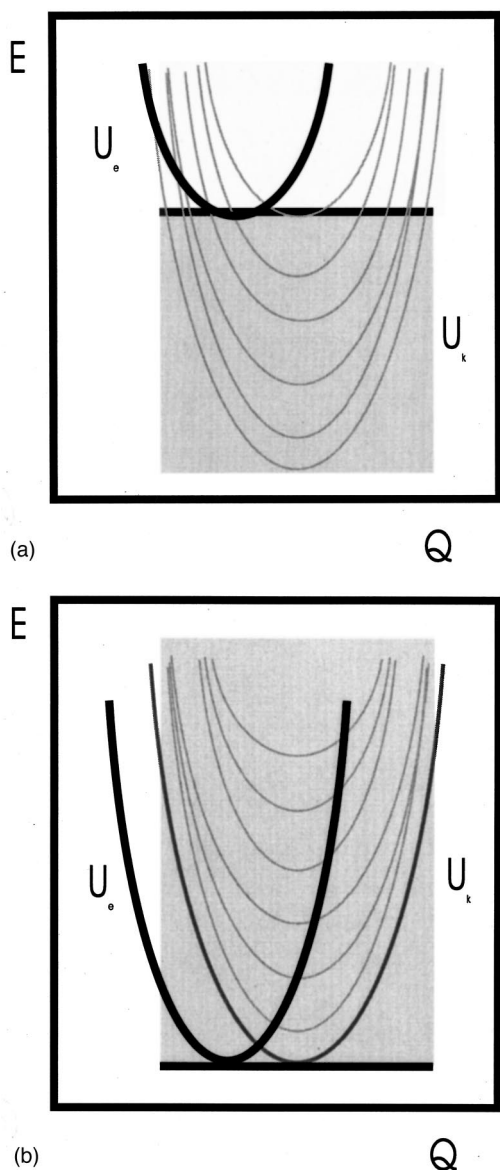


FIG. 5. Scheme of PES for the excited molecular level with PES U_e coupled to the limited continuum of PES U_k corresponding to a finite conduction band. Part a: Bottom of U_e is degenerate with the upper band edge. Part b: Bottom of U_e is degenerate with the lower band edge.

However when one is close to a band edge, different Poisson distributions can give rise to different decay times. For instance, when one is close to the lower band edge ($\epsilon_e = 0.1$ eV), a distribution ($g_p = 1$) in which the lower vibronic levels of the excited state have most of the initial probability of occupancy, the excited state decay as seen in Fig. 6 (see dotted line) is much slower, with the clear signature of the step-wise decay. On the other hand when the Poisson distribution is shifted to higher vibronic levels ($g_p = 2$), the decay can be faster as is seen in Fig. 6 (see dashed line). When the excited state is close to the upper band edge ($\epsilon_e = 1.3$ eV), as in Fig. 7, the exact opposite behavior is to be expected, i.e., lower vibronic populations ($g_p = 1$) decay faster (see dotted line in Fig. 7) whereas higher vibronic populations ($g_p = 2$) decay more slowly (see dashed line in Fig. 7). Thus unless the excited state is in the middle of a

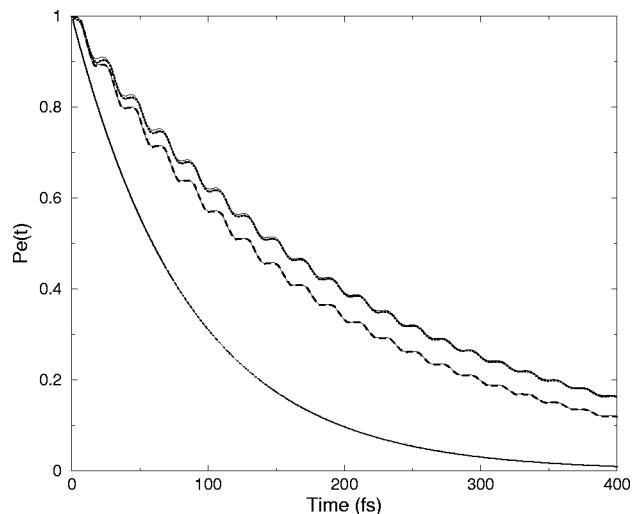


FIG. 6. Excited-state decay from ϵ_e positioned 0.1 eV above the bottom of a 1.4 eV wide band (reorganization energy $\lambda = 0.2$ eV). Solid line: wide-band limit, dotted line: lower vibronic levels populated ($g_p = 1$), dashed line: higher vibronic levels populated ($g_p = 2$). The slender solid line represents fit for the corresponding calculations from Eq. (26).

large band or the reorganization energy is rather small, it should be possible in principle to obtain different excited-state decay with the modulation of transfer probability by changing the wavelength of the laser pulse. In such cases one can control the excited state decay by appropriate variation of the wavelength of the laser pulse.

E. Excited-state decay in the presence of two vibrational modes

In order to understand the decay in realistic situations where more than one vibrational mode can actively partici-

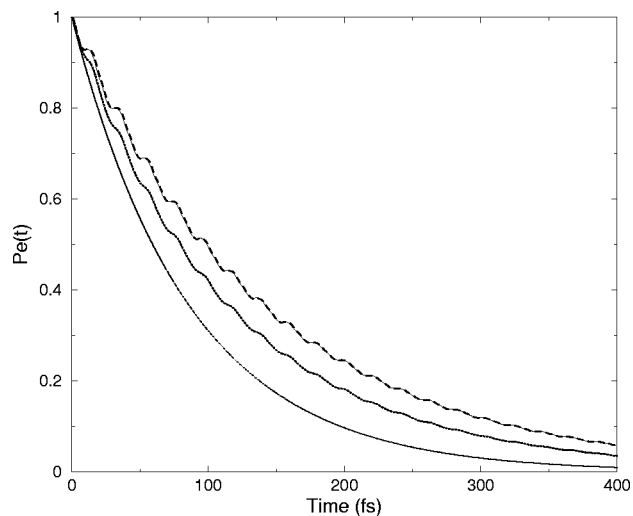


FIG. 7. Excited-state decay from ϵ_e positioned 1.3 eV above the bottom of a 1.4 eV wide band (reorganization energy $\lambda = 0.2$ eV). Solid line: wide-band limit, dotted line: lower vibronic levels populated ($g_p = 1$), dashed line: higher vibronic levels populated ($g_p = 2$). The slender solid line represents fit for the corresponding calculations from Eq. (26).

pate in electron transfer, two vibrational modes will be explicitly included in the analysis of the excited state population dynamics. As the numerical results have been shown to be equivalent to the decay expression one can extend Eq. (26) to a two mode case and draw inferences from its time behavior when several modes are actively involved in the electron transfer process. Accordingly

$$\begin{aligned}
 P_{e\{v_1 v_2\}}(t) \approx & \sum_{v_1, v_2} |A_{ev_1}(t=0)|^2 |A_{ev_2}(t=0)|^2 \exp(-k_{v_1 v_2} t) - \sum_{v_1, v_2, \bar{v}_1} A_{ev_1}(t=0) A_{e\bar{v}_1}(t=0) \times |A_{ev_2}(t=0)|^2 \\
 & \times \exp(-[k_{v_1 v_2} + k_{\bar{v}_1 v_2}]t/2) \frac{2\kappa S_{v_1 \bar{v}_1} S_{v_2 v_2}}{\varepsilon_{ev_1} - \varepsilon_{e\bar{v}_1}} \sin(\varepsilon_{ev_1} - \varepsilon_{e\bar{v}_1})t - \sum_{v_1, v_2, \bar{v}_2} |A_{ev_1}(t=0)|^2 A_{ev_2}(t=0) A_{e\bar{v}_2}(t=0) \\
 & \times \exp(-[k_{v_1 v_2} + k_{v_1 \bar{v}_2}]t/2) \frac{2\kappa S_{v_1 v_1} S_{v_2 \bar{v}_2}}{\varepsilon_{ev_2} - \varepsilon_{e\bar{v}_2}} \sin(\varepsilon_{ev_2} - \varepsilon_{e\bar{v}_2})t - \sum_{v_1, v_2} \sum_{\bar{v}_1, \bar{v}_2} A_{ev_1}(t=0) A_{e\bar{v}_1}(t=0) \\
 & \times A_{ev_2}(t=0) A_{e\bar{v}_2}(t=0) \exp(-[k_{v_1 v_2} + k_{\bar{v}_1 \bar{v}_2}]t/2) S_{v_1 \bar{v}_1} S_{v_2 \bar{v}_2} \frac{2\kappa \sin[(\varepsilon_{ev_1} - \varepsilon_{e\bar{v}_1}) + (\varepsilon_{ev_2} - \varepsilon_{e\bar{v}_2})]t}{(\varepsilon_{ev_1} - \varepsilon_{e\bar{v}_1}) + (\varepsilon_{ev_2} - \varepsilon_{e\bar{v}_2})}, \quad (28)
 \end{aligned}$$

where

$$k_{v_1 v_2} = 2\kappa S_{v_1 v_1} S_{v_2 v_2} \quad (29)$$

and

$$S_{v_i \bar{v}_i} = \sum_{\bar{\mu}} \langle \chi_{i\bar{\mu}} | \chi_{ev_i} \rangle \langle \chi_{e\bar{v}_i} | \chi_{i\bar{\mu}} \rangle. \quad (30)$$

The dominant terms of decay for a two mode case can thus be cast into a purely diagonal term for both the modes (the first term), and three off-diagonal terms arising from cases wherein one or the other mode is diagonal while the other is off-diagonal (the second and third summation terms) and the wholly off-diagonal contribution as signified by the last term. Depending on the frequency of each mode and the displacement of its PES with respect to the ground state a sub-set of modes can satisfy the wide band limit. For such modes the following relationship will hold namely, $S_{v_i \bar{v}_i} = \delta_{v_i \bar{v}_i}$. The consequences of this can be seen from Eq. (28). For instance if both the modes satisfy the criteria for the wide band limit then, Eq. (28) becomes identical to that of decay into a pure electronic QC. Thus for two modes of frequencies, $\hbar\omega_1 = 0.08$ eV and $\hbar\omega_2 = 0.06$ eV one finds that the wide band criteria is satisfied and the decay coincides completely with the decay into an electronic QC as in Fig. 8. On the other hand if only one of the frequencies satisfy the wide band limit ($\hbar\omega_1 = 0.08$ eV) whereas the other one does not ($\hbar\omega_2 = 0.2$ eV), Eq. (28) reduces to that of a single mode case [i.e., Eq. (26)] as can also be seen from Fig. 8. Thus all the modes which satisfy the wide band limit have no role in the decay and even a large number of such low-frequency modes will not smear out the oscillations of the high-frequency modes which modulate electron transfer. When both the modes do not satisfy the wide band limit, one obtains a genuine case of a two mode result as is seen from the slowest decay curve of Fig. 8. If more than one mode does not satisfy the wide band limit, the decay gets slower with the inclusion of every such mode.

V. EFFECT OF VARYING THE DENSITY OF STATES AND THE ELECTRONIC COUPLING

In the previous section various facets of the decay into an electronic vibronic QC were studied including that of its control by different, initial, laser prepared populations. However, the entire analysis including all the previous work done on pure electronic QC have always assumed a constant density of states, i.e., a uniform spacing, as well as a constant coupling strength. It is well known that the density of states of the conduction band varies with energy and this can be ignored only if the variation is extremely slow over the energy range that is resonant with the life time broadened energy of the injecting level. For a pure electronic QC tending

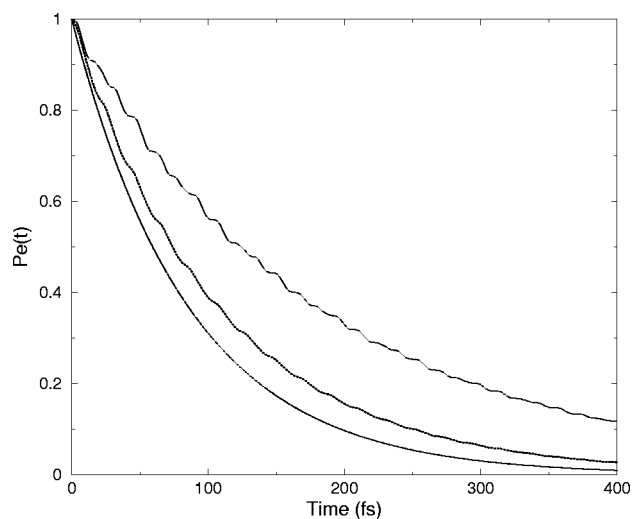


FIG. 8. Excited-state decay for constant coupling two mode system. $\varepsilon_e = 0.5$ eV above band edge. Solid line: Wide band limit as well as decay with modes of frequencies $\hbar\omega_1 = 0.08$ eV and $\hbar\omega_2 = 0.06$ eV. Dotted line: $\hbar\omega_1 = 0.08$ eV and $\hbar\omega_2 = 0.2$ eV. This coincides with numerical calculation obtained for the decay of a single mode where $\hbar\omega_0 = 0.2$ eV (dashed). Solid line with slowest decay: $\hbar\omega_1 = 0.28$ eV and $\hbar\omega_2 = 0.2$ eV.

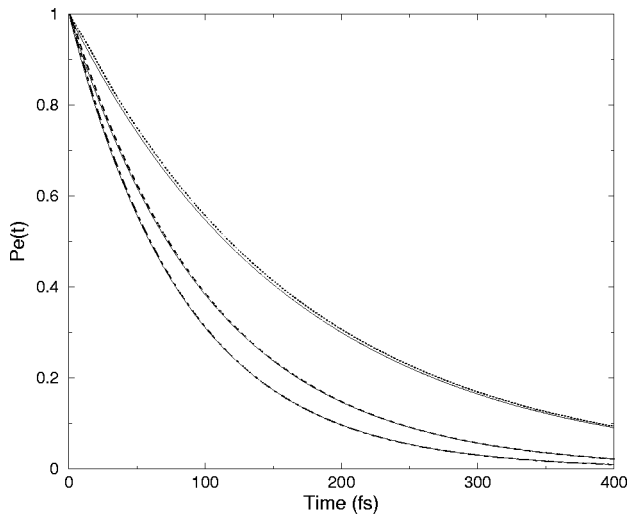


FIG. 9. Excited-state decay for various energetic positions ε_e from the bottom of a 1.4 eV wide band of electronic QC. Solid line: wide-band limit, dotted line: 1.3 eV above the bottom, dot-dashed line: 0.7 eV above the bottom (mid-band and coincides with wide-band limit), dashed line: 0.3 eV above the bottom. The slender solid line represents fit for the corresponding calculations from Eq. (32) for ε_e values 1.3 eV, and 0.3 eV from bottom of the band.

towards the wide band limit one may be justified in ignoring such variations but since in this work one is considering the effects arising from the finite nature of an electronic–vibronic QC it will be of interest to explore the effects of a varying density of states and/or a varying electronic coupling.

In order to mimic a simple case of a local density of states on the first atom of a semi-infinite chain in a tight-binding model,³³ the electronic coupling $|V_{ke}|^2$ is defined for the pure electronic QC as

$$|V_{ke}|^2 = |v|^2 \frac{(w^2 - (\varepsilon_k - w)^2)^{1/2}}{w}, \quad (31)$$

where w is the value of ε_k at the mid-point of the QC band. The electronic coupling is now a parabolic function which reaches its maximum value in the middle of the band and goes to zero at the band edges. Since one is in the infinite band limit (Fermi's Golden rule regime), the injecting level senses a value of the coupling appropriate to the k level that is energetically resonant with it. The time-dependent occupancy of the injecting level, therefore, follows an exponential decay at a rate 2κ where:

$$\kappa = \frac{\pi |v|^2}{\Delta} \frac{(w^2 - (\varepsilon_e - w)^2)^{1/2}}{w}. \quad (32)$$

As can be ascertained from Fig. 9, the decay into an electronic QC with an electronic coupling which varies as in Eq. (31) is indeed given by the above expression where the rate depends on the energetic location of the injecting level ε_e . But this is similar to the expression one obtains in the wide band limit for a level injecting into a continuum of levels which has a quadratic energy dependence for its density of states.²² In this manner by a suitable choice of the electronic coupling one can bring variation in the density of states as well as in the electronic coupling into the QC approach.

Extending the above method to the electronic–vibronic QC one can now incorporate the variations in the effective coupling into the expression for the decay of the excited state (for a single mode case and for $t < \tau_r$)

$$P_e(t) \approx \sum_v |A_{ev}(t=0)|^2 \exp(-k_v t) - \sum_{v \neq \bar{v}} \sum_{\bar{\mu}} A_{ev}(t=0) A_{e\bar{v}}(t=0) \times \exp(-[k_v + k_{\bar{v}}]t/2) \frac{2\kappa_{v\bar{\mu}} \hbar}{\varepsilon_v - \varepsilon_{\bar{v}}} \langle \bar{\mu} | v \rangle \langle \bar{v} | \bar{\mu} \rangle \times \sin(\varepsilon_v - \varepsilon_{\bar{v}})t, \quad (33)$$

where

$$k_v = 2 \sum_{\bar{\mu}} \kappa_{v\bar{\mu}} |\langle v | \bar{\mu} \rangle|^2 \quad (34)$$

and

$$\kappa_{v\bar{\mu}} = \frac{\pi |v|^2}{\Delta} f(\{w_i\}, v, \bar{\mu}). \quad (35)$$

Now $f(\{w_i\}, v, \bar{\mu})$ is a function which includes not only the vibrational quantum numbers of the excited and the ionized molecule (that help to locate the electronic level in the QC into which the electron is injected) but also the band parameters of the semiconductor model ($\{w_i\}$). One can use for instance the functional form from a one-dimensional (1D) chain of atoms for compound semiconductors with a constant coupling for the molecular excited state at the end of the semi-infinite chain³⁴ or where the coupling is also varying.²³ However, for purposes of illustrating the general physics, the simple case that was considered in the pure electronic QC will be taken up namely

$$f(w, v, \bar{\mu}) = \frac{\sqrt{w^2 - [w - (\varepsilon_v - \bar{\mu} \hbar \omega_0)]^2}}{w}. \quad (36)$$

The band parameters in this case just reduces to w which is nothing but the value of the energy level of the QC in the middle of the band, i.e., $w = \varepsilon_k(\text{mid-point})$. One has to note that $\bar{\mu}$ signifies a restricted summation indicating the finite nature of the electronic vibronic QC.

The accuracy of using the modified decay expression Eq. (33) is seen from Fig. 10 wherein the decay is plotted for different injecting positions for the excited electronic state. Since the effective electronic coupling given by Eq. (31) is decreasing away from the middle of the band, the decay gets progressively slower when the excited state is shifted towards the lower band edge, whereas remains more or less the same when it is shifted to the upper part. The latter trend is obvious since the largest terms in the summation leading to the overall rate [Eq. (34)], is included once the level is positioned above the middle of the band. For this reason the decays plotted in Fig. 10 are different from the one into the pure electronic QC where the decays are symmetrical below and above the middle of the band [see Eq. (32)]. In any case the decays that are obtained here are slower than what one would obtain for the case of a constant coupling (compare

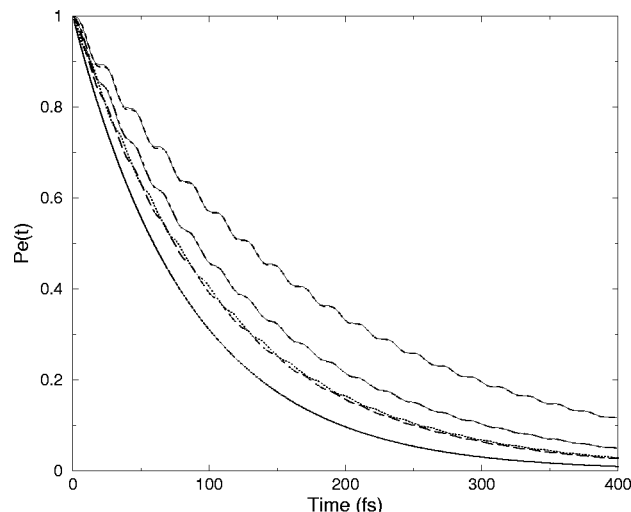


FIG. 10. Excited-state decay for various energetic positions of ε_e from the bottom of a 1.4 eV wide band (reorganization energy $\lambda = 0.2$ eV). Solid line: electronic wide-band limit. Dotted line: 1.1 eV above the bottom as well as long dashed line: 0.7 eV above the bottom (mid-band case), have similar time scales are shown just above the solid line. Dashed-dotted line: 0.5 eV above the bottom, dashed line: 0.3 eV above the bottom (which shows the slowest decay). The slender solid line represents fit for the corresponding calculations using the modified rate given by Eq. (34) for ε_e values 0.5 eV, and 0.3 eV above the bottom of the band.

with Fig. 3). This is clear from Eq. (34) since the presence of the $\bar{\mu}$ index in $\kappa_{v\bar{\mu}}$ implies that the Franck–Condon factors can never be summed to unity (which leads to the maximum rate, i.e., the wide band or the pure electronic QC limit) but to some value which is less than unity. For the same reason the coherence effects from the off-diagonal terms cannot completely disappear though they can be considerably reduced as can be seen when the position of the injecting level is close to the mid-band region and above it in Fig. 10.

The extension to a two mode case is straight forward as in the case of constant coupling and the results are depicted in Fig. 11. The two low-frequency modes which satisfy the wide band conditions in the constant coupling case have a slower decay than the wide band limit showing mild residual oscillations, since the effective varying coupling does not allow for the complete cancellation of the Franck–Condon terms. Similarly, the reduction of two modes to a single mode when one mode satisfies wide band limit in the constant coupling case ($\hbar\omega_1 = 0.08$ eV), whereas the other does not ($\hbar\omega_1 = 0.2$ eV) is not seen when the effective coupling is varying. Thus lower frequencies do play a role in the decay, in the case of varying effective coupling (or equivalently the case of varying density of states and/or electronic coupling strength), especially in slowing it down. It is likely that although lower frequencies are damped (because of the partial cancellation of Franck–Condon terms), a large number of them may still smear the higher frequency oscillations.

Therefore one obtains the important result namely that when one has a density of states and/or an electronic coupling which is varying significantly, then the decay into the band states will not be independent of Franck–Condon factors and hence cannot be determined by the electronic coupling alone. Hence any attempt to obtain the injection rate

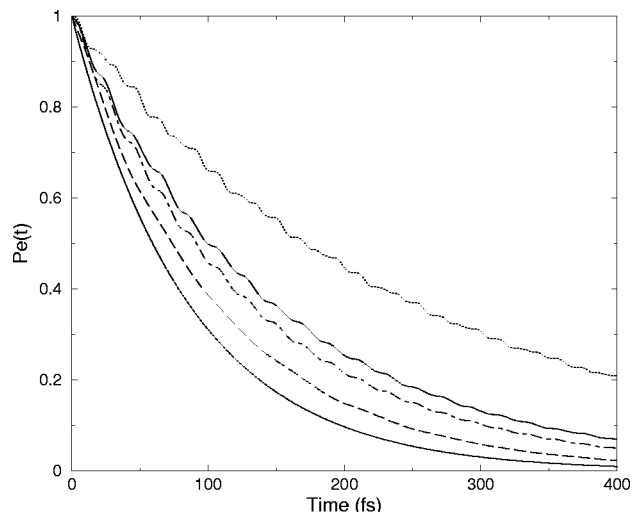


FIG. 11. Excited-state decay for variable coupling two mode system. $\varepsilon_e = 0.5$ eV above band edge. Solid line with fastest decay: Wide band limit. Dashed line: $\hbar\omega_1 = 0.08$ eV and $\hbar\omega_2 = 0.06$ eV. Dashed-dotted line: Single mode $\hbar\omega_0 = 0.2$ eV. Solid line with modulation: $\hbar\omega_1 = 0.08$ eV and $\hbar\omega_2 = 0.2$ eV. Dotted line: $\hbar\omega_1 = 0.28$ eV and $\hbar\omega_2 = 0.2$ eV.

solely from the electronic coupling while adopting a varying density of states as well as electronic coupling^{22,23} would in principle, lead to its overestimation. However for negligible reorganization energy and/or very slowly varying density of states one can indeed be very close to the pure electronic tunneling limit. Going back to the question of whether negligible reorganization is the same as the wide band limit, the answer is that this would be true only if the density of states and electronic coupling were to vary only marginally over the relevant energy range. Otherwise this assumption²² would be incorrect. Consequently the excited-state decay will always have a residual temperature dependence even in the wide band limit if the density of states and/or the electronic coupling were to vary significantly.

VI. SUMMARY AND CONCLUSIONS

Photoinduced charge-transfer from molecule to solid has been modeled and studied via an electronic–vibronic QC. Essential differences between the electronic QC and its generalization namely the electronic–vibronic QC have been illustrated. Utilizing the properties of the QC namely that (i) the QC behaves like a continuum in the early time window before the onset of recurrences and (ii) this time region can be extended to longer times by varying the QC spacing, an approximate expression for the decay of the excited state has been obtained. This expression can be utilized to describe decay from an initial thermal distribution as well as when one has an initial vibrational wave packet. The expression for the decay valid for a finite band also includes the wide-band as a limiting case and accurately reproduces all the numerical results concerning the decay of vibronic coherence as a function of band-width, energetic position of the injecting level, reorganization energy as well as initial population profiles in the excited state. Making use of this fact, the case of two vibrational modes has also been studied via the decay expression and inferences have been drawn when one can have

several modes actively involved in the electron transfer process. In the last section it was also extended to include realistic variations in the density of states as well as in the electronic coupling both of which can be incorporated in the decay expression as an effective variable electronic coupling.

The decay expression has been obtained using the assumption that the infinity limit for the pure electronic transition is attained within a much shorter span of energy width than for vibrational transitions. Thus one can assume the infinity limit for the electronic transitions (Fermi's Golden rule) while still retaining a finite band for the vibronic transitions. When the electronic coupling gets even stronger to induce life time broadening which spills over the finite band edge, Fermi's golden rule can no longer be used to describe the population decay of the excited state as has been shown from continuum calculations.²² In such cases the decay becomes oscillatory and has to be numerically calculated and the decay expression is no longer valid.

Whenever the decay is modulated by vibrational coherence, the amplitude of modulation gradually attenuates during the course of the decay and dies out as the process of electron transfer is completed. The amplitude of modulation is determined both by the initial conditions (laser preparation) of the excited vibrational states, and by the energy and transfer parameters of the model. For instance, energetic position of the injecting vibronic level of a given mode with respect to the band edges, and its corresponding reorganization energy, will determine whether the quantity $\sum_{\bar{\mu}} |\chi_{i\bar{\mu}}| \langle \chi_{i\bar{\mu}} | \chi_{i\bar{\mu}} \rangle$ is close to, or less than unity. Accordingly, the amplitude of modulation can be small or significant. Static inhomogeneous effects not considered here, can lead to a distribution of injecting positions and reorganization energies (via the PES displacements), resulting in a possible smearing of oscillations. Such effects and anharmonicity can also result in nonuniform vibrational energy spacing and smoothen out modulation. Interestingly, varying the coupling strength in order to mimic a specific density of states results in enhancing the amplitude of modulation vis-a-vis constant coupling since invariably $\sum_{\bar{\mu}} \kappa_{v\bar{\mu}} |\chi_{i\bar{\mu}}| \langle \chi_{i\bar{\mu}} | \chi_{i\bar{\mu}} \rangle < 1$. At the same time some amount of smearing of high-frequency oscillations can be expected from a large number of low-frequency modes for this case, unlike for constant coupling. From a study of the off-diagonal terms in the decay expression, it was seen that the oscillations are dominated essentially by the fundamental harmonics of the modulating frequencies.

The results indicate ET from the excited state to the surface is fastest in the wide-band limit which is shown to be equivalent to the zero re-organization limit when one has a constant effective electronic coupling. Under these conditions namely, (1) constant electronic coupling and (2) all vibrational modes participating in the electron transfer fulfill the criteria for the wide band, the transfer time is determined only by the combination of electronic coupling and the available density of states in the semiconductor and will be temperature independent. Also in this situation, ET is not modulated by vibrational wave packets nor can it be manipulated by varying the initial population profiles by means of appropriate laser pulses. However, for the case when the finite nature of the band plays a role in determining ET, it becomes

slower compared to the above limit but can be modulated by appropriately prepared vibrational wave packets and will show temperature dependent decays.

The finite nature of the electronic–vibronic QC manifests when (1) one or more active vibrational modes do not satisfy the wide band limit or equivalently, the reorganization energy associated with respective mode (or modes) is comparable to the energetic distance of the injecting level from the lower edge of the band and (2) irrespective of the active modes satisfying the wide band limit, if the effective electronic coupling varies significantly over this energy range. In such cases to consider the electron injection process as purely electronic would lead to overestimation of the injection times.^{22,23}

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APPENDIX A: GOLDEN RULE TRANSITION RATE

In order to have a reference rate expression at hand, one computes the rate for the transition from a particular vibrational state χ_{ev} into the QC according to the Golden Rule of quantum mechanics. The rate reads

$$k_{ev} = \frac{2\pi}{\hbar^2} \sum_{k\mu} |V_{ek}|^2 |\langle \chi_{ev} | \chi_{i\mu} \rangle|^2 \delta(\varepsilon_{ev} - \varepsilon_{k\mu}). \quad (\text{A1})$$

Noting the definition of the density of states, Eq. (7) and the inverse Fourier transformed spectral density, Eq. (19) one easily obtains

$$k_{ev} = \sum_{\mu} |\langle \chi_{ev} | \chi_{i\mu} \rangle|^2 J_{ec}(\varepsilon_{ec} + \omega_{v\mu}). \quad (\text{A2})$$

APPENDIX B: EQUATION OF MOTION FOR THE ELECTRONIC QC AMPLITUDE

The equations of motion for the amplitude $A_e(t)$ of the excited state can be directly obtained from Eq. (17) by dropping all vibrational quantum numbers, i.e.

$$\frac{\partial}{\partial t} A_e(t) = - \int_0^t d\tau M(\tau) A_e(t-\tau). \quad (\text{B1})$$

The kernel, Eq. (18) is thereby reduced to the quantity $J_{ec}(\tau)$ [Eq. (19)], which can be calculated analytically for the present case of a regular as well as an infinite QC that has a constant transfer coupling. One notes that

$$\rho(\omega) = \sum_{n=-\infty}^{\infty} \delta(\omega - n\Delta), \quad (\text{B2})$$

and obtain ($v = V_e/\hbar$)

$$J_{ec}(\tau) = |v|^2 \sum_{n=-\infty}^{\infty} e^{-in\Delta\tau} \equiv 2\kappa \sum_{n=-\infty}^{\infty} \delta(\tau - n\tau_r). \quad (\text{B3})$$

For the last step the Poisson summation formula³⁵ has been used

$$\sum_{n=-\infty}^{\infty} \exp(-i2\pi nx) = \sum_{n=-\infty}^{\infty} \delta(x-n), \quad (\text{B4})$$

and the following namely, the recurrence time $\tau_r = 2\pi/\Delta$ and the decay rate $\kappa = |v|^2\tau_r/2$ have been introduced.

If one inserts this expression into Eq. (B1) it follows:

$$\begin{aligned} \frac{\partial}{\partial t} A_e(t) = & -\kappa A_e(t) - 2\kappa \sum_{n=1}^{\infty} \theta(t-n\tau_r) \\ & \times \exp(in\varepsilon_{ec}\tau_r) A_e(t-n\tau_r). \end{aligned} \quad (\text{B5})$$

The solution for $A_e(t)$ is given as²⁵⁻²⁷

$$\begin{aligned} A_e(t) = & e^{-\kappa t} \left(1 - \sum_{n=1}^{\infty} \theta(t-n\tau_r) \exp((i\varepsilon_e + \kappa)n\tau_r) \right. \\ & \left. \times 2\kappa(t-n\tau_r) \frac{1}{n} L_{n-1}^1(2\kappa(t-n\tau_r)) \right). \end{aligned} \quad (\text{B6})$$

Here, the L_{n-1}^1 are associated Laguerre polynomials. The first term of Eq. (B6) gives rise to dynamics associated with the continuum aspect of the QC whereas the infinite summation gives rise to dynamics related to the discrete nature of the QC. This is evident, since the first term alone contributes to pure exponential decay in the lifetime, which is characteristic of continuum behavior. Also the contribution of the terms grouped in the summation can be shifted to infinitely later times by making the discrete QC tend towards a continuum (i.e., $\Delta \rightarrow 0$ which results in $\tau_r \rightarrow \infty$). The presence of the Heaviside functions lead to sudden periodic interruptions in the time development, at various multiples of τ_r .

The decay rate κ corresponds to the Golden Rule expression $k_e/2 = J_{ec}/2 = \pi|v|^2\rho$. This is similar to what is obtained from either Eq. (A1) or Eq. (A2), for a pure electronic case with a constant coupling v as well as a constant density of states ρ that is set equal to $1/\Delta$.

APPENDIX C: EQUATION OF MOTION FOR THE ELECTRONIC-VIBRONIC QC AMPLITUDE

As a first step Eq. (17) is solved for the case of a regular electronic QC with a constant coupling as used in Sec. III. The respective spectral density is given in Eq. (B3), and consequently Eq. (17) becomes

$$\begin{aligned} \frac{\partial}{\partial t} A_{ev}(t) = & -\kappa A_{ev}(t) - 2\kappa \sum_{n=1}^{\infty} \theta(t-n\tau_r) \exp(in\varepsilon_{ec}\tau_r) \\ & \times \sum_{\bar{v}} \exp(i\omega_{\bar{v}t}) \mathcal{P}_{ev\bar{v}}(n\tau_r) A_{ev}(t-n\tau_r). \end{aligned} \quad (\text{C1})$$

For the first term on the right-hand side, $\mathcal{P}_{ev\bar{v}}(0) = \delta_{v,\bar{v}}$ which can be directly deduced from Eq. (20). This result shows that in the time region $t < \tau_r$ all vibrational levels decay with the same rate 2κ .

Next it is assumed that for all vibrational modes involved, the ratio $s_\xi = \omega_\xi/\Delta$ is an integer. Then the argument $-i\omega_{\bar{v}t}$ of the exponential function in $\mathcal{P}_{ev\bar{v}}(n\tau_r)$ becomes equal to $-i2\pi n \sum_\xi s_\xi (\mu_\xi - \bar{v}_\xi)$ [compare Eq. (20)]. This

yields 1 for the complete exponential function and one obtains $\mathcal{P}_{ev\bar{v}}(n\tau_r) = \delta_{v,\bar{v}}$. As a result Eq. (C1) reduces to

$$\begin{aligned} \frac{\partial}{\partial t} A_{ev}(t) = & -\kappa A_{ev}(t) - 2\kappa \sum_{n=1}^{\infty} \theta(t-n\tau_r) \\ & \times \exp(in\varepsilon_{ec}\tau_r) A_{ev}(t-n\tau_r). \end{aligned} \quad (\text{C2})$$

Thus, the equation of motion for $A_{ev}(t)$ for all possible sets of v become identical to each other and to the equation of motion for the amplitude of the excited state decaying into a pure electronic QC, namely Eq. (B5).

As already clarified the two essential conditions to be fulfilled for the entire time-behavior of the electronic QC to coincide with that of the electronic-vibronic QC are an infinite electronic-vibronic QC and s_ξ should be an integer. If the condition of wide-band alone is satisfied then the two QC have identical behavior for times $t < \tau_r$. The second condition is an intrinsic property of the electronic-vibronic QC. It is interesting to note that if $\omega_\xi < \Delta$ then even though the first condition will usually be fulfilled the time behavior for $t > \tau_r$ will always be different from that of the pure electronic QC.

APPENDIX D: DIFFERENT SOLUTIONS TO EQUATION OF MOTION FOR THE ELECTRONIC-VIBRONIC QC AMPLITUDE

As a third example for a solution of the basic equation of motion Eq. (17), one can derive an approximate expression for the state population [Eq. (16)], which is valid in the time-region of interest before any recurrence has occurred. As an initial approximation one neglects retardation effects in Eq. (17) and obtains

$$\frac{\partial}{\partial t} A_{ev}(t) = -\frac{1}{2} \sum_{\bar{v}} \exp(i\omega_{\bar{v}t}) K_{v\bar{v}} A_{ev}(t), \quad (\text{D1})$$

where the general rate

$$K_{v\bar{v}} = 2 \int_0^\infty d\tau \exp(i\varepsilon_{ec}\tau) J_{ec}(\tau) \mathcal{P}_{ev\bar{v}}(\tau), \quad (\text{D2})$$

has been introduced. The neglect of retardation effects in determining A_{ev} is justified if the expansion coefficients do not change substantially during the time period when retardation is important [decay time of $M_{v\bar{v}}(t, \tau)$ with respect to its τ -dependence]. The rate, Eq. (D2) can be understood as a half-sided Fourier transformed function which, in the general case, becomes an expression with a real and an imaginary part. Although the latter can be accounted for in the following computation one concentrates on the real part and arrives at:

$$k_{v\bar{v}} = \text{Re } K_{v\bar{v}} \equiv \delta_{v,\bar{v}} k_v + (1 - \delta_{v,\bar{v}}) k_{v\bar{v}}. \quad (\text{D3})$$

This separation is introduced in Eq. (D1) and a perturbation expansion with respect to the off-diagonal rates $k_{v\bar{v}}$ is carried out. The zero-order solution is simply $A_{ev}^{(0)}(t) = A_{ev}(0) \times \exp(-k_v t/2)$. The equation of motion for the first-order coefficients reads

$$\frac{\partial}{\partial t} A_{ev}^{(1)}(t) = -\frac{1}{2} k_v A_{ev}^{(1)}(t) - \frac{1}{2} \sum_{\bar{v} \neq v} \exp(i\omega_{v\bar{v}} t) k_{v\bar{v}} A_{e\bar{v}}^{(0)}(t). \quad (\text{D4})$$

This equation is simply integrated [by taking into account $A_{ev}^{(1)}(0) = 0$]. If the first and zero-order solution for the expansion coefficients A_{ev} is inserted into expression (16) and a linearization with respect to $k_{v\bar{v}}$ is carried out, one obtains [note the assumption of real initial values $A_{ev}(0)$]

$$P_e(t) = \sum_{v, \bar{v}} A_{ev}(0) A_{e\bar{v}}(0) \exp\left(-\frac{k_v + k_{\bar{v}}}{2} t\right) \times \left(\delta_{v, \bar{v}} - (1 - \delta_{v, \bar{v}}) \frac{\sin(\omega_{v\bar{v}} t)}{\omega_{v\bar{v}}} k_{v\bar{v}} \right). \quad (\text{D5})$$

Noting that it is Eq. (20) which determines the vibrational part of the integral kernel [Eq. (18)], one arrives at

$$k_{v\bar{v}} = \sum_{\mu} \langle \chi_{ev} | \chi_{i\mu} \rangle \langle \chi_{i\mu} | \chi_{e\bar{v}} \rangle J_{ec}(\varepsilon_{ec} + \omega_{\bar{v}\mu}). \quad (\text{D6})$$

Equation (D5) incorporates the decay of the diagonal part of the initial “density matrix” $A_{ev}(0)A_{e\bar{v}}(0)$ as well as the coherence effects arising from the interferences between the various off-diagonal elements. Such coherent effects lead to modulation of the population in the excited state in the course of its decay. To arrive at the wide-band limit one can replace J_{ec} in Eq. (D6) by 2κ , since this is what has been obtained in considering the case of a regular and infinite electronic QC. For a finite band-width the dependence of J_{ec} on $\omega_{\bar{v}\mu}$ imposes restrictions on the \bar{v} -summation and thereby prevents one from obtaining the trivial result $\mathcal{P}_{ev\bar{v}}(0) = \delta_{v, \bar{v}}$. In order to reproduce the results of the numerical simulations one has to set $J_{ec} = 2\kappa$, even for the finite band case since electronic transitions are already in the infinite band limit for the weak electronic coupling regime explored in this work.

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