

Photoinduced ultrafast electron injection from a surface attached molecule: Control of electronic and vibronic distributions via vibrational wave packets

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Photoinduced femtosecond electron transfer from a chromophore attached via a molecular group to a semiconductor surface is discussed theoretically. For an early time region after ultrafast photoexcitation and for a specific range of electron transfer times, the occurrence of remarkable electronic and vibrational distributions is proposed. The energetic structure and range of the related electronic wave packets can be controlled by the shape of a vibrational wave packet which has been prepared by laser excitation of the attached molecule.

Electron injection from a light absorbing molecule (chromophore) into an electrode (heterogeneous ET) is of particular interest in AgBr photography, dye-sensitized solar cells, etc.^{1,2} Apart from the technological importance, studies in photoinduced processes are relevant in understanding the basic physics of charge injection at interfaces. For instance, immobilizing the donor molecules at specific distances from the electrode by attaching anchor groups of appropriate lengths one can systematically investigate the effects of molecule-surface distance variation on the charge-injection process.³ Furthermore, one may control the initial vibronic states of the donor by an appropriate optical preparation and more importantly accurately determine the time scale of charge injection into the electrode.

Recent experiments have shown that electron injection from a molecularly anchored chromophore to a nanoporous TiO₂ electrode proceeds on a sub-ps time scale.^{3–7} Pump-probe spectroscopy has been employed to time resolve (i) the decay of the excited state,⁴ (ii) the formation of the molecular ion,⁴ and (iii) the arrival of the injected electron in the empty conduction band of the semiconductor electrode.^{6,7} The ultrafast nature of the photoinduced charge injection process implies that the electron is transferred from the molecule to the electrode well before vibrational relaxation can occur in the donor molecule. This has been recently confirmed by the observation of oscillations in the probe absorption signal due to vibrational wave-packet motion during heterogeneous electron transfer.⁸ In the above experimental system electron transfer proceeds in 80 fs from the excited singlet state of the perylene chromophore, through the molecular anchor group (-CH₂-phosphonate), into the conduction band of a TiO₂ electrode.

Compared to the amount of theoretical work done in the whole field of ET reactions (for a recent overview see, e.g., Refs. 9,10) little attention has been paid to modeling photoinduced charge transfer from a molecule to a semiconductor surface. Up to now only parts of this latter process have been considered, for example, electron injection into a quasicontinuum (QC) of pure electronic levels (see, e.g. Ref. 11) or into a vibronic QC (compare Ref. 12). A proper combination of these processes which is essential for describing heteroge-

neous ET has not been explored until now. A recent work on obtaining pump-probe signals using a density-matrix approach ($\chi^{(3)}$ theory) has addressed the issue of excited-state probe absorption when the electron undergoes an ultrafast injection into a continuum of band states.¹³ In all the above cases the focus has been on the dynamics associated with the decay of the injecting (excited) state.

In this paper a detailed description of ultrafast electron-vibrational dynamics accompanying photoinduced heterogeneous ET, valid for times prior to onset of relaxation processes, will be given. We discuss the time-dependent probability distributions in the electronic QC and among the vibronic states of the ionized molecule, their interrelationship, and also the role played by vibrational wave packets in the excited state in engendering a unique series of electronic wave packets in the electronic QC. To obtain the probability distributions a time-dependent Schrödinger equation approach is utilized. Neglect of the relaxation processes in the early time region is justified since for the above experimental system, injected hot electrons have been found to relax in about 150 fs.¹⁴ Furthermore, the vibrational wave packet in the excited state of the chromophore lasts at least one ps,⁸ also indicating weak anharmonic coupling.

The Hamiltonian which is responsible for the ultrafast and coherent part of the charge injection dynamics contains the electronic states $|\varphi_a\rangle$ (diabatic states) as well as the set of vibrational coordinates Q_ξ participating in the ET process. The Q_ξ are governed by the vibrational Hamiltonian H_a , where the electronic quantum number comprises the molecular ground and excited state, $a=g$ and $a=e$, respectively, as well as the QC of band states ($a=k$). Correspondingly, the whole Hamiltonian reads

$$H = \sum_a H_a |\varphi_a\rangle \langle \varphi_a| + \sum_k (V_{ke} |\varphi_k\rangle \langle \varphi_e| + \text{H.c.}). \quad (1)$$

To elucidate the main features, a case of harmonic potential energy surface (PES), and a single vibrational coordinate with a vibrational quantum of $\hbar\omega_{\text{vib}}=0.1$ eV, that is common to all electronic states will be considered. Although the coherent oscillations in the perylene chromophore (using a

pulse width of 20 fs) was dominated by two modes of energy around 0.05 eV,⁸ with shorter pulses one can indeed excite the modes around 0.1 eV. The transfer integral V_{ek} couples the electron in the excited donor state to the semiconductor QC. V_{ek} has been chosen as a constant, i.e., independent of k , a usual assumption in surface molecule interactions.¹⁵ The implicit assumption here is that normal mode oscillations do not modify the surface-molecule distance and hence the transfer integral V_{ek} (justified for the above experimental system in view of the rigid anchor group).

To include the photoexcitation process (into the excited donor level) Eq. (1) has to be completed by the coupling to the radiation field. This will be described in the electric dipole (and Condon) approximation where the molecular transition matrix element is denoted by \mathbf{d}_{eg} (direct excitation into the band continuum can be neglected).

To study the system dynamics one has to solve the time-dependent Schrödinger equation for the electron-vibrational wave function $|\Psi(t)\rangle = \sum_{av} A_{av}(t) |\chi_{av}\rangle |\varphi_a\rangle$. The time-dependent expansion coefficients are characterized by the electronic as well as vibrational quantum numbers, a and ν , respectively (χ_{av} is the related vibrational wave function). Accordingly, one obtains the time-dependent occupation probability of an electronic state k in the quasicontinuum $P(E,t) \equiv P_k(t) = \sum_{\nu} |A_{k\nu}(t)|^2$ and that of a vibronic level ν of the ionized molecule $P_{\nu}(t) = \sum_k |A_{k\nu}(t)|^2$. The QC states (800 levels) have been shown to behave exactly like a continuum until the occurrence of the first recurrence.¹¹ For the level spacing of the QC assumed here (2.5 meV), the first recurrence occurs after 1.6 ps. Since a box like uniform level density is assumed for the QC, its behavior is similar to a two-dimensional continuum of semiconductor substrate states of width 2 eV.

The distribution $P(E,t)$ versus the energy of the conduction band is shown in Fig. 1. One notices in part (a) of Fig. 1 a number of peaks separated from one another by $\hbar\omega_{\text{vib}}$. It seems obvious that their heights are determined by the Franck-Condon factors of the vibronic levels between the excited and ionized molecular state. This can be confirmed by estimating the structure of the electronic distributions from Golden Rule arguments. For times well separated from the laser pulse action and less than the time the first recurrence appears, the probability structure in the QC is related to $\sim \sum_{\nu\mu} P_{\mu}^{(i)} |\langle \chi_{e\mu} | \chi_{k\nu} \rangle|^2 \delta(E_e + \mu\hbar\omega_{\text{vib}} - E - \nu\hbar\omega_{\text{vib}})$ ($P_{\mu}^{(i)}$ is the field-pulse-induced initial donor-level distribution). Accordingly, for a given value of μ one obtains transitions into the band state with energy $E = E_e + \mu\hbar\omega_{\text{vib}}$ and multiples of $\hbar\omega_{\text{vib}}$ below. The whole structure in Fig. 1(a) is obtained by adding contributions for different μ , and by incorporating the Franck-Condon factors as a weight. Thus the probability distribution in the QC appears as a Franck-Condon progression, but with each member broadened according to the electronic interaction of the excited molecular state [leading to a lifetime of 85 fs, since the measured value is around 80 fs (Ref. 8)]. The laser pulse width (Gaussian width of 60 fs) has been chosen such that very little vibronic coherence is formed in the excited state.

When a vibrational wave packet is created on the excited state with a laser pulse width that is much shorter than the period of vibrational motion (41 fs) one obtains, as shown in Fig. 1(b), a more uniform spread of probabilities due to tran-

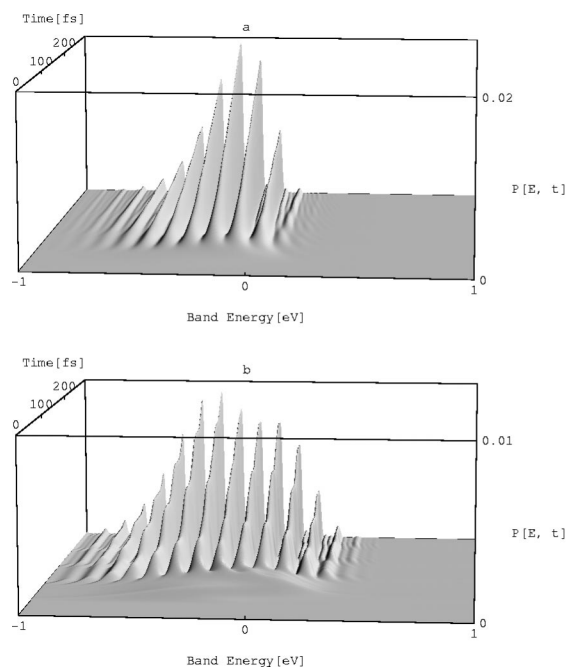


FIG. 1. Probability distribution of the injected electron versus the energy of the conduction band. $E=0$ denotes position of excited donor level. Exciting wavelength corresponds to a 0-0 transition with a Gaussian pulse-width of (a) 60 fs and (b) 2 fs.

sitions from the higher states combined in the vibrational wave packet. More importantly, oscillations in the probability distribution $P(E,t)$ due to definite phase relations between members of the Franck-Condon progression appear as displayed in Fig. 1(b). Therefore, the energetic spacing as well as the time period of the oscillations in the Franck-Condon dictated structure are both related to the fundamental harmonic of the single vibrational mode.

It is shown in Fig. 2 that the occupancy $P(E,t)$ of a few selected levels E from the electronic QC is built up in an oscillatory fashion due to vibrational wave-packet motion in the donor molecule. This is similar to the experimental results in certain donor-acceptor complexes¹⁶ where there is some evidence that vibrational wave-packet motion modulates donor-acceptor occupancies (see also Ref. 12). However, in the wide band limit, the total rise in probability of the entire electronic QC (obtained as a result of summing

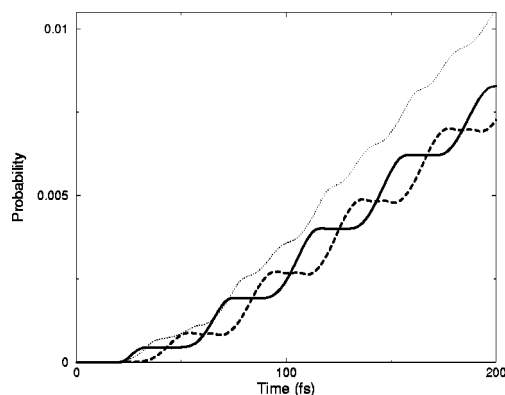


FIG. 2. The rise of probability in three selected levels of the QC for conditions similar to Fig. 1(b): The dotted line $E = -0.2$ eV, the solid line $E = -0.5$ eV, and the dashed line $E = 0.1$ eV.

over all QC states) turns out to be a smooth function as individual oscillatory contributions undergo destructive interference. The curve with the fastest rise in Fig. 2 oscillates at $2\omega_{\text{vib}}$ since the vibrational wave packet transits the crossing region (of the respective PES) for this QC level twice within one period. The other two curves which oscillate at ω_{vib} are clearly out of phase with respect to each other since their respective curve crossing regions are at opposite classical turning points of the excited state vibrational wave packet.

It is interesting to note that the information corresponding to the location of the wave packet in vibrational coordinate-ordinate space is transformed upon injection into phase information of the electronic energetic distribution. In an energy and time-resolved experiment (e.g., a two-photon photoemission experiment) this information is retained whereas in an energy-integrated but time-resolved experiment (standard pump-probe experiments) this information is lost, and one obtains a smooth rise (wide band limit), in agreement with the experimental result.⁸

It is clear that by varying the laser pulse, e.g., the width, one can create different types of vibrational wave packets in the excited state of the molecule. However, the results in Fig. 1 indicate that different types of vibrational wave packets upon ultrafast electron injection, will lead to different electronic wave packets in the semiconductor. Thus, by varying the laser pulse one has control over the type of electronic wave packet injected into the semiconductor.

It is instructive to relate $P(E, t)$ to the spatial probability distribution in the electronic QC (the electronic wave packet). This quantity can be expressed in terms of the respective wave functions $\varphi_k(\mathbf{r})$ as (\mathbf{r} is the spatial electronic coordinate)

$$P_{\text{QC}}(\mathbf{r}, t) = \sum_{\nu} \left| \sum_k A_{k\nu}(t) \varphi_k(\mathbf{r}) \right|^2. \quad (2)$$

In order to numerically calculate the electronic wave packet one needs the $\varphi_k(\mathbf{r})$ (but this will not be attempted in this paper). As seen from Eq. (2) the electronic wave packet is a linear combination of subwave packets whose number depends on the maximum value of ν . When the laser pulse populates for instance, only a single vibrational level in the excited donor state, one obtains for each value of ν in Eq. (2) a particular k value governed by the energy conservation condition $E = E_e + \mu\hbar\omega_{\text{vib}} - \nu\hbar\omega_{\text{vib}}$. Each value of ν gives rise to an electronic subwave packet in the electronic QC whose energy spread is determined by the excited-state lifetime broadening around a specific value of E (a cluster of values around E). The ET into an electronic-vibronic QC leads to a series of electronic wave packets even for the simplest case, where each electronic subwave packet is akin to what is obtained from an injection into a pure electronic QC. With a vibrational wave packet in the excited donor state, μ is multivalued leading to a series of overlapping electronic subwave packet of similar energy span. The enhancement of the energetic spread of the electronic subwave packets as well as the extent of their consequent overlap in the electronic QC can thus be controlled by an appropriate preparation of a vibrational wave packet in the excited molecular state.

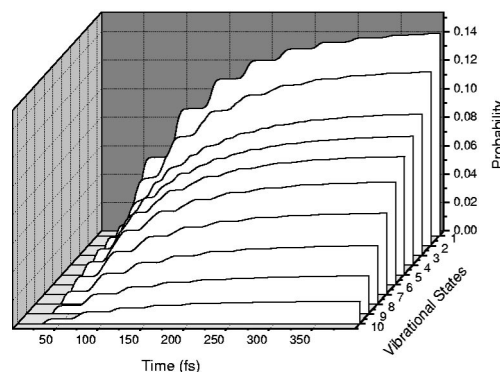


FIG. 3. The probability distributions among the vibronic states of the ionized molecule as in Fig. 1(b).

The case wherein several normal modes participate in ET would lead to a more complex electronic distribution in the QC. It would be the result of a superposition of electronic wave packets both from modes which have acquired a vibrational wave packet for the given laser pulse width as well as from those which have only a single vibronic level occupancy. Even so, it is important to have the reference picture of the single mode case at hand while analyzing distributions which arise from several modes (currently under study). Furthermore, it would be of central interest for further studies to clarify how the overall coherence decays on a somewhat longer time scale where dissipation becomes predominant.

For a large electronic coupling the lifetime broadening can be much larger than $\hbar\omega_{\text{vib}}$ that leads to a loss of the Franck-Condon structure in the energy spectrum of the QC. An overall energetic shift occurs towards the bottom of the QC, which is typical for injection into a pure electronic QC (as in the case of a Fano-Anderson model¹⁷). The electronic wave packet in this case is not affected by a presence or absence of an initial vibrational wave packet. The time scale of electron injection in photodesorption studies for small molecules,¹⁸ usually corresponds to this limit.

The probability distribution of the occupancy of the vibronic levels of the ionized molecule $P_{\nu}(t)$ is shown in Fig. 3. It can be related to the expression $\sim \sum_{\mu} P_{\mu}^{(i)} |\langle \chi_{e\mu} | \chi_{k\nu} \rangle|^2$ with the restriction $E_e + (\mu - \nu)\hbar\omega_{\text{vib}} \geq 0$. Since the energy lost by the electron in the QC is equivalent to the energy gained by the vibrational part of the ionized molecule, the two distributions are linked by energy conservation. Indeed a one-to-one correspondence between the two distributions can be obtained in the case when only a single vibronic level is initially populated in the donor excited state. With an initial vibrational wave packet however, this simplicity is lost as can be seen by comparing Figs. 1(b) and 3. (This vibrational energy gain is the crucial quantity to be determined in describing desorption yields.¹⁸)

Experimental data pertaining to the theoretical results predicted here have not yet been reported. However, time and energy-resolved measurements such as two photon photoemission (2PPE) can probe the oscillatory buildup of the occupancy of the vibrational modes in the ionized molecule and of the occupancy of electronic levels in the semiconductor as discussed in this paper [Figs. 1(b)–3]. Such experiments appear feasible in view of the 2PPE experiments

where electron transfer dynamics were probed in molecular adsorption layers on a metal surface.¹⁹

To summarize, this paper reports model calculations pertaining to electron injection into an electronic-vibronic QC. The main highlight of this work is the control of the structure and energetic range of electronic distributions/wave packets by a suitable preparation of a vibrational wave packet in the excited molecular state. The rich structure presented by the probability distribution in the electronic QC may be achievable only by ultrafast charge injection from a molecule to a

semiconductor, thus highlighting a unique role played by such heterogeneous charge-transfer processes. The subsequent propagation, dephasing, and relaxation of the electronic wave packet in the semiconductor calls for further study.

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