

Inducing Coherent Oscillations in the Electron Transfer Dynamics of a Strongly Dissipative System with Pulsed Monochromatic Light

D. G. Evans,¹ R. D. Coalson,¹ H. J. Kim,² and Yu. Dakhnovskii²

¹*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

²*Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213*

(Received 28 April 1995)

Calculations are presented that suggest coherent oscillations in the electronic state populations of an electron transfer reaction in a polar solvent can be induced by subjecting the system to a sequence of monochromatic laser pulses on the picosecond time scale. These oscillations are produced by pumping the system between different steady state distributions attained in the presence and absence of a strong continuous-wave electric field. The amplitude and rise time of these time-dependent oscillations may be altered by changing the pulse duration and the electric field strength. The experimental realization of the proposed scheme will require strong electric fields ($\approx 10^7$ V/cm), and the effect will be most pronounced for activationless reactions.

PACS numbers: 33.80.Be

The effect of a many-body environment on the quantum dynamics of a two-state system is a much studied theoretical problem whose results may readily be applied to processes such as electron transfer reactions in condensed phase media. Electron coherence in these systems is an important and interesting effect. With no dissipation, an electron oscillates between two (donor and acceptor) sites within the electron transfer complex. When the interaction with the bath becomes stronger, these oscillations will decay in time. At some critical value of the system-bath coupling, irreversible decay will be attained. This coherence-incoherence transition has been studied in the small polaron problem by Holstein [1] and in the two-site problem by Chakravarty and Leggett [2] and others [3]. Coherence in quantum well heterostructures with weak electron-phonon coupling [4] has been observed experimentally. In this work, we will suggest a new physical situation where coherence, albeit based on a different mechanism than the one responsible for coherent oscillations in the systems considered in Refs. [1–4], might be observed.

In electron transfer (ET) reactions in polar solvents, incoherent quantum transport due to the strong electron-solvent dipole interaction is always observed. The rate constant may be described in the framework of the spin-boson Hamiltonian [2]

$$\hat{H}_{\text{SB}} = -\frac{1}{2} \hbar \Delta \hat{\sigma}_x + \frac{1}{2} \epsilon \hat{\sigma}_z + \frac{1}{2} \sum_k (p_k^2 + \omega_k^2 q_k^2) + \frac{1}{2} \hat{\sigma}_z \sum_k g_k q_k, \quad (1)$$

where $\hbar \Delta$ is the electronic coupling parameter, ϵ is the bias (the reaction heat) between two equilibrium positions, $\hat{\sigma}_{x,z}$ are Pauli spin matrices, and ω_k and g_k are, respectively, the frequency and coupling constant of the k th bath oscillator described by coordinate q_k and momentum p_k . The electronic state associated with the $|+\rangle$ eigenstate of $\hat{\sigma}_z$ (with eigenvalue $+1$) shall be designated as the donor

electronic state. It corresponds to the state in which a mobile electron is localized on the donor site. The other electronic base state is then the acceptor state. Within the framework of the noninteracting blip approximation [2], assuming a small electronic hopping matrix element and strong electron-medium coupling (as in many mixed valence electron transfer complexes immersed in polar solvents), the system decays exponentially with an inverse time constant given by the sum of the forwards (donor \rightarrow acceptor) and backwards (acceptor \rightarrow donor) rate constants obtained from the golden rule. In the high temperature limit, Levich-Dogonadze [5] and Marcus [6] obtained the following expressions for the forwards and backwards rate constants:

$$k_f = \frac{\hbar \Delta^2}{4} \left(\frac{\pi}{k_B T E_r} \right)^{1/2} e^{-(E_r - \epsilon)^2 / 4 E_r k_B T},$$

$$k_b = \frac{\hbar \Delta^2}{4} \left(\frac{\pi}{k_B T E_r} \right)^{1/2} e^{-(E_r + \epsilon)^2 / 4 E_r k_B T}, \quad (2)$$

where E_r is the reorganization energy defined as $E_r \equiv \frac{1}{2} \sum_k g_k^2 / \omega_k^2$. The relevant kinetic equation for the evolution of the difference in electron populations of the donor and acceptor states, $x(t) \equiv P_d(t) - P_a(t)$, is

$$\dot{x}(t) = -k_-^0 - k_+^0 x(t), \quad (3)$$

where the constants k_{\pm} are given in terms of the forwards and backwards golden rule rate constants as $k_{\pm}^0 = k_f \pm k_b$.

The solution to Eq. (3),

$$x(t) = (x_0 + k_-^0 / k_+^0) e^{-k_+^0 t} - k_-^0 / k_+^0, \quad (4)$$

where x_0 is the initial value of x , is elementary but instructive: The population relaxes exponentially with inverse time constant k_+^0 , and the population difference reaches an asymptotic value of $-k_-^0 / k_+^0$ independent of initial populations.

When a strong time-dependent electric field is applied, the dynamics may be described by the Hamiltonian $\hat{H} = \hat{H}_{\text{SB}} - \frac{1}{2} \hat{\sigma}_z V(t)$, where $V(t)$ is proportional to the electric

field strength (c.f. below). The equation of motion within the noninteracting blip approximation for the electronic population difference $x(t)$ is then given as [7,8]

$$\dot{x}(t) = -\Delta^2 \left[\int_0^t dt' \sin[F(t) - F(t') + \epsilon(t - t')] \sin[Q_1(t - t')/\pi] \exp[-Q_2(t - t')/\pi] + \int_0^t dt' \cos[F(t) - F(t') + \epsilon(t - t')] \cos[Q_1(t - t')/\pi] \exp[-Q_2(t - t')/\pi] x(t') \right], \quad (5)$$

where $F(t) \equiv \int_0^t dt' V(t')$, and at high temperatures $Q_1(t)/\pi \equiv E_r t/\hbar$ and $Q_2(t)/\pi \equiv E_r k_B T t^2/\hbar^2$.

In the case of an electron transfer complex, application of an external electric field $E(t)$ produces a coupling potential $V(t) = \mu_0 E(t)$, where μ_0 is the difference between the dipole moments of the reactant (donor) and product (acceptor) states. It has been shown [7,8] that in the presence of a monochromatic, continuous-wave (cw) field, i.e., for $E(t) = E_0 \cos(\omega_0 t)$, $x(t)$ still relaxes exponentially without any large scale oscillations. Moreover, the forwards and backwards rate constants are in general *modified to different extents* by the applied cw field. A range of asymptotic donor and acceptor distributions spanning orders of magnitude can be obtained by varying the field parameters. A reaction that favors occupation of one electronic state can be altered to favor the other state when the field is applied. Hence, it is plausible that a simple "on-off" sequence of monochromatic pulses could be utilized to drive oscillations between the populations of the donor and acceptor excited states. A precise description of this scenario and demonstration of its validity within the spin-boson model introduced above is presented in what follows.

The electric field profile motivated by the above observations is shown in Fig. 1. The monochromatic cw field is switched on for intervals of time τ_p , which alternate with "field-off" intervals of duration T_0 . The key point

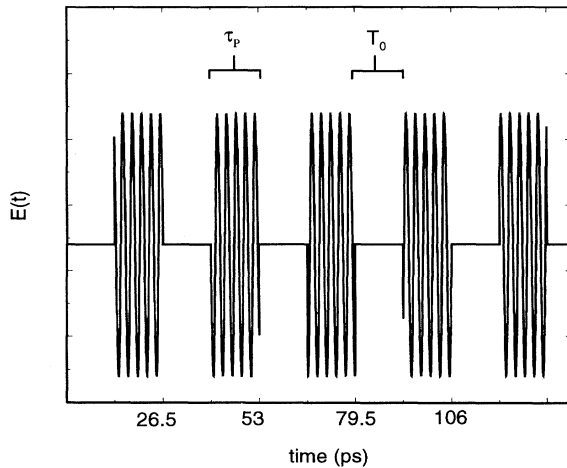


FIG. 1. The electric field $E(t)$ is a sequence of monochromatic pulses of duration τ_p at intervals T_0 apart.

is that in the absence of the applied field, one set of rate constants (and the associated equilibrium constant) will be operative, while when the ac field is turned on, a *different* set of rate and equilibrium constants is actuated.

Assuming that the evolution of the system is much slower than the typical relaxation time of the bath excitations, Eq. (5) may be simplified [9] to

$$\dot{x}(t) = -K_-(t) - K_+(t)x(t), \quad (6)$$

where

$$K_-(t) \equiv \Delta^2 \int_0^t dt' \sin[F(t) - F(t') + \epsilon(t - t')] \times \sin[Q_1(t - t')/\pi] \exp[-Q_2(t - t')/\pi], \quad (7)$$

$$K_+(t) \equiv \Delta^2 \int_0^t dt' \cos[F(t) - F(t') + \epsilon(t - t')] \times \cos[Q_1(t - t')/\pi] \exp[-Q_2(t - t')/\pi]. \quad (8)$$

In the absence of any applied field, Eqs. (7) and (8) yield (in the high temperature regime and neglecting short-time transients) the time-independent Marcus rate constants; specifically, $K_- = k_-^0$ and $K_+ = k_+^0$. When an intense monochromatic field is applied, these values are modified to [7,8]

$$k_{\pm} = \frac{\hbar \Delta^2}{4} \left(\frac{\pi}{E_r k T} \right)^{1/2} \sum_{m=-\infty}^{\infty} J_m^2 \left(\frac{\mu_0 E_0}{\hbar \omega_0} \right) \times \left\{ \exp \left[\frac{-(E_r + \hbar m \omega_0 - \epsilon)^2}{4 E_r k T} \right] \pm \exp \left[\frac{-(E_r + \hbar m \omega_0 + \epsilon)^2}{4 E_r k T} \right] \right\}, \quad (9)$$

where J_m is the m th order Bessel function.

In Ref. [8] it was shown that the ratio $-k_-/k_+$, which determines the asymptotic steady state donor and acceptor populations, can vary strongly with field parameters. The key design feature for our purposes is to choose molecular and field parameters such that $-k_-^0/k_+^0$ is close to -1 (acceptor state is favored), while $-k_-/k_+$ with the field on is close to $+1$ (donor state is favored). In this way, pronounced oscillations in the electronic populations of the ET system can be achieved.

In Fig. 2 we demonstrate how the sequence of monochromatic laser pulses in Fig. 1 gives rise to electron coherence in a chemical reaction of electron transfer in a polar solvent. We take a typical polar solvent reorganization energy, $E_r = 1$ eV and $\hbar\omega_0 = E_r$. The transition matrix element is chosen to be equal to 100 cm^{-1} , which is typical for nonadiabatic ET reactions. The electric field strength is chosen such that $\mu_0 E_0 / \hbar\omega_0 = 2$. In Fig. 2(a), the electronic population oscillates between the donor and acceptor sites despite the strong environmental dissipation and the fact that this reaction is activationless and strongly exothermic. At $\epsilon = E_r/2$ (with an activation energy $E_r/8$), the amplitude of the oscillations is smaller. These oscillations disappear for the symmetric reaction (where $\epsilon = 0$). The pulses in this case (1.325 ps) were much shorter, since relaxation rates for the unbiased system were much larger.

The bias parameter ϵ chosen ensures that the initial decay will be an exponential relaxation to the product state. After the pulse is turned on, the system dynamics is controlled by the field, and the population is driven toward the long time product distribution that would be obtained by application of a monochromatic cw field. The rate at which the population of reactants grows depends on the value of k_+ . At the completion of the pulse, the system relaxes according to the rate constant k_+^0 , which is appropriate in the absence of the field. The reactive system therefore oscillates between two steady-state distributions: $x = -k_-/k_+$ while the pulse is on

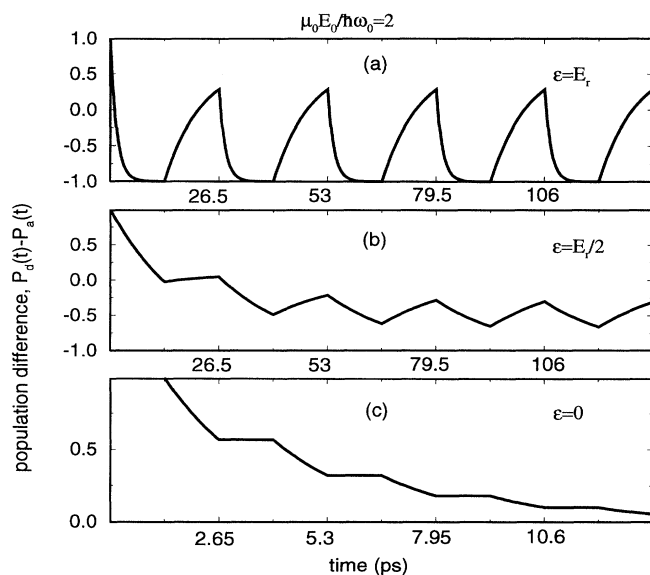


FIG. 2. Electron population difference $x(t) = P_d(t) - P_a(t)$ for three electron transfer reactions in the presence of the pulsed laser field depicted in Fig. 1. The frequency of the field is $\hbar\omega_0 = E_r = 1$ eV and the field strength is such that $\mu_0 E_0 / \hbar\omega_0 = 2$. (a) Activationless reaction, $\epsilon = E_r$; (b) reaction with $\epsilon = E_r/2$; and (c) symmetric electron transfer with no bias.

and $x = -k_-^0/k_+^0$ after the pulse. Subsequent periodic oscillations are produced by a periodic sequence of pulses on the picosecond time scale. For the symmetric reaction, the application of a laser pulse alters the evolution rate of the electronic populations, but, since the steady state distributions are unchanged, oscillations cannot be achieved by the proposed switching mechanism.

In Fig. 3 the electric field strength of the pulses is altered by changing the parameter $a = \mu_0 E_0 / \hbar\omega_0$ from 2.5 to 1.5 when $\epsilon = E_r$. At $a = 2.5$, maximum amplitude of population oscillation is obtained since this is the field strength for which the probability of electron transfer to the product state is lowest [8].

In Fig. 4 we show how the population profile may easily be manipulated by changing the pulse duration from $\tau_p = 53$ to 6.625 ps for the biased system, $\epsilon = E_r$ with an electric field strength related to $a = 2.0$. When the pulse duration is much longer than the rise time of the system upon application of the electric field, the system saturates at the long time reactant-product distribution. When the pulse is shorter than the rise time, pumping to the equilibrium population distribution is not achieved, and a sequence of oscillations of smaller amplitude is obtained.

From Figs. 2–4, we can also see how the electric field strength, the time duration of the pulses, and the bias of the chemical system affect the mean population (which is the average of the long-time population distributions in the absence and presence of the light field) about which the electron density oscillates.

In conclusion, coherent electronic oscillations in a dissipative environment may be observed by irradiating an ET

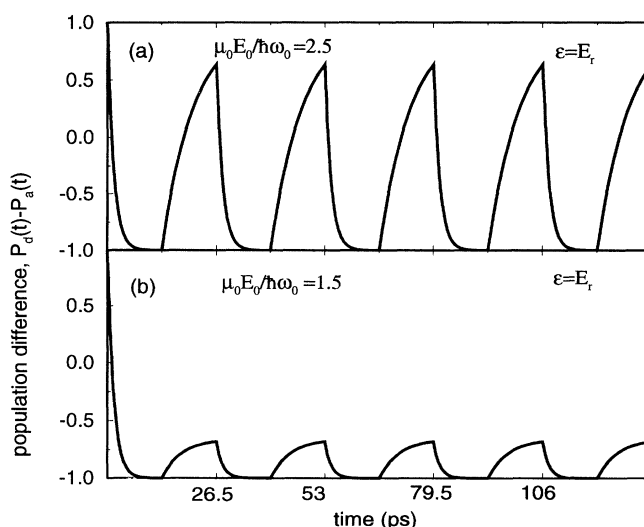


FIG. 3. Effect of electric field strength on the population difference $x(t) = P_d(t) - P_a(t)$. The parameter $a = \mu_0 E_0 / \hbar\omega_0$ is changed from (a) $a = 2.5$ to (b) $a = 1.5$ for the activationless reaction $\epsilon = E_r$, with $\tau_p = T_0 = 13.25$ ps and $\hbar\omega_0 = E_r = 1$ eV.

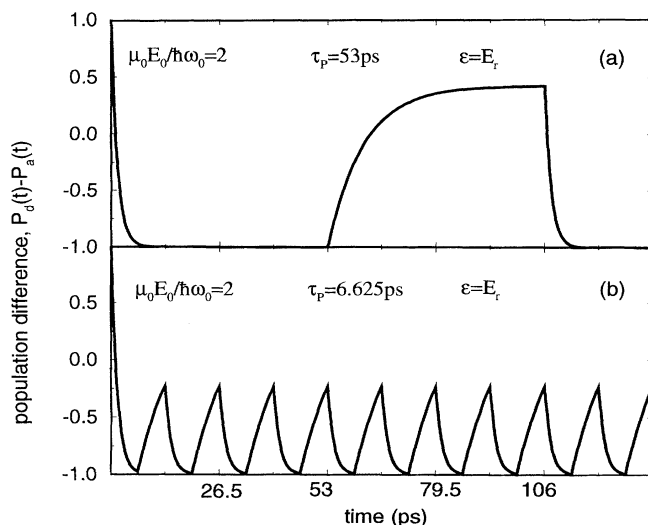


FIG. 4. Effect of the pulse profile on the population difference $x(t) = P_d(t) - P_a(t)$ for activationless reaction: (a) pulses of duration $\tau_p = 53$ ps separated by $T_0 = 53$ ps and (b) pulses of duration $\tau_p = 6.625$ ps separated by $T_0 = 6.625$ ps.

complex in a polar solvent with a sequence of laser pulses on the picosecond-nanosecond time scale, which drive oscillations in the electron population. We have found an analytical expression for the time-dependent behavior of the electron population, and shown that activationless ET systems are good candidates for the observation of significant oscillations. The physics of this phenomenon is simple: The electronic population oscillates between two steady-state distributions, one dependent on an external driving field and the other the Gibbs-Boltzmann equilibrium distribution. These oscillations will not be observable in a symmetric electron transfer process.

A value of $a = \mu_0 E_0 / \hbar \omega_0 \sim 2.1$ would require (for a reorganization energy E_r of 1 eV) an electric field strength of $E_0 \approx 3 \times 10^7$ V/cm, assuming a photon energy of 1 eV and a $\pm e$ charge pair separated by a distance on the order of 5–7 Å. This distance range is commensurate with those of mixed valence electron transfer systems [10] and electron transfer reactions along chains of rigid organic ring systems [11]. Although the required field strengths are high, they are experimentally attainable [12], and it is unlikely that they would result in dielectric breakdown of the solvent since the pulses are of very short duration. Detection of the electronic state populations would be possible via transient absorption measurements using a probe laser if either the products

or reactants had significant absorption coefficients in the IR or the visible region of the spectrum.

The coupling between the electric field and the electric dipole of the ET complex depends on the orientation of the ET complex as $\vec{\mu}_0 \cdot \vec{E}(t)/2$. To avoid dilution of the effects predicted by our analysis due to orientational averaging, it may be advantageous to embed a collection of aligned ET complexes using thin film techniques. We have not considered direct coupling between the electric field and the solvent. It is difficult to estimate the strength of this coupling without detailed molecular analysis, but we expect that it should not overwhelm the direct coupling of the field to the ET complex when the dipole moment of the ET complex is much larger than that of the solvent. Thus, mixed valence transition metal complexes with many spacer groups separating the donor and acceptor sites may serve as optimal systems for realizing the effects described in this work.

We wish to thank Gilbert Walker for extensive discussions. The authors acknowledge the financial support of the NSF, Grants No. CHE-9101432 (R. D. C.) and No. CHE-9412035 (H. J. K.). D. G. E. wishes to thank the University of Pittsburgh for the award of a predoctoral Andrew D. Mellon Fellowship.

- [1] T. Holstein, *Ann. Phys. (N.Y.)* **8**, 324 (1959).
- [2] (a) S. Chakravarty and A. Leggett, *Phys. Rev. Lett.* **52**, 5 (1984); (b) A. Leggett *et al.*, *Rev. Mod. Phys.* **59**, 1 (1987).
- [3] M. P. A. Fisher and A. T. Dorsey, *Phys. Rev. Lett.* **54**, 1609 (1985); H. Grabert and U. Weiss, *Phys. Rev. Lett.* **54**, 1605 (1985).
- [4] H. G. Roskos *et al.*, *Phys. Rev. Lett.* **68**, 2216 (1992).
- [5] V. G. Levich and R. R. Dogonadze, *Dokl. Acad. Nauk SSSR* **124**, 123 (1959); **133**, 158 (1960); V. G. Levich, *Adv. Electrochem. Eng.* **4**, 249 (1966).
- [6] R. A. Marcus, *Annu. Rev. Phys. Chem.* **15**, 155 (1964).
- [7] Yu. Dakhnovskii, *J. Chem. Phys.* **100**, 6492 (1994).
- [8] Yu. Dakhnovskii and R. D. Coalson, *J. Chem. Phys.* **103**, 2908 (1995).
- [9] R. D. Coalson, D. G. Evans, and A. Nitzan, *J. Chem. Phys.* **101**, 436 (1994).
- [10] G. C. Walker *et al.*, *J. Phys. Chem.* **95**, 5712 (1991); P. F. Barbara, G. C. Walker, and T. P. Smith, *Science* **256**, 975 (1992).
- [11] M. J. Shephard, M. N. Padden-Row, and K. D. Jordan, *Chem. Phys.* **176**, 289 (1993).
- [12] S. Franzen and S. G. Boxer, *J. Phys. Chem.* **97**, 6340 (1993); S. Franzen, R. F. Goldstein, and S. G. Boxer, *J. Phys. Chem.* **94**, 5135 (1990).