Theory of coherent thermal photoinduced electron transfer reactions in polyatomic molecules.

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Abstract

The second order perturbation theory expression for the time dependent populations and rates of photoinduced electron transfer reactions has been previously derived by R.D. Coalson, D. G. Evans and A. Nitzan (J. Chem. Phys. **101**, 436 (1994)) and by M. Cho and R. J. Silbey (J. Chem. Phys. **103**, 595 (1995)). Here, we adapt these expressions for the study and analysis of the excitation laser frequency dependence of the time dependent populations and rates. Our model consists of a molecule with three electronic states, each supporting a manifold of harmonic internal vibrations of the molecule. In contrast to previous expectations, we find that in the region of significant absorption, the photoinduced electron transfer rate is almost independent of the frequency and the temporal width of the excitation laser. This conclusion implies that control of the excitation rate through the excitation laser frequency is possible only if external noise destroys the coherence of the excitation process.

I. INTRODUCTION

Photoinduced electron transfer is a three state process [1,2]. A (thermal) molecule in the ground state is excited by a laser to an electronically excited donor state. This donor state then interacts with an acceptor state, leading to a transfer of an electron. Electronic excitation of a molecule is usually accompanied by a weakening of vibrational bonds in the excited state. We have recently shown [3,4] that, depending on the photoexcitation wavelength and temporal properties, such a weakening may lead to a cooling of the vibrational population in the excited state. This cooling may then lead to an exponential reduction of the electron transfer rate in the activated regime [5,6]. Changing the excitation wavelength may thus change the electron transfer rate by orders of magnitude, either slowing it down or speeding it up.

These results [5,6] were derived by using an approximate incoherent two step approach. First the photoexcitation process was considered to prepare a nascent energy dependent distribution in the excited donor state. Then this distribution was used as input in the Golden rule expression for the electron transfer rate. This theory was an approximate one, valid provided that the electron transfer process is decoupled from the photoexcitation.

Coalson, Evans and Nitzan [7] and Cho and Silbey [8] derived the leading order term in a perturbation expansion for the photoinduced electron transfer rate. In their applications, they assumed that the excitation pulse is a delta function in time, that it includes all excitation frequencies. Here, we will use the formalism of Refs. [7,8] but apply it to study the photoinduced electron transfer process as a function of laser frequency and pulse shape. We will compare the results of the present theory, which allows for coherence between the photoexcitation step and the electron transfer step and the previous theory presented in Refs. [5,6] which assumed that the two processes are incoherent.

We find in the present study that the coherent process creates a situation in which the transfer rate of the electron from the locally excited donor to the acceptor state, as a function of the wavelength, is very similar to the excitation process from the ground state

to the locally excited donor state. As a result, the photoinduced electron transfer rate is almost independent of the excitation frequency and the temporal width of the pulse.

In Section II we will review the theory and apply it to a model of harmonic vibrational Hamiltonians for the ground, locally excited donor and acceptor states. A numerical example will be studied in Section III, and we end with a discussion which attempts to reconcile the present coherent results with the previous incoherent theory of photoinduced electron transfer.

II. THEORY OF PHOTOINDUCED ELECTRON TRANSFER

A. Review of perturbation theory results.

Following the formalism presented by Cho and Silbey [8] we assume that we are dealing with three different orthogonal electronic states representing the ground state ($|g>$) the locally excited donor state ($|D>$) and the acceptor state ($|A>$). The nuclear Hamiltonians for the three electronic states will be denoted h_g, h_D and h_A respectively. The full Hamiltonian (H) of the system is composed of three parts:

$$H = H_0 + V(t) + J \tag{2.1}$$

where H_0 is diagonal in the three electronic states:

$$H_0 = |g> h_g <g| + |D> h_D <D| + |A> h_A <A|. \tag{2.2}$$

$V(t)$ is the laser field that induces the excitation from the ground state to the locally excited donor state:

$$V(t) = \mu E(t) \cos(\omega t)|D><g| + \mu^* E^*(t) \cos(\omega t)|g><D| \tag{2.3}$$

where μ is the dipole operator which may depend on the nuclear coordinates and $E(t)$ is the time profile of the optical field whose central frequency is ω. The final term in the Hamiltonian (J) induces the electron transfer between the donor and the acceptor states:

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$$J = \Delta|A><D| + \Delta^*|D><A| \tag{2.4}$$

and Δ is the coupling strength.

As shown in Ref. [8], to leading order in μ^2 the time dependent population of the locally excited donor state, assuming that the field is turned on at time t_0 is given by the expression:

$$P_D(t,\omega) = \frac{2}{\hbar^2 Z_g} Re \left(Tr e^{-\beta h_g} \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \tilde{V}_1^\dagger(t') \tilde{V}_1(t'') \right) \tag{2.5}$$

where $\beta \equiv \frac{1}{k_B T}$, Z_g is the partition function of the ground state nuclear Hamiltonian at the inverse temperature β:

$$Z_g = Tr e^{-\beta h_g} \tag{2.6}$$

and $\tilde{V}_1$ comes from the representation of the field Hamiltonian in the interaction picture with respect to the zero-th order Hamiltonian [9]:

$$\tilde{V}_1(t) = e^{ih_D(t-t_0)/\hbar} \mu e^{-ih_g(t-t_0)/\hbar} E(t) \cos(\omega t) \tag{2.7}$$

The rate of change of the population of the acceptor state may be assumed naively (for a formal justification see Refs. [8,10]) to be linearly proportional to the population of the locally excited donor state:

$$\frac{dP_A(t,\omega)}{dt} = k(t,\omega) P_D(t,\omega) \tag{2.8}$$

where the time dependent rate constant, which is the central quantity to be evaluated in this paper is given by the expression:

$$k(t,\omega) = \frac{Re \left(\int_{t_0}^{t} dt'' \int_{t_0}^{t} d\tau' \int_{t_0}^{\tau'} d\tau'' Tr \left(e^{-\beta h_g} \tilde{V}_1^\dagger(t'') \tilde{J}_1^\dagger(t) \tilde{J}_1(\tau') \tilde{V}_1(\tau'') \right) \right)}{\hbar^2 Re \left(\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' Tr \left(e^{-\beta h_g} \tilde{V}_1^\dagger(t') \tilde{V}_1(t'') \right) \right)} \tag{2.9}$$

and $\tilde{J}_1(t)$ comes from the interaction representation of the electron transfer coupling term:

$$\tilde{J}_1(t) = e^{ih_A(t-t_0)/\hbar} \Delta e^{-ih_D(t-t_0)/\hbar} \tag{2.10}$$

After a short initiation time, $k(t,\omega)$ goes to a constant ($k(\omega)$) which is well approximated by allowing $t_0 \to -\infty$ and $t \to \infty$.

B. Application to a harmonic model

The harmonic model for photoinduced electron transfer is not trivial to solve and allows for a variety of interesting physical limits. It is also true that for 'medium sized' polyatomic (10-40 atoms) at room temperature, the harmonic assumption is valid at least on a qualitative level. Due to the electronic excitation, one may expect that the frequencies in the locally excited donor state will differ somewhat from those of the ground state. We assume that the molecule under consideration has N degrees of freedom. Using mass weighted coordinates q_j and momenta p_j the harmonic model will take the form:

$$h_g = \sum_{j=1}^{N} \frac{1}{2} \left(p_j^2 + \omega_{gj}^2 q_j^2 \right) \tag{2.11}$$

$$h_D = \sum_{j=1}^{N} \frac{1}{2} \left(p_j^2 + \omega_j^2 q_j^2 \right) + \epsilon_{Dg} \tag{2.12}$$

$$h_A = \sum_{j=1}^{N} \frac{1}{2} \left(p_j^2 + \omega_j^2 (q_j - q_{j0})^2 \right) + \epsilon_{Ag} \tag{2.13}$$

where $\epsilon_{Dg}, \epsilon_{Ag}$ are the energies at the bottom of the well of the locally excited donor state and the acceptor state, relative to the ground state. One may make this model more general by allowing the frequencies ω_j of the acceptor state to differ from the donor state, by introducing position shifts to the locally excited donor state relative to the ground state and by allowing for Dushinskii rotations [14] of the normal modes in each of the electronic states. For the purpose of this paper we will remain with the above simplified model, since it has in it the essential physics.

For this model, the partition function for the ground state is:

$$Z_g = \prod_{j=1}^{N} \frac{1}{2 \sinh(\hbar \beta \omega_{gj}/2)}. \tag{2.14}$$

As shown in Ref. [11], the thermal correlation function of the ground state and locally excited donor state is:

$$\chi_{Dg}(t; \beta) \equiv Tr e^{-i \frac{t_c}{\hbar} h_g} e^{-i \frac{t}{\hbar} h_D}$$

$$= \sqrt{ \prod_{j=1}^{N} \left(\frac{a_{gj}(t_c) a_j(t)}{(b_{gj}(t_c) + b_j(t))^2 - (a_{gj}(t_c) + a_j(t))^2} \right)}. \tag{2.15}$$

Here, the a's and b's are:

$$a_{gj}(t_c) = \frac{\omega_{gj}}{\sin(\omega_{gj}t_c)} \tag{2.16}$$

$$b_{gj}(t_c) = \frac{\omega_{gj}}{\tan(\omega_{gj}t_c)} \tag{2.17}$$

$$a_j(t) = \frac{\omega_j}{\sin(\omega_j t)} \tag{2.18}$$

$$b_j(t) = \frac{\omega_j}{\tan(\omega_j t)} \tag{2.19}$$

and

$$t_c = -i\hbar\beta - t. \tag{2.20}$$

The field is assumed to have been turned on in the infinite past $(t_0 \rightarrow -\infty)$. One then readily finds (within the Condon approximation) that the time dependent population in the locally excited donor state (Eq. 2.5), at the central excitation frequency ω is:

$$P_D(t,\omega) = \frac{2|\mu|^2}{\hbar^2 Z_g} Re \int_0^\infty dt'' \chi_{Dg}(t'';\beta)\eta(t,t'';\omega) \tag{2.21}$$

where the field function $\eta(t,t'';\omega)$ is:

$$\eta(t,t'';\omega) = \int_{-\infty}^t dt' E^*(t')E(t'-t'')\cos(\omega t')\cos(\omega(t'-t'')) \tag{2.22}$$

Computation of the time and frequency dependent population in the locally excited donor state is thus reduced to two quadratures. If the temporal profile of the field $(E(t))$ is a Gaussian, than an analytic expression is obtained for the field function η and one remains with a single quadrature.

From Eqs. 2.7-2.10, one finds with a bit of manipulation, that within the Condon approximation, the rate of change of population of the acceptor state is:

$$\frac{dP_A(t,\omega)}{dt} = \frac{2|\mu|^2|\Delta|^2}{\hbar^4 Z_g} \int_0^\infty dz \int_0^\infty dy \int_0^\infty dx \cdot$$
$$Re\left(\chi(z-x-y-i\hbar\beta, -z,y,x)E^*(t-z)E(t-y-x)\cos(\omega(t-z))\cos(\omega(t-y-x))\right).$$
$$\tag{2.23}$$

The correlation function χ is defined as:

$$\chi(t_0, t_1, t_2, t_3) = Tr\left(e^{-\frac{i}{\hbar}t_0 h_g} e^{-\frac{i}{\hbar}t_1 h_D} e^{-\frac{i}{\hbar}t_2 h_A} e^{-\frac{i}{\hbar}t_3 h_D}\right). \tag{2.24}$$

For a harmonic oscillator Hamiltonian, the matrix element of the propagator is known [12]:

$$< x|e^{-i\frac{t}{\hbar}h_{ho}}|y> = \left(\frac{a(t)}{2\pi i\hbar}\right)^{\frac{1}{2}} e^{\frac{ib(t)}{2\hbar}(x^2+y^2)-\frac{ia(t)}{\hbar}xy} \tag{2.25}$$

where $a(t) = \frac{\omega}{\sin(\omega t)}$ and $b(t) = \frac{\omega}{\tan(\omega t)}$. The correlation function of Eq. 2.24 is thus expressed as a four fold Gaussian integral for each vibrational degree of freedom. Defining the 4 integration variables of the j-th degree of freedom as a vector $\underline{x}_j$, the integral can be put in the following matrix form

$$\chi(t_0, t_1, t_2, t_3) = e^{-\frac{i}{\hbar}(\epsilon_{Dg}(t_1+t_3)+\epsilon_{Ag}t_2)}$$
$$\prod_{j=1}^{N} \sqrt{\frac{a_{gj}(t_0)a_{Dj}(t_1)a_{Dj}(t_2)a_{Dj}(t_3)}{(4\pi i\hbar)^4}} \int d\underline{x}_j e^{\frac{i}{\hbar}[\frac{1}{2}\underline{x}_j^T \mathbf{A}_j \underline{x}_j + q_{j0}\underline{B}_j^T \underline{x}_j + q_{j0}^2 C_j]}, \tag{2.26}$$

where the boldfaced values are matrices, the underlined values are vectors and the superscripts T mean transpose. The matrix $\mathbf{A}_j$ is given by

$$\mathbf{A}_j = \begin{bmatrix} b_{gj}(t_0) + b_j(t_3) & -a_{gj}(t_0) & 0 & -a_j(t_3) \\ -a_{gj}(t_0) & b_{gj}(t_0) + b_j(t_1) & -a_j(t_1) & 0 \\ 0 & -a_j(t_1) & b_j(t_1) + b_j(t_2) & -a_j(t_2) \\ -a_j(t_3) & 0 & -a_j(t_2) & b_j(t_2) + b_j(t_3) \end{bmatrix}, \tag{2.27}$$

the vector $\underline{B}_j^T$ is

$$\underline{B}_j^T = \begin{bmatrix} 0, & 0, & b_{Dj}(t_2) - a_{Dj}(t_2), & b_{Dj}(t_2) - a_{Dj}(t_2) \end{bmatrix} \tag{2.28}$$

and C_j is given by

$$C_j = b_{Dj}(t_2) - a_{Dj}(t_2) \tag{2.29}$$

Completing the square in the exponent of Eq. 2.26, using the fact that $\mathbf{A}_j$ is symmetric, and the well known formula $\int d\underline{x} e^{-\underline{x}^T \mathbf{P}\underline{x}} = \sqrt{\pi^N/\det(\mathbf{P})}$, we obtain the following expression for the correlation function

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$$\chi(t_0, t_1, t_2, t_3) = e^{-\frac{i}{\hbar}(\epsilon_{Dg}(t_1+t_3)+\epsilon_{Ag}t_2)}$$

$$\prod_{j=1}^{N} \sqrt{\frac{a_{gj}(t_0)a_{Dj}(t_1)a_{Dj}(t_2)a_{Dj}(t_3)}{\det(\mathbf{A}_j)}} e^{-\frac{i}{\hbar}q_{j0}^2(\frac{1}{2}\underline{B}_j^T \mathbf{A}_j^{-1}\underline{B}_j - C)} \qquad (2.30)$$

The remaining time integrals appearing in Eq. 2.23 which are needed for obtaining the time and frequency dependent rate must be evaluated numerically.

III. MODEL COMPUTATIONS OF PHOTOINDUCED COHERENT ELECTRON TRANSFER

A. The model

The theory worked out in the previous section will be applied to the same model studied in Refs. [5,6]. The system is chosen to have 45 degrees of freedom, divided into three groups - low, medium and high frequencies. The low frequencies of h_g range from 50 to 470 cm^{-1} with an equal spacing of 30 cm^{-1}. The medium frequencies range from 800 cm^{-1} to 1220 cm^{-1} with the same spacing and the high frequencies range from 2000 cm^{-1} to 2700 cm^{-1} with an equal spacing of 50 cm^{-1}. These three groups mimic the typical frequency distribution of a polyatomic molecule. In the locally excited donor state, the frequencies of the low frequency group are reduced by a constant factor of 0.95, the medium frequency group by the factor 0.98 and the high frequency group by 0.99.

The energy gap between the ground and excited donor states ϵ_{Dg} is unimportant (except for justifying the rotating wave approximation, see below), since it simply sets the scale of frequencies for the photo-excitation laser. The energy gap between the excited donor and acceptor states is ϵ_{Ag} and is taken to be 0. Thus for the excitation frequency we use the difference $\omega - \epsilon_{Dg}$. The constants Δ and μ are set to 1.

The position shifts q_{j0} in the acceptor Hamiltonian are chosen such that the shift energy for a given mode $\frac{1}{2}\omega_j^2 q_{j0}^2 = x\hbar\omega_j$. The parameter x is chosen to be 0 for the medium frequency and high frequency groups of modes and is 2 [2] for the low frequency group of modes. This choice is made to assure that we are not in the tunneling limit, where the electron transfer

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rate becomes temperature independent. The intramolecular reorganization energy is thus 7,410 cm^{-1}. This implies an activation energy of approximately a quarter of an electron volt for a symmetric transfer process.

An analysis of the rate of change of the acceptor population, based on Eq. 2.23 shows that the main contribution to the dz and dx integrals comes from the region where $x = z = t$. This implies that as t increases the effective integration range adapts accordingly, and we expect to have a non-zero asymptotic result for $\frac{dP_A(t,\omega)}{dt}$ when $t \to \infty$.

For numerical reasons it will be convenient to use a Gaussian pulse width for the incident laser field $[E(t) = \frac{1}{\sqrt{\pi}\sigma}e^{-(t/\sigma)^2}]$. The time pulse width σ was first chosen to be wide enough so as not to broaden significantly the absorption spectrum. In Figures 1 to 6, $\sigma = 0.05\ cm$ (we use cm as the unit of time, inverse to the frequency unit cm^{-1}) , this broadens the spectrum by only 20 cm^{-1}, which is small in comparison with the absorption spectrum width for this case, known to be about 200 cm^{-1} [4]. Variation of the width is then studied in Figures 7 and 8.

B. A rotating wave approximation

To further simplify the four fold time integration, we use a rotating wave approximation, which is well justified, due to the large energy gap between the ground state and the locally excited donor state. Specifically, by expressing the $\cos(\omega t)$ term of the field (see Eq. 2.7) as a sum of exponents, one may separate the product of the cos functions in Eqs. 2.22 and 2.23, into two contributions: half cos of the sum and half cos of the difference. Asymptotic analysis of Eqs. 2.22 and 2.23 then shows that the term with the half cos of the sum is very oscillatory, having no stationary point, and so this term may be neglected. The remaining half cos difference term may be expressed as $\frac{1}{4}$ of the sum of 2 exponents, one which contributes around the frequency $\omega = \epsilon_{Dg}/\hbar$ the other contributes in the vicinity of the frequency $\omega = -\epsilon_{Dg}/\hbar$. Since ϵ_{Dg} is positive and so is ω, the latter term can again be neglected so that we will use only the first exponent. Using this rotating wave approximation,

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the integral in Eq. 2.22 simplifies to:

$$\eta(t, t''; \omega) = \frac{1}{8\sigma\sqrt{2\pi}} e^{i\omega t''} e^{-\frac{t''^2}{2\sigma^2}} \left[1 + erf\left(\frac{t - 0.5t''}{\sigma/\sqrt{2}} \right) \right]$$ (3.1)

C. Numerical results

We will examine the time evolution of the frequency dependent rate $k(t, \omega)$ (cf. Eq. 2.9). For this purpose it is necessary to compute the population in the locally excited donor state $P_D(t, \omega)$ and the rate of change of population in the acceptor state $dP_A(t, \omega)/dt$. Given the pulse width of $\sigma = 0.05$ it suffices to study the time interval [-0.2cm 0.2cm] for several values of $\omega - \omega_{00}$. This is shown in Figures 1 to 3 where we plot the time dependence of the locally excited donor state population (as defined in Eq. 2.21); the rate of change of the acceptor population (as defined in Eq. 2.23) and the time dependent rate constant (cf. Eq. 2.8), respectively. All the quantities are computed for three frequencies $\omega - \omega_{00} = -280, -80$, and 120 cm^{-1} corresponding respectively to the red edge, the peak and the blue edge of the absorption spectrum. One notes that all three quantities reach their asymptotic in time limit by the time $t = 0.1$ cm.

The frequency dependence of the population of the locally excited donor state is plotted in Fig. 4 for the four times -0.12, -0.04, 0.04 and 0.2 cm. One notes that the asymptotic in time limit of the population in the locally excited donor state is up to a constant identical to the absorption spectrum. As already mentioned and as seen from the Figure, the width of the absorption spectrum is approximately 200 cm^{-1}. Initially the absorption occurs for a much larger spread in frequencies, which then narrows with time.

The frequency dependence of the rate of change of the population in the acceptor state is plotted in Fig. 5. The similarity of these results to those shown for the population in the locally excited donor state in Figure 4 is striking. The frequency dependence of the rate of change of the acceptor population is slightly broader than the locally excited donor state population, but the differences are not very large.

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All of this implies that the asymptotic in time limit of the rate constant is almost independent of the excitation frequency of the laser in the frequency region for which the absorption is significant. This central result of this paper is shown in Figure 6, which depicts the frequency dependence of the rate constant k for the same values of time as in Figures 4 and 5.

The dependence of the photoexcitation process on the incident field time width σ is shown in Figures 7 and 8. In Figure 7 we plot the donor state population, which as expected, broadens with decreasing temporal width. Figure 8 then presents the frequency dependent rate constant for a few different values of the temporal width, at the asymtotic time t=0.2cm.

As σ increases, the incident pulse is sharper in frequency, hence the frequency region for which the absorption is significant is narrower, and approaches the 200 cm^{-1} width. P_D depicted in Figure 7 is calculated after normalizing $E(t)$ so that the peak population is equal for all σ, but k, which is the ratio between dP_A/dt and P_D does not depend on any normalization of the field. The asymptotic value for $k(\omega)$ in the frequency region for which the absorption is significant does not depend on σ and as mentioned before is also almost independent of ω.

Finally we remark that an estimate for the asymptotic value of the rate constant may be evaluated rather simply, provided that the ground state and locally excited state Hamiltonians are identical and the excitation frequency is $\omega = \epsilon_{Dg}/\hbar$. One then finds that:

$$k_{asymptotic} = \frac{2\Delta^2}{\hbar^2 Z_g} \int_0^\infty dy Tr \left\{ e^{i(y-i\beta)h_g} e^{-iyh_A} \right\} \tag{3.2}$$

Numerical computation of Eq. 3.2 confirms the asymptotic value for k observed in Figure 3, for $\omega - \omega_{00}$=-80 and t>0.1cm, which is about 5x10^{-5}cm^{-1}.

IV. DISCUSSION

A numerical study of the frequency and pulse width dependence of photoinduced electron transfer in a model harmonic polyatomic model was presented. In contrast to previous

work, here we used a three state Hamiltonian and within leading order perturbation theory treated the quantum dynamics exactly. The resulting excitation frequency dependence of the electron transfer rate differs significantly from the results of a previous study, in which the photoexcitation of the locally excited donor state was decoupled from the subsequent electron transfer step. In the latter study [5], we found for the same harmonic Hamiltonian as used in the present study, that the rate changes by up to two orders of magnitude as the photoexcitation freqency sweeps through the frequency region where absorption is not negligible.

The two step approach was based on finding first the nascent energy dependent distribution in the excited donor state, created by photoexcitation and then using this distribution as input in the Golden rule expression for the electron transfer rate. This analysis showed that the rate constant k is smaller for frequencies for which the donor state is cooled, and higher for frequencies for which the donor is heated. The results presented in this paper show that this two step approach is incorrect for the isolated molecule. In the absorption region, the rate is almost independent of the excitation frequency. When the photoabsorption and the electron transfer processes are treated on the same footing, it would seem that the intermediate dynamics is not very important.

Does this imply that our former results are wrong? Yes, for the isolated molecule, but not necessarily for a molecule interacting even weakly with a surrounding bath. One may expect that if the bath dephases the nascent distribution in the locally excited donor state on a time scale which is rapid compared to the electron transfer process, then the electron transfer will indeed be decoupled from the photoexcitation step and the two step model would be correct. If however, the interaction with the bath leads to an energy thermalization on a time scale which is faster than the electron transfer time, then this thermalization will again cause the rate to be independent of the excitation frequency. In other words, sensitive dependence on the photoexcitation frequency can be expected provided that the interaction with the bath leads to a fast dephasing time but a slow energy relaxation time as compared with the electron transfer time.

Can one show this type of a behavior using a model system? In principle yes, one must add a bilinear coupling of the vibrational modes of the molecule to a harmonic bath and then repeat the same type of computation as presented in the present paper, with an initial thermal distribution of the bath modes. Such a computation has been done for the photoexcitation process [13], which involved only two electronic states. It is much more difficult to carry it out for a three state system with 10 to 100 vibrational degrees of freedom, as in this case it becomes very difficult to obtain a simple analytic expression for the four point correlation function.

Even after the present study there are a number of questions which should still be answered. We did not allow for position shifts or Dushinskii rotations of the locally excited donor state with respect to the ground state. But perhaps even more interesting is what happens when using a strong field. A theory of strong field coherent photoexcited electron transfer remains a challenge for future work.

ACKNOWLEDGMENT

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[9] Note the typographical error in Eqs. 6 of Ref. [8]. The correct version of the first equation is $\tilde{V} = \tilde{V}_1(t)|D><g| + \tilde{V}_1^\dagger(t)|g><D|$ where $\tilde{V}_1(t)|D><g|$ is as defined in Eq. 2.7. The second equation, giving the electron transfer coupling in the interaction picture is correct as it stands.

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Figure captions

FIG. 1 Time evolution of the locally excited donor population for several excitation frequencies.

FIG. 2 Time evolution of the acceptor population rate of change for several excitation frequencies.

FIG. 3 Time evolution of the rate constant k for several excitation frequencies.

FIG. 4 Frequency dependence of the locally excited donor population at different times.

FIG. 5 Frequency dependence of the acceptor population rate of change at different times.

FIG. 6 Frequency dependence of the rate constant k at different times. Note that at the asymptotic time, the rate is almost independent of the excitation frequency.

FIG. 7 Frequency dependence of the absorption spectrum for several incident pulse widths.

FIG. 8 Frequency dependence of the rate constant k for several incident pulse widths.
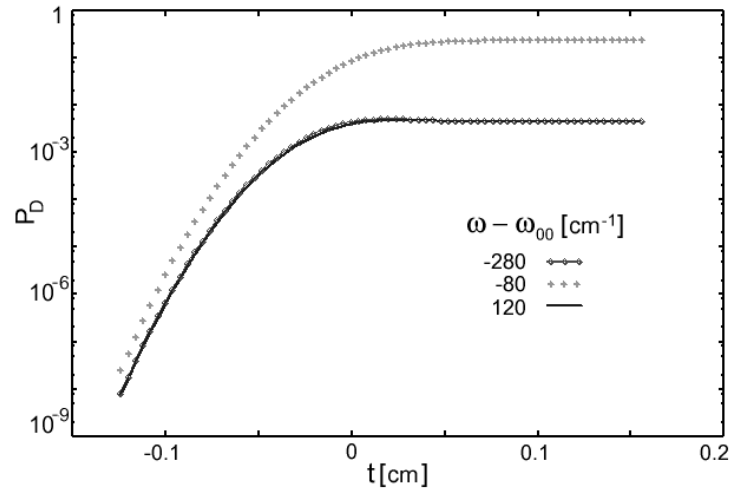
Figure 1, Ianconescu and Pollak
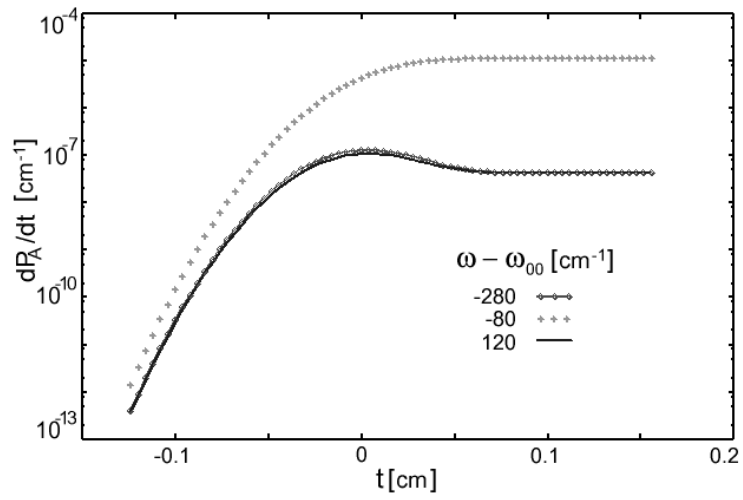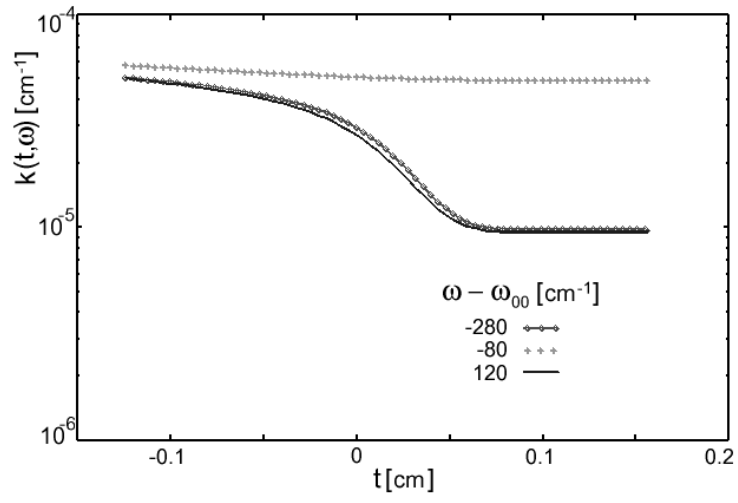

Figure 2, Ianconescu and Pollak
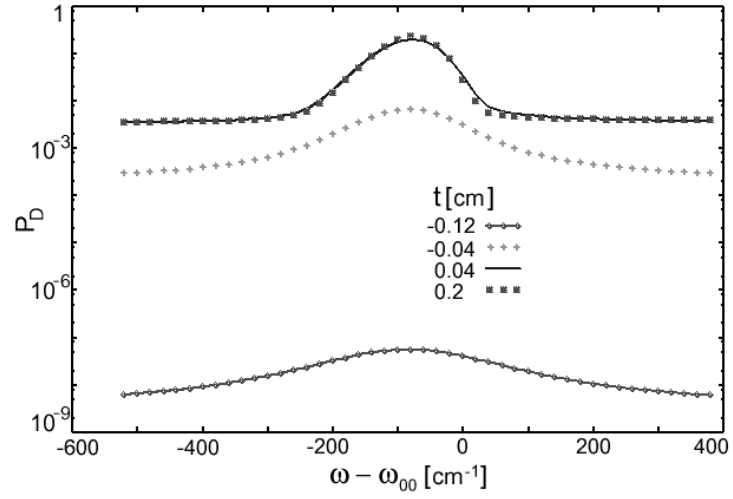
Figure 3, Ianconescu and Pollak

Figure 4, Ianconescu and Pollak

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Figure 5, Ianconescu and Pollak

Figure 6, Ianconescu and Pollak

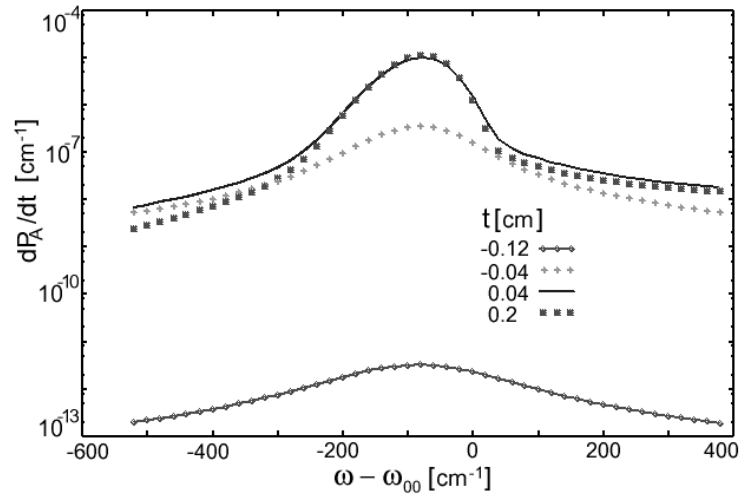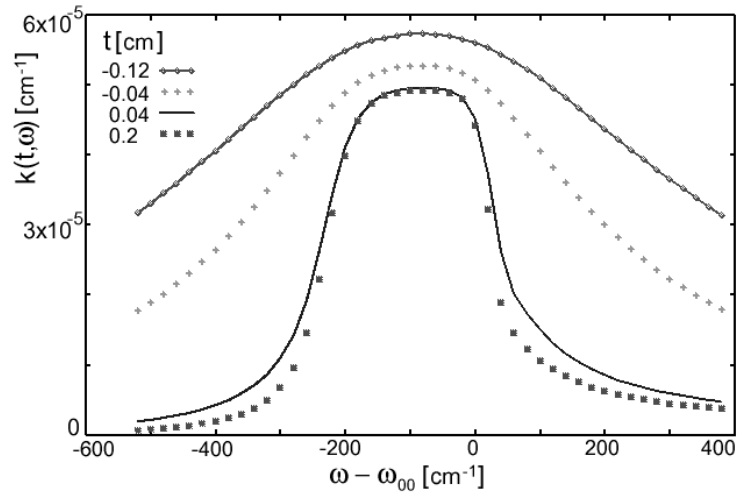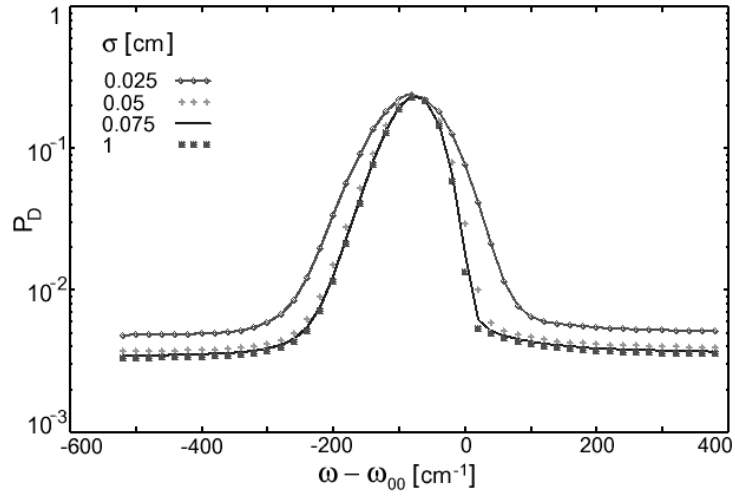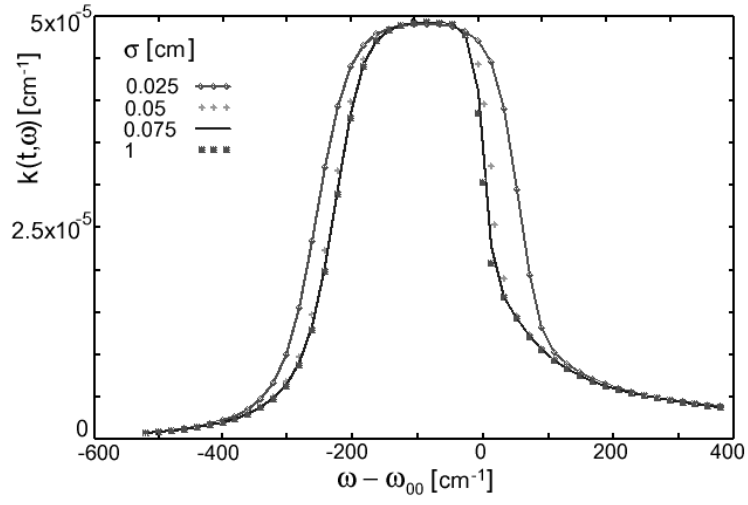**Figure 7, Ianconescu and Pollak**

Figure 8, Ianconescu and Pollak