

Multistate quantum Fokker–Planck approach to nonadiabatic wave packet dynamics in pump–probe spectroscopy

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The quantum Fokker–Planck equation of Caldeira and Leggett is generalized to a multistate system with anharmonic potentials and a coordinate dependent nonadiabatic coupling. A rigorous procedure for calculating the dynamics of nonadiabatic transitions in condensed phases and their monitoring by femtosecond pump–probe spectroscopy is developed using this equation. Model calculations for a harmonic system with various nonadiabatic coupling strengths and damping rates are presented. Nuclear wave packets in phase space related to electronic coherence are shown to provide an insight into the mechanism of nonadiabatic transitions. The Green's function expression for these wave packets is used to explore possible algorithms for incorporating electronic dephasing in molecular dynamics simulations of curve crossing processes.

I. INTRODUCTION

Femtosecond nonlinear optical spectroscopies provide a powerful tool for studying the dynamics of nonadiabatic curve crossing¹ and electron transfer processes.^{2–4} A tremendous insight has been gained by comparing qualitative arguments,⁵ quantitative analytical calculations,^{6–8} and numerical studies^{9–15} with experiment. As far as theoretical work goes, the fully quantum treatment poses some difficult problems. Quantum nonadiabatic transitions, in the absence of dissipation, can be studied by a wide variety of numerical methods based on the wave function.^{9–14} When dissipation is important, wave function-based methods are not practical since the calculation requires the incorporation of many nuclear degrees of freedom (a bath). Integrating out the bath degrees of freedom can be performed using path integral,^{16–18} or projection operator¹⁹ techniques. The path integral approach is particularly powerful for systems with harmonic potentials, where the necessary functional integrations can be carried out and analytical expressions for density matrix elements may be derived.^{8,20} Numerical evaluation of the path integrals using Monte Carlo methods is possible.^{21,22} This approach, however, is computationally intensive and its applicability is still limited. The projection operator approach is applicable if an interaction between the system and the bath is weak. It leads to an equation of motion for density matrix elements (the master equation), which can be solved numerically.^{15,23–25} The master equation approach requires the computation of the vibronic eigenstates, which makes it difficult to apply to curve crossing in systems such as alkali halides,^{26,27} where the potentials and nonadiabatic couplings are complicated functions of nuclear coordinates, and we need to incorporate many vibronic eigenstates.

An alternative, and perhaps more natural way to solve the problem is using the phase space representation (instead of eigenstate expansions) for the density matrix. Sparpagli-

one, Yan, and Mukamel developed Green's function techniques in phase space^{15,24} and semiclassical equations of motion based on the Langevin equation to treat nonadiabatic transitions in the weak coupling limit. For a single potential surface, the equation of motion for phase space distribution functions is known as the quantum Fokker–Planck equation.^{28–30} In this paper, we extend the quantum Fokker–Planck equation to a multistate system with anharmonic potentials and coordinate-dependent nonadiabatic coupling. The multistate Fokker–Planck equation obtained by Garg *et al.*⁶ was limited to harmonic potentials with a constant nonadiabatic coupling. The present equation provides a microscopic picture of nonadiabatic processes using nuclear wave packets in phase space. Like the master equation, this approach is applicable only for weak coupling to the bath. In Appendix A, we generalize this equation to a strong system–bath coupling by introducing a hierarchy of kinetic equations.^{31–33} We then present a rigorous procedure for calculating femtosecond pump–probe curve crossing spectroscopy using reduced wave packets in phase space, where bath degrees of freedom have been traced out. Previous theoretical treatments of this problem were based on the wave functions and were limited to isolated molecules (no bath) and further employed an approximate procedure for calculating the absorption spectrum.³⁴ We also use our results to examine possible semiclassical of molecular dynamics (MD) simulations of curve crossing problems.^{35–40} The incorporation of dephasing effects in nonadiabatic transitions in MD is usually phenomenological. Using the Green's function of electronic coherence obtained from the quantum Fokker–Planck equation, we can pinpoint the approximations made in current procedures and establish a firm theoretical basis for possible generalizations. Our procedure is illustrated by model calculations. The dynamics of nuclear wave packets and its signature in the pump–probe spectrum are discussed.

The organization of this paper is as follows: the multistate Fokker–Planck equation is presented in Sec. II. In Sec. III, we develop the procedure for calculating the pump–probe spectrum. Numerical results for a harmonic system are

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presented in Sec. IV. The implications of our results on molecular dynamics simulations of nonadiabatic processes are discussed in Sec. V.

II. THE MULTISTATE QUANTUM FOKKER-PLANCK EQUATION

Consider a molecular system with several electronic states $|j\rangle$ strongly coupled to a single primary nuclear coordinate R . The Hamiltonian of the system is

$$H_s = \frac{P^2}{2M} + \sum_j \sum_k |j\rangle U_{jk}(R) \langle k|, \quad (1)$$

where P is the conjugate momentum of R . The diagonal element $U_{jj}(R)$ is the potential surface of the j th electronic surface, and the off-diagonal elements $U_{jk}(R)$ with $j \neq k$ represent the nonadiabatic coupling between the j th and the k th states. In addition, the primary nuclear coordinate is coupled to a bath which is represented by a set of harmonic oscillators with frequencies ω_n , masses m_n , coordinate x_n , and momenta p_n . The interaction between the primary nuclear coordinate and the n th bath oscillator is assumed to be linear with a coupling strength c_n . The total Hamiltonian is then given by

$$H = H_s + H', \quad (2)$$

where

$$H' = \sum_n \left[\frac{p_n^2}{2m_n} + \frac{m_n \omega_n^2}{2} \left(x_n - \frac{c_n R}{m_n \omega_n^2} \right)^2 \right]. \quad (3)$$

All information about the bath which is required for a reduced description of the system dynamics is contained in its initial temperature and its spectral density

$$J(\omega) \equiv \omega \sum_n \left(\frac{c_n^2}{4m_n \omega_n^3} \right) [\delta(\omega - \omega_n) + \delta(\omega + \omega_n)]. \quad (4)$$

$J(\omega)$ is related to the symmetric correlation function of a collective bath coordinate ($X = \sum c_n x_n$),^{16,31}

$$\frac{1}{2} \langle X(t)X + XX(t) \rangle = \hbar \int d\omega J(\omega) \coth\left(\frac{\beta \hbar \omega}{2}\right) \cos(\omega t), \quad (5)$$

where $\beta = 1/k_B T$ is the inverse temperature of the bath, and the time evolution of X is determined by the pure bath Hamiltonian [Eq. (3) with $R=0$]. If the spectral distribution is given by $J(\omega) = M \zeta \omega / 2\pi$ (the Ohmic distribution) and the bath temperature is high (i.e., $\coth(\beta \hbar \omega / 2) \approx 2 / \beta \hbar \omega$), we have $\frac{1}{2} \langle X(t)X + XX(t) \rangle = 2M \zeta \delta(t) / \beta$. This correlation function corresponds to the Gaussian-white noise Brownian oscillator. In this case, we obtain an equation of motion for the reduced system density matrix $\rho(t)$ (the quantum Fokker-Planck equation). In an operator form, it reads²⁸

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} H_s \hat{\rho}(t) - \frac{\zeta}{2\hbar} \hat{R} \times \left(i \hat{P} \circ + \frac{2M}{\beta \hbar} \hat{R} \times \right) \hat{\rho}(t). \quad (6)$$

Here, \hat{P} is the momentum operator, and we have defined for any two operators \hat{A} and \hat{B} ,

$$\hat{A} \times \hat{B} \equiv \hat{A} \hat{B} - \hat{B} \hat{A}, \quad \hat{A} \circ \hat{B} \equiv \hat{A} \hat{B} + \hat{B} \hat{A}. \quad (7)$$

The symbol \times stands for a commutator and \circ for an anti-commutator. This equation of motion is valid only when the following high temperature condition applies:³⁰

$$\beta \hbar \omega_c \ll 1, \quad (8)$$

where ω_c is a characteristic frequency of the system. When this condition is not satisfied, the quantum Fokker-Planck equation may yield unphysical results such as negative diagonal elements $\langle R | \hat{\rho}(t) | R \rangle < 0$. The limitation [Eq. (8)] can be relaxed if we consider a Gaussian-Markovian bath where $J(\omega) = M \zeta \omega \gamma^2 / 2\pi (\gamma^2 + \omega^2)$.³² With the assumption of the high temperature bath $\beta \hbar \gamma \ll 1$, this spectral density represents a Gaussian-Markovian noise where the symmetric correlation function of the noise induced by the heat bath is given by $\frac{1}{2} \langle X(t)X + XX(t) \rangle = 2M \zeta \exp(-\gamma t) / \beta$. Thus, ζ and γ correspond to the friction and the relaxation time of the noise, respectively. The generalized equation of motion holds in this case provided $\beta \hbar \gamma \ll 1$ and is presented in Appendix A. The important point is that now the restriction does not involve the system frequencies (which can be small or large compared to β^{-1}), but only a high temperature requirement with respect to the bath, which is much easier to meet. The calculations presented below will, however, be limited to the simpler Gaussian-white noise case.

For the multistate system [Eq. (1)], the density matrix may be expanded in the electronic basis set as

$$\hat{\rho}(t) = \sum_{j,k} |j\rangle \rho_{jk}(R, R'; t) \langle k|. \quad (9)$$

Here, $\rho_{jk}(R, R'; t)$ is expressed in the coordinate representation. Alternatively, we can switch to the Wigner (phase space) representation

$$W_{jk}(P, R; t) \equiv \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dr e^{iPr/\hbar} \rho_{jk}(R - r/2, R + r/2; t), \quad (10)$$

and the density matrix may then be written as

$$\hat{W}(t) = \sum_{j,k} |j\rangle W_{jk}(P, R; t) \langle k|. \quad (11)$$

By performing the Wigner transformation on Eq. (6) with the Hamiltonian (1), the multistate Fokker-Planck equation assumes the form

$$\begin{aligned}
& \frac{\partial}{\partial t} W_{jk}(P, R; t) \\
&= -\frac{P}{M} \frac{\partial}{\partial R} W_{jk}(P, R; t) - \frac{1}{\hbar} \int \frac{dP'}{2\pi\hbar} \\
&\quad \times \sum_m [X_{jm}(P-P', R) W_{mk}(P', R; t) \\
&\quad + X_{mk}^*(P-P', R) W_{jm}(P', R; t)] + \Gamma W_{jk}(P, R; t). \quad (12)
\end{aligned}$$

Here

$$\begin{aligned}
X_{ij}(P, R) &= i \int_{-\infty}^{\infty} dr \exp\left(\frac{iPr}{\hbar}\right) U_{ij}\left(R - \frac{r}{2}\right), \\
X_{ij}^*(P, R) &= i \int_{-\infty}^{\infty} dr \exp\left(\frac{-iPr}{\hbar}\right) U_{ij}\left(R - \frac{r}{2}\right) \\
&= -i \int_{-\infty}^{\infty} dr \exp\left(\frac{iPr}{\hbar}\right) U_{ij}\left(R + \frac{r}{2}\right), \quad (13)
\end{aligned}$$

and the Ornstein-Uhlenbeck operator which describes Brownian motion in momentum space is

$$\Gamma \equiv \zeta \frac{\partial}{\partial P} \left(P + \frac{M}{\beta} \frac{\partial}{\partial P} \right). \quad (14)$$

Note that the present equations hold even if $U_{jk}(R)$ are time dependent, as is the case, e.g., in optical spectroscopy. A semiclassical approximation for these equations is given in Appendix B.

It is possible to keep the density matrix in the coordinate representation and solve the equation of motion for $\rho_{jk}(R, R'; t)$ [Eq. (6)]. In that case, the equation is somewhat simpler since it is local in coordinate space. Nevertheless, the Wigner representation has few advantages. First it allows us to compare the quantum density matrix directly with its classical counterpart. Second, using phase space distribution functions, we can further easily impose the necessary boundary conditions (e.g., periodic or open boundary conditions, where particles can move in and out of the system). This is much more difficult in the coordinate representation (see Ref. 29).

III. IMPULSIVE PUMP-PROBE SPECTROSCOPY IN A DISPLACED HARMONIC SYSTEM

Our equation of motion is not limited to a particular functional form of the potentials and the coordinate dependent nonadiabatic couplings. For simplicity, we apply it to a harmonic system. We study a pump-probe experiment⁴¹ in a four-level system denoted by g , e , e' , and f (Fig. 1). The electronic energy gaps between ge and ef are denoted by ω_{eg} and ω_{ef} ($\omega_{ef} = \omega_{e'f}$), respectively. The potentials are given by $U_{jj}(R)$ ($j = g, e, e',$ and f). We assume that only the e and e' states are coupled by a coordinate independent nonadiabatic coupling setting $U_{ee'}(R) = \Delta$.

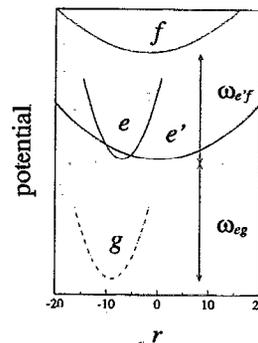


FIG. 1. Potential surfaces of the four level system.

The system is initially in the ground state. At time $t=0$, a pump pulse which couples the g and e states is applied, bringing the molecule to the e state. This primary coordinate R then moves in the U_{ee} potential. As a result of the nonadiabatic coupling $U_{ee'}$, some of the e state population transfers to e' . At $t=\tau$, a probe pulse which couples only the e' and f states is applied, and the induced coherence between e' and f is detected by the probe absorption. Thus, by observing the probe absorption spectrum and its variation with τ , we can monitor the vibrational motions in the e' state.

The coupling of our system with the laser field is given by

$$\begin{aligned}
H_E &= E_I(\mathbf{r}, t) (|g\rangle\langle e| + |e\rangle\langle g|) \\
&+ E_T(\mathbf{r}, t) (|e'\rangle\langle f| + |f\rangle\langle e'|), \quad (15)
\end{aligned}$$

where $E_I(\mathbf{r}, t)$ and $E_T(\mathbf{r}, t)$ are the pump and the probe (test) pulses

$$\begin{aligned}
E_I(\mathbf{r}, t) &= E_1(t) \exp(i\mathbf{k}_1 \mathbf{r} - i\Omega_1 t) + \text{c.c.}, \\
E_T(\mathbf{r}, t) &= E_2(t) \exp(i\mathbf{k}_2 \mathbf{r} - i\Omega_2 t) + \text{c.c.} \quad (16)
\end{aligned}$$

The pulses are assumed to be resonant $\Omega_1 = \omega_{eg}$ and $\Omega_2 = \omega_{e'f}$ and impulsive, i.e.,

$$E_1(t) = \theta_1 \delta(t), \quad E_2(t) = \theta_2 \delta(t - \tau), \quad (17)$$

where θ_1 and θ_2 are their areas and we take $\theta_1 = \theta_2 = 1$. Since the pump is impulsive, the wave packet ρ_{ee} created initially in the e state has the same shape as the ground state equilibrium density matrix. This allows us to eliminate the ground state from our calculations and the effect of the pump excitation can be simply taken into account by setting the initial condition in the e state as

$$W_{ee}(P, R; 0) = \exp\left[-\beta \left(\frac{P^2}{2M} + U_{gg}(R) \right)\right], \quad (18)$$

where $U_{gg}(R)$ is the ground state potential. Since nonadiabatic coupling exists only between the e and e' states, we need to calculate the wave packets W_{ee} , $W_{e'e'}$, and $W_{ee'}$ ($W_{e'e'}$ is the Hermitian conjugate of $W_{ee'}$) and we need not consider the f state until the probe pulse is applied. For harmonic potentials, the multistate quantum Fokker-Planck equation coincides with the semiclassical equation (see Appendix B) and we have

$$\begin{aligned} \frac{\partial}{\partial t} W_{ee}(P, R; t) &= -(L_{ee} - \Gamma) W_{ee}(P, R; t) \\ &\quad - \frac{i\Delta}{\hbar} [W_{e'e}(P, R; t) - W_{ee}(P, R; t)], \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t} W_{e'e'}(P, R; t) &= -(L_{e'e'} - \Gamma) W_{e'e'}(P, R; t) \\ &\quad + \frac{i\Delta}{\hbar} [W_{e'e}(P, R; t) - W_{ee}(P, R; t)], \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{\partial}{\partial t} W_{ee'}(P, R; t) &= -(L_{ee'} - \Gamma) W_{ee'}(P, R; t) \\ &\quad - \frac{i\Delta}{\hbar} [W_{e'e'}(P, R; t) - W_{ee}(P, R; t)], \end{aligned}$$

where

$$\begin{aligned} L_{jk} &\equiv \frac{P}{M} \frac{\partial}{\partial R} - \frac{1}{2} \left[\frac{\partial U_{jj}(R)}{\partial R} + \frac{\partial U_{kk}(R)}{\partial R} \right] \frac{\partial}{\partial P} \\ &\quad + \frac{i}{\hbar} [U_{jj}(R) - U_{kk}(R)] \quad (j, k = e, e'). \end{aligned} \quad (20)$$

Here, $U_{ee}(R)$ and $U_{e'e'}(R)$ are the potential surfaces of the e and e' states, respectively, and Δ is their nonadiabatic coupling.

Finally, at time $t = \tau$, the impulsive probe pulse which connects the e' and f states is applied. The polarization induced by the third-order interaction with the external field with wave vector $\mathbf{k}_2 = -\mathbf{k}_1 + \mathbf{k}_1 + \mathbf{k}_2$ is given by

$$P_{k_2}(t) = \int dP \int dR W'_{fe'}(P, R, \tau), \quad (21)$$

where $W'_{e'f}(P, R; t)$ satisfies the equation of motion

$$\frac{\partial}{\partial t} W'_{fe'}(P, R; t) = -(L_{fe'} - \Gamma) W'_{fe'}(P, R; t). \quad (22)$$

The impulsive probe interaction leads to the following initial condition:

$$W'_{fe'}(P, R, \tau) = -i W_{e'e'}(P, R, \tau). \quad (23)$$

The probe absorption spectrum is commonly detected by spectrally dispersing the transmitted probe, and the signal, measured as a function of the dispersed frequency ω_2 , is given by⁴²

$$S(\omega_2) = -2 \operatorname{Im} E_2^*(\omega_2) P_{k_2}(\omega_2). \quad (24)$$

Here, $E_2(\omega_2)$ is the Fourier transform of the probe field amplitude

$$E_2(\omega_2) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt \exp[i(\omega_2 - \omega_{e'f})t] E_2(t), \quad (25)$$

and for the present impulsive probe case $E_2(\omega_2) = \text{const}$. $P_{k_2}(\omega_2)$ is the Fourier transform of the polarization

$$P_{k_2}(\omega_2) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt \exp[i(\omega_2 - \omega_{e'f})t] P_{k_2}(t). \quad (26)$$

In summary, the probe absorption can be calculated by the following three steps: (1) calculate W_{ee} , $W_{e'e'}$, and $W_{ee'}$ by solving Eqs. (19) with the initial condition (18) between $t=0$ and $t=\tau$, (2) calculate $W'_{fe'}$ using Eq. (22) with the initial condition (23), then trace it over P and R [Eq. (21)] to obtain $P_{k_2}(t)$; (3) the absorption spectrum $S(\omega_2)$ is finally obtained using Eq. (24) by performing Fourier transform of $P_{k_2}(t)$.

To obtain a clear picture in phase space for the dynamics of nonadiabatic problem, we found it instructive to rearrange Eqs. (19) by formally eliminating the off-diagonal elements $W_{ee'}$,

$$\begin{aligned} \frac{\partial}{\partial t} W_{ee}(P, R; t) &= -(L_{ee} - \Gamma) W_{ee}(P, R; t) - \frac{2\Delta^2}{\hbar^2} \operatorname{Re} \int_0^t d\tau \exp[-(L_{ee'} - \Gamma)(t - \tau)] W_{ee}(P, R; \tau) \\ &\quad + \frac{2\Delta^2}{\hbar^2} \operatorname{Re} \int_0^t d\tau \exp[-(L_{ee'} - \Gamma)(t - \tau)] W_{e'e'}(P, R; \tau) \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{\partial}{\partial t} W_{e'e'}(P, R; t) &= -(L_{e'e'} - \Gamma) W_{e'e'}(P, R; t) + \frac{2\Delta^2}{\hbar^2} \operatorname{Re} \int_0^t d\tau \exp[-(L_{ee'} - \Gamma)(t - \tau)] W_{ee}(P, R; \tau) \\ &\quad - \frac{2\Delta^2}{\hbar^2} \operatorname{Re} \int_0^t d\tau \exp[-(L_{ee'} - \Gamma)(t - \tau)] W_{e'e'}(P, R; \tau). \end{aligned}$$

Denoting the second and the third terms on the right-hand side of the above equations by K_{ee} and $K_{e'e'}$, respectively, and taking the time derivatives of these terms, we can recast Eq. (27) in a form that is local in time

$$\begin{aligned} \frac{\partial}{\partial t} W_{ee}(P, R; t) &= -(L_{ee} - \Gamma) W_{ee}(P, R; t) - K_{ee}(P, R; t) \\ &\quad + K_{e'e'}(P, R; t), \\ \frac{\partial}{\partial t} W_{e'e'}(P, R; t) &= -(L_{e'e'} - \Gamma) W_{e'e'}(P, R; t) \\ &\quad + K_{ee}(P, R; t) - K_{e'e'}(P, R; t), \\ \frac{\partial}{\partial t} K_{ee}(P, R; t) &= -(L_{ee} - \Gamma) K_{ee}(P, R; t) \\ &\quad + \frac{2\Delta^2}{\hbar^2} W_{ee}(P, R; t), \\ \frac{\partial}{\partial t} K_{e'e'}(P, R; t) &= -(L_{e'e'} - \Gamma) K_{e'e'}(P, R; t) \\ &\quad + \frac{2\Delta^2}{\hbar^2} W_{e'e'}(P, R; t). \end{aligned} \quad (28)$$

The kernel K_{ee} represents the *nonadiabatic transition flux density in phase space* from e to e' , whereas $K_{e'e'}$ represents the flux density for the reverse transition. If the frequencies of the harmonic potentials in the e and e' state are the same, we may evaluate the exponential kernel in Eq. (27) using path integrals.⁸ For anharmonic potentials, we need to solve the equations of motion numerically. Although Eqs. (19) are somewhat simpler than Eq. (28) (three vs four equations), in this paper, we use the latter since K_{ee} and $K_{e'e'}$ provide a unique visualization of the coordinate and momentum dependence of nonadiabatic transitions, as will be demonstrated in Sec. V.

IV. NUMERICAL CALCULATIONS

Hereafter we use dimensionless coordinate and momentum defined by $r = R\sqrt{M\omega_A/\hbar}$ and $p = P\sqrt{1/M\hbar\omega_A}$, respectively, where ω_A is the ground state frequency. We assume the following harmonic potentials (see Fig. 2):

$$\begin{aligned} U_{gg}(r) &= \frac{\hbar}{2} \omega_A (r - d_g)^2 - \hbar \omega_{ge}, & U_{ee}(r) &= \frac{\hbar}{2} \omega_A (r - d_e)^2, \\ U_{e'e'}(r) &= \frac{\hbar}{2} \bar{\omega}_B r^2, & U_{ff}(r) &= \frac{\hbar}{2} \bar{\omega}_B (r - d_f)^2 + \hbar \omega_{e'f}. \end{aligned} \quad (29)$$

The parameters used are $\omega_A = 1000 \text{ cm}^{-1}$, $\bar{\omega}_B = 100 \text{ cm}^{-1}$, $d_g = -9.0$, $d_e = 7.0$, and $d_f = -2.0$. Note that the frequency of the e' and f potentials is not $\bar{\omega}_B$, but rather $\omega_B = \sqrt{\bar{\omega}_B \omega_A} = 333 \text{ cm}^{-1}$ since we defined the dimensionless coordinate using ω_A . We chose the initial temperature $T = 300 \text{ K}$, which satisfies the condition (8) for the higher frequency ω_A (i.e., $\beta\hbar\omega_A/2 = 0.38 < 1$). The numerical integration of Eqs. (28) was performed by the fourth order Runge-Kutta method for

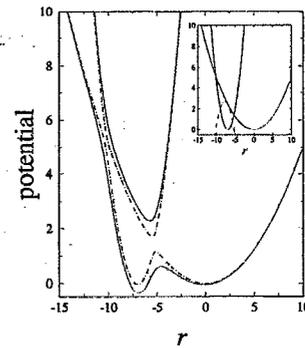


FIG. 2. Adiabatic potential surfaces $U_{ee} + U_{e'e'} \pm \sqrt{(U_{ee} + U_{e'e'})^2 - 4(U_{ee}U_{e'e'} - U_{ee}^2)}$ for the strong nonadiabatic coupling (solid line) and the weak nonadiabatic coupling (dashed line). The inset shows nonadiabatic potentials U_{ee} and $U_{e'e'}$ and their difference (dashed line).

finite difference expression of momentum and the coordinate space (we used 40×100 mesh for $-7.5 < p < 7.5$ and $-19 < r < 19$).²⁹ We have used two values of the nonadiabatic coupling $\Delta = 300 \text{ cm}^{-1}$ (weak) and $\Delta = 1000 \text{ cm}^{-1}$ (strong). We also used two values of the friction $\zeta = 25 \text{ cm}^{-1}$ (weak) and $\zeta = 500 \text{ cm}^{-1}$ (strong).

In the following, we show the wave packets $W_{ee}(p, r; t)$ and $W_{e'e'}(p, r; t)$, the nonadiabatic transition fluxes $K_{ee}(p, r; t)$ and $K_{e'e'}(p, r; t)$ and the pump-probe spectra. The results are shown in four groups: (1) weak coupling and weak friction (Figs. 3–5); (2) strong coupling and weak friction (Figs. 6–8); (3) weak coupling and strong friction (Figs. 9–11); (4) strong coupling and strong friction (Figs. 12–14).

Figure 3 shows the time evolution of the W_{ee} and $W_{e'e'}$ wave packets for a weak nonadiabatic coupling and weak friction. A Gaussian wave packet centered at $r = -9$ and $p = 0$ is created in the e state at time $\tau = 0$. At $\tau = 0.05 \text{ ps}$ [Fig. 3(a)], the wave packet in the e state moves in the positive coordinate direction. We observe a small wave packet in the e' state at about the same position as the e state wave packet. The wave packet in the e state then reaches [Fig. 3(b)] and passes [Fig. 3(c)] the curve crossing point ($r = -4.9$). Although we have used a coordinate independent nonadiabatic coupling, the transition mainly takes place in the vicinity of the curve crossing point, and the e' population suddenly increases when the e wave packet passes the crossing point [in Fig. 3(c)]. This is because of the $i[U_{ee}(r) - U_{e'e'}(r)]$ factor in the Liouville operator (20) for $W_{e'e'}$. As can be seen from Eq. (19), W_{ee} and $W_{e'e'}$ are highly oscillatory functions of time at positions far from the curve crossing point, where the phase $i[U_{ee}(r) - U_{e'e'}(r)]$ is large. Thus, $W_{e'e'}$ can be large only near the crossing point, where the phase is small. After passing the crossing point, the transferred wave packet starts to move in the e' state potential surface [Fig. 3(d)]. Since the frequency of the e' potential (333 cm^{-1}) is lower than that of the e state (1000 cm^{-1}); the wave packet centered at $r = 0$ is broadened. In Fig. 3(e), we observe a second wave packet in the e' state, centered at the same position of the wave packet in the e state ($r = 8$). Each time the e state wave packet passes through the curve crossing point, a small wave packet

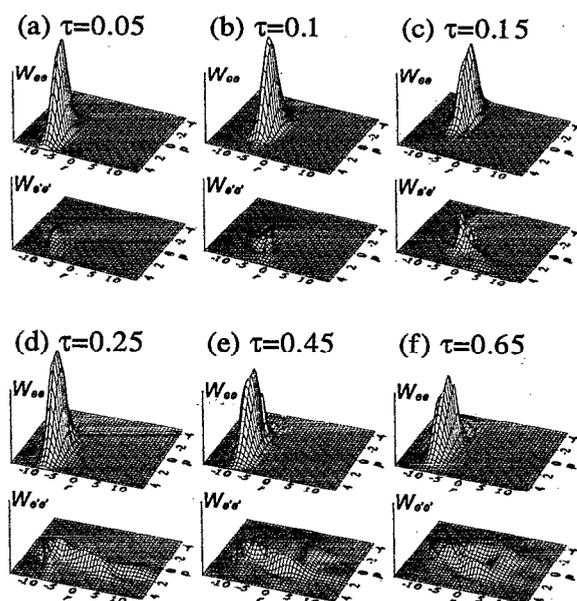


FIG. 3. The time evolution of the wave packet of the e and e' states for a weak nonadiabatic coupling ($\Delta=300\text{ cm}^{-1}$) and weak friction ($\zeta=25\text{ cm}^{-1}$).

is formed in the e' state, and we thus observe three wave packets moving in the e' state in Fig. 3(f).

To gain further insight into the nonadiabatic transition mechanism, we plotted K_{ee} and $K_{e'e'}$ in Fig. 4. The magnitude of K_{ee} gives the differential flux (per unit volume in phase space) from e to e' (and $K_{e'e'}$ for the reverse processes). At time $t=0.05\text{ ps}$ [Fig. 4(a)], the transition is from e to e' and the reverse flux is negligible since the e' population [$W_{e'e'}$ in Fig. 3(a)] is very small. When the e wave packet approaches the curve crossing point [Figs. 4(b) and 4(d)], K_{ee} grows in the vicinity of the curve crossing position, where the nonadiabatic transition takes place. $K_{e'e'}$ also shows a small peak in Figs. 4(b) and 4(c), reflecting the reverse transition. Since K_{ee} and $K_{e'e'}$ are coupled to W_{ee} and $W_{e'e'}$, their shape depends strongly on the profiles and magnitudes of W_{ee} and $W_{e'e'}$. Thus, we expect to observe a peak in K_{ee} at the same position where W_{ee} is peaked. In addition to this peak corresponding to the W_{ee} wave packet, we see a small peak at the crossing point in Figs. 4(d)–4(f). Since the $W_{e'e'}$ wave packet is broadened, we cannot observe a clear peak in $K_{e'e'}$ in Figs. 4(d)–4(f) as we observed in K_{ee} , and instead we see a small peak at the curve crossing point. To highlight the region where the nonadiabatic coupling takes place, we need to eliminate the influence of W_{ee} or $W_{e'e'}$. This will be done at the end of this section for different nonadiabatic coupling and damping rates.

The pump–probe spectra corresponding to Figs. 3 and 4 are displayed in Fig. 5. Here, we set $\Delta\omega_2 \equiv \omega_2 - \omega_{e'f}$. The motion of the e' wave packet is observed as a shift of the absorption peak. It is, however, difficult to separate the peaks corresponding to the second and the third wave packets observed in Figs. 3(d)–3(f) from the first peak in Fig. 5 since the spectrum only reflects the $W_{e'e'}$ wave packet in the co-

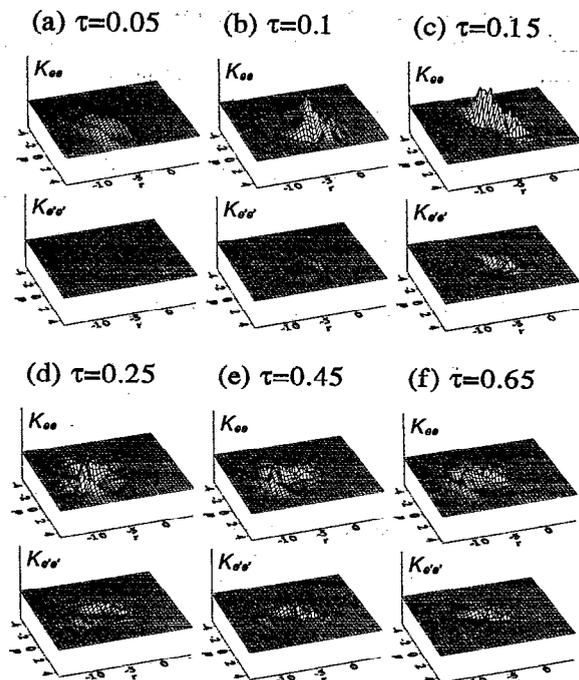


FIG. 4. The time evolution of the nonadiabatic transition flux density in phase space from e to e' and from e' to e for the system of Fig. 3.

ordinate space, whereas Fig. 5 contains information on the coordinate as well as the momentum. The phase space distribution thus provides a useful means for analyzing the spectrum.

We next consider a strong nonadiabatic coupling and weak damping. Figure 6 shows the time evolution of W_{ee} and $W_{e'e'}$. In Fig. 6(a), the e wave packets move initially in the e potential surface. Due to the strong constant nonadiabatic coupling, we already observe the e' wave packet at this early time. Once the e wave packet reaches the curve crossing point, most of it transfers to the e' state. The population of W_{ee} then decreases, whereas $W_{e'e'}$ increases [Fig. 6(b) and 6(c)]. The transferred wave packet in the e' state then moves in the e' potential surface [Fig. 6(d) and 6(e)]. Since

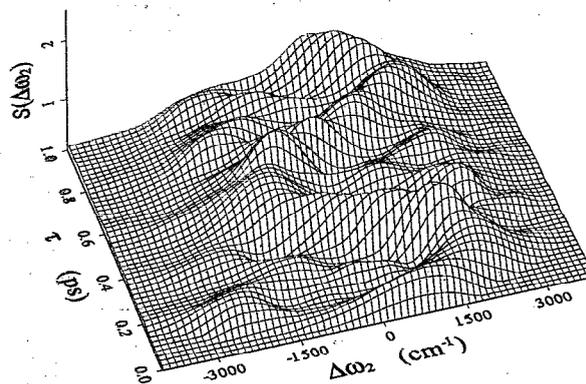


FIG. 5. The impulsive pump–probe spectrum for the system of Fig. 3.

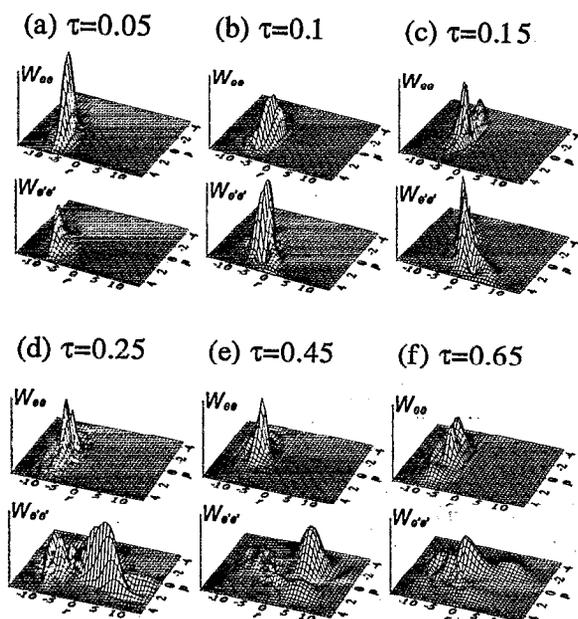


FIG. 6. The time evolution of the wave packets for a strong nonadiabatic coupling ($\Delta=1000 \text{ cm}^{-1}$) and weak friction ($\zeta=25 \text{ cm}^{-1}$).

most of the e wave packet is transferred to e' when it passes the curve crossing point, then the second and the third wave packets of $W_{e'e'}$, appearing in Figs. 3(d) and 3(e) are hardly observed in Figs. 6(d) and 6(e). In Fig. 6(f), the e' wave

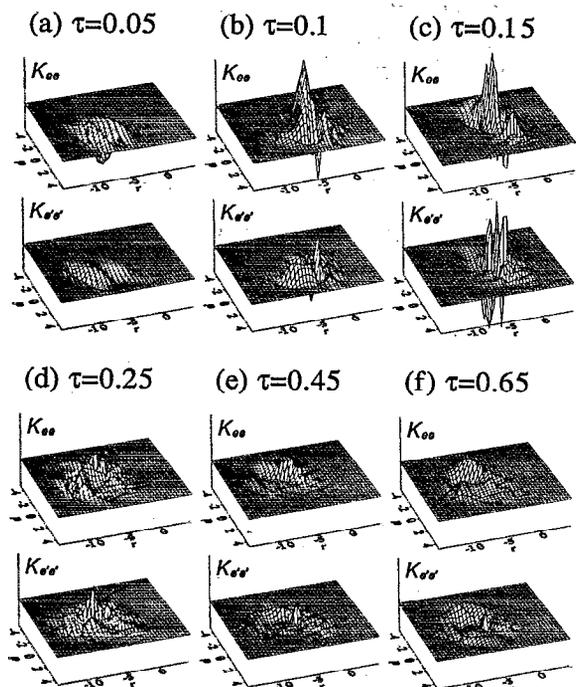


FIG. 7. The time evolution of the nonadiabatic transition flux density in phase space for the system of Fig. 6.

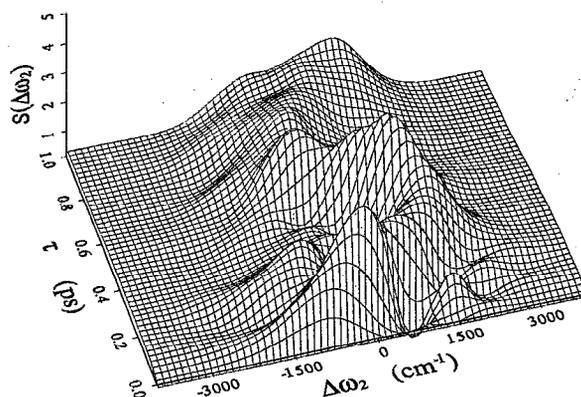


FIG. 8. The impulsive pump-probe spectrum for the system of Fig. 6.

packet again reaches the curve crossing point and it recrosses to the e state. The differential fluxes K_{ee} and $K_{e'e'}$ are plotted in Fig. 7. In Figs. 7(a)–7(d), the peaks in K_{ee} and $K_{e'e'}$ are higher than those in Fig. 6 corresponding to the stronger nonadiabatic coupling, but overall the wave packets are similar. This indicates that the coordinate dependence of the nonadiabatic process does not vary strongly with the nonadiabatic coupling strength. However, the shapes of K_{ee} [Figs. 7(e) and 7(f)] are quite different from those in Fig. 4, since W_{ee} is strongly perturbed. The corresponding pump-probe spectra are given in Fig. 8, where the e' wave packet is clearly observed. Since it recrosses to e at $\tau=0.7$ ps, the height of the peak decreases at this time.

We next consider the time evolution for strong damping and a weak nonadiabatic coupling. Since the motion is now considerably slower, we display the wave packets only at times $t=0.15, 0.25,$ and 0.45 ps. Due to the strong damping; the e wave packet quickly relaxes to the bottom of the potential, resulting in a Gaussian peak centered at $r=7$ and $p=0$ [Fig. 9(a)]. Since the shape of W_{ee} is equilibrated after it reaches the bottom of the e potential, the transition from e to e' does not show an oscillatory motion as observed in the weak damping case [Figs. 9(b) and 9(c)]. The transition between e and e' occurs near the crossing point ($r=-4.9$) and

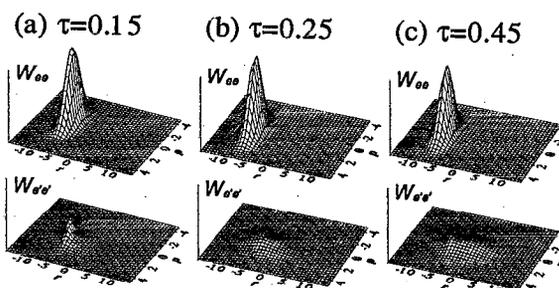


FIG. 9. The time evolution of the wave packets for a weak nonadiabatic coupling ($\Delta=300 \text{ cm}^{-1}$) and strong friction ($\zeta=500 \text{ cm}^{-1}$).

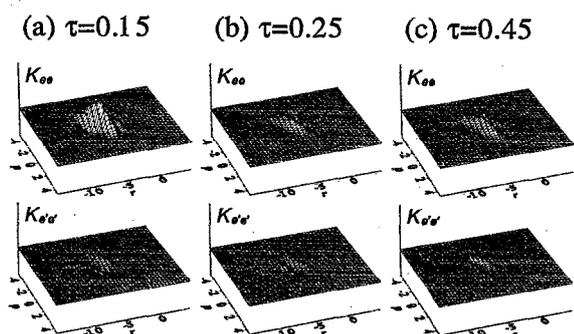


FIG. 10. The time evolution of the nonadiabatic transition flux density in phase space for the system of Fig. 9.

we observe the wave packet in the e' state [Fig. 9(a)]. The shape of W_{ee} is stationary and it acts as a source for the e' state. The transferred wave packet then relaxes toward the minimum of the e' state potential $r=0$ [Figs. 9(b) and 9(c)]. K_{ee} and $K_{e'e'}$ are shown in Fig. 10. We observe a peak near the crossing point ($r=-4.9$). The shape of the distribution depends, however, on both coordinate and momentum. As can be seen from Fig. 10, the nonadiabatic transition can take place far from the crossing point if the momentum is large. The corresponding pump-probe spectrum is shown Fig. 11. We observe a slowly shifting peak corresponding to the motion of the wave packet transferred to e' from e .

Figure 12 shows the time evolution of the wave packet for strong damping and strong nonadiabatic coupling. In this case, the magnitude of the e' wave packet quickly decreases compared with the weak nonadiabatic coupling case [Figs. 12(a)–12(c)]. The spatial dependence of the nonadiabatic transition, however, does not seem to change, and the shape of $W_{e'e'}$ is similar to that of Fig. 9. This similarity is confirmed by plotting K_{ee} and $K_{e'e'}$ (Fig. 13) and comparing with Fig. 10. This indicates that the geometry of the nonadiabatic coupling is not affected by the damping strength. The pump-probe spectrum is shown in Fig. 14. The shape of the spectrum is similar to Fig. 11, except for the very early

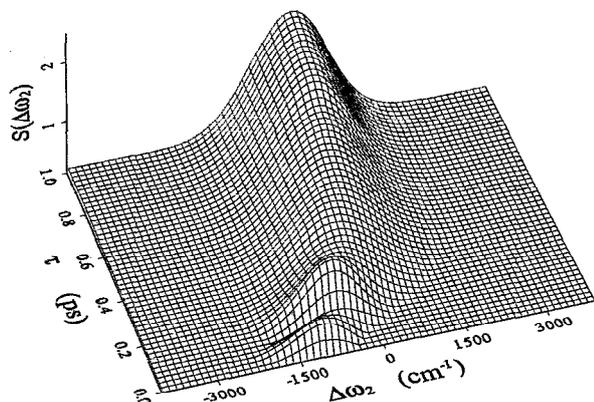


FIG. 11. The impulsive pump-probe spectrum for the system of Fig. 9.

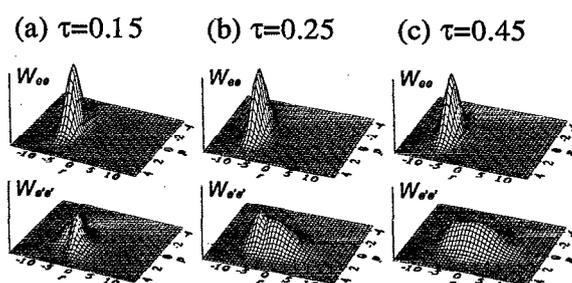


FIG. 12. The time evolution of the wave packets for a strong nonadiabatic coupling ($\Delta=1000 \text{ cm}^{-1}$) and strong friction ($\zeta=500 \text{ cm}^{-1}$).

time, where a large portion of the wave packet is transferred to e' because of the strong nonadiabatic coupling.

We have also followed the time evolution of the spectrally integrated probe absorption as a function of the damping and nonadiabatic coupling strength

$$I(\tau) = \int_{-\infty}^{\infty} d\Delta \omega_2 S(\Delta \omega_2; \tau), \quad (30)$$

where τ is the time delay between the pump and the probe.

Figure 15 shows $I(\tau)$ for a weak nonadiabatic coupling. All curves are oscillating with period $T=0.18 \text{ ps}$ corresponding to the e state vibration. These oscillatory features disappear at long time due to the damping. The change in spectral intensity reflects the transition rate between e and e' . It is small for weak damping ($\zeta=25$) and it increases at larger damping $\zeta=100$. It decreases again, however, if ζ becomes very large. This is reminiscent of the activation and diffusion regimes of chemical reactions.⁴³

The strong nonadiabatic coupling case is displayed in Fig. 16. Here, we observe a decreased intensity at $t=0.7$ for weak damping $\zeta=25$ and 100 corresponding to the recrossing from e' to e . The activation and diffusion regime-like features observed in Fig. 15 do not show up here because the changes of population due to wave packets switching back and forth between e and e' are very large.

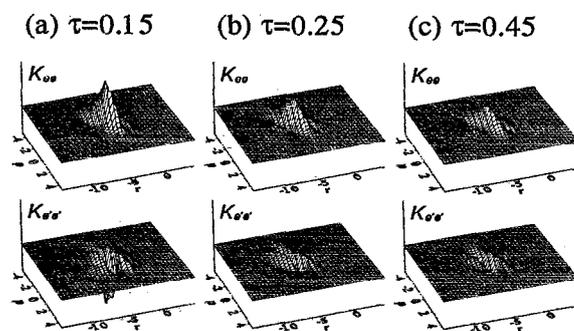


FIG. 13. The time evolution of the nonadiabatic transition flux density in phase space for the system of Fig. 12.

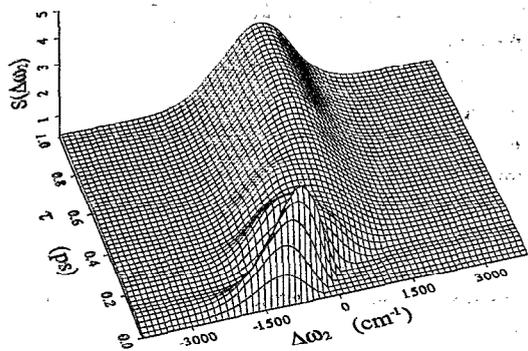


FIG. 14. The impulsive pump-probe spectrum for the system of Fig. 12.

The distribution of the differential fluxes K_{ee} and $K_{e'e'}$ in phase space reflects the time evolution of the populations W_{ee} or W_{gg} , as well as the intrinsic curve crossing rate. In order to separate these effects (approximately) and focus solely on the intrinsic rate, we found it helpful to define the following normalized fluxes:

$$\bar{K}_{ee}(p,r) = \int_0^T d\tau K_{ee}(p,r;\tau) / \int_0^T d\tau W_{ee}(p,r;\tau),$$

$$\bar{K}_{e'e'}(p,r) = \int_0^T d\tau K_{e'e'}(p,r;\tau) / \int_0^T d\tau W_{e'e'}(p,r;\tau). \tag{31}$$

Here, T is an averaging time taken to be $T=1$ ps. Figure 17 shows $\bar{K}_{ee}(p,r)$ and $\bar{K}_{e'e'}(p,r)$ for the previous four cases (Figs. 3–14). $\bar{K}_{ee}(p,r)$ in Fig. 17(a) is peaked around $r=-4$ and $r=-10$, which coincide with the curve crossing points (see Fig. 2). For $\bar{K}_{e'e'}(p,r)$ of Fig. 17(a), we observe a ring-like structure in phase space. This can be rationalized using energy conservation. Consider a particle moving in the e' state which transfers from e at position r . Energy conservation implies that the particle should acquire a kinetic energy corresponding to the difference of the potential $U_{e'e'}(r) - U_{ee}(r)$. Thus, the momentum of the transferred e'

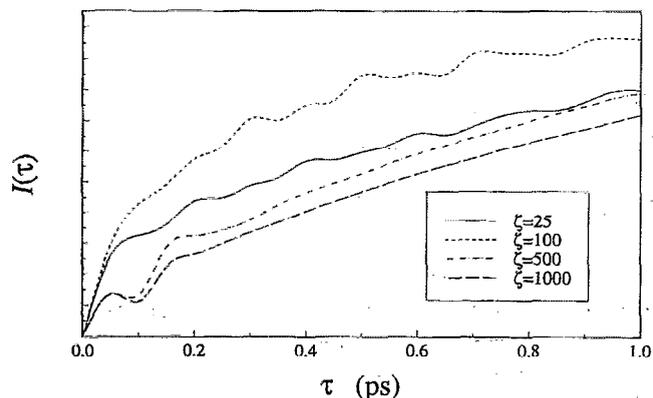


FIG. 15. The time evolution of the integrated probe absorption spectrum for a weak nonadiabatic case for different frictions.

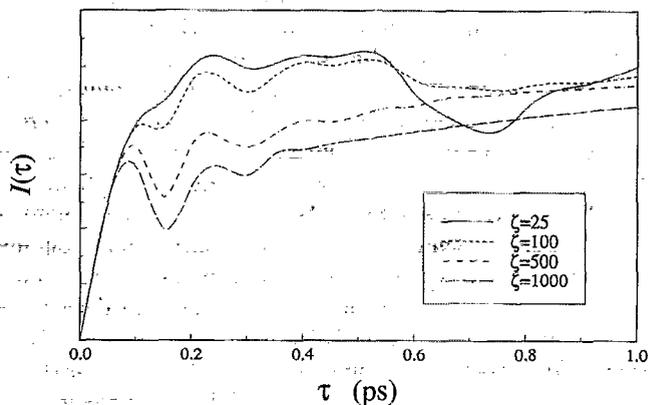


FIG. 16. The time evolution of the integrated probe absorption spectrum for a strong nonadiabatic case for different frictions.

particle must be larger than $\pm \sqrt{2M[U_{e'e'}(r) - U_{ee}(r)]}$. As seen from the inset of Fig. 2, the difference $U_{e'e'}(r) - U_{ee}(r)$ has the maximum at $r=-7.6$ and becomes negative at $r < -10$ and $-5.2 < r$, and thus the distribution of $\bar{K}_{e'e'}(p,r)$ shows a ring-like structure. In Fig. 17(b), the peaks are higher than those in Fig. 17(a) because of the strong nonadiabatic coupling. The shape of the peaks

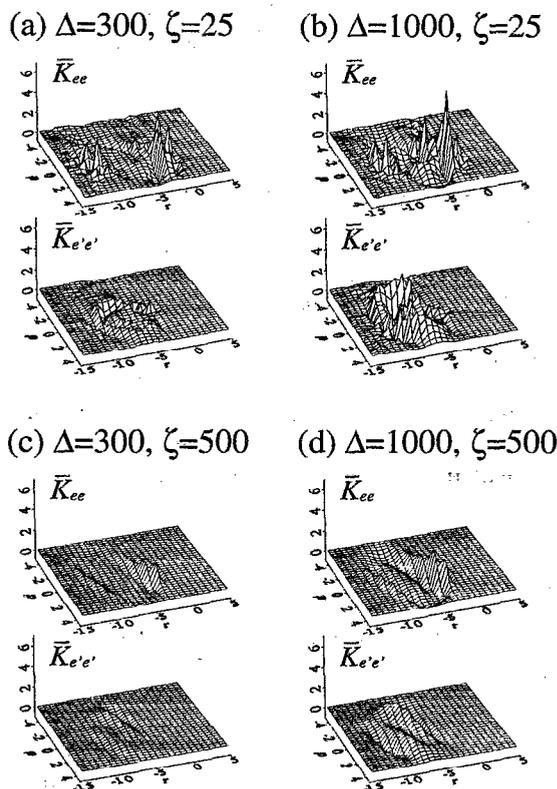


FIG. 17. Normalized fluxes for different nonadiabatic couplings and frictions.

is more complicated than those in Fig. 17(a), since the wave packets W_{ee} and W_{gg} have substantially changed.

Figures 17(c) and 17(d) show the normalized fluxes for the strong damping cases. Since W_{ee} and W_{gg} quickly lose their momentum and are equilibrated, the shapes of $\bar{K}_{ee}(p, r)$ and $\bar{K}_{e'e'}(p, r)$ calculated from Eq. (31) are rather simple. In these figures, we see that the distribution of nonadiabatic coupling is a function both of the coordinate and the momentum. If the momentum is large, the nonadiabatic coupling can take place far from the curve crossing points $r = -5$ and $r = -10$. This shows that it is not sufficient to discuss the nonadiabatic transitions in the coordinate space and it is essential to consider the momentum as well. In the next section, we explore the possibility of developing molecular dynamics algorithms which make use of this observation.

V. APPLICATION OF NONADIABATIC GREEN'S FUNCTIONS TO MOLECULAR DYNAMICS SIMULATIONS

In the present paper, we calculated phase space wave packets by solving equations of motions. This approach correctly incorporates quantum coherence between the two electronic states (e and e'). However, it is difficult to apply such a scheme in molecular dynamics simulations, where particle motions are governed by classical or semiclassical kinetic equations. In this section, we explore the possible use of the present results to construct effective molecular dynamics algorithms.

By introducing Green's functions corresponding to electronic coherence,²⁴ we can rewrite the equations of motion (19) in the form

$$\begin{aligned} \frac{\partial}{\partial t} W_{ee}(P, R; t) = & -(L_{ee} - \Gamma) W_{ee}(P, R; t) - \int dP' \int dR' \int_0^t d\tau G_{e'e'}(P, R; P', R'; t - \tau) W_{ee}(P', R', \tau) \\ & + \int dP' \int dR' \int_0^t d\tau G_{e'e}^*(P, R; P', R'; t - \tau) W_{e'e'}(P', R', \tau), \end{aligned} \quad (32)$$

$$\begin{aligned} \frac{\partial}{\partial t} W_{e'e'}(P, R; t) = & -(L_{e'e'} - \Gamma) W_{e'e'}(P, R; t) - \int dP' \int dR' \int_0^t d\tau G_{e'e}(P, R; P', R'; t - \tau) W_{ee}(P', R', \tau) \\ & + \int dP' \int dR' \int_0^t d\tau G_{e'e}^*(P, R; P', R'; t - \tau) W_{e'e'}(P', R', \tau), \end{aligned}$$

where the Green's function is defined in phase space by

$$G_{e'e}(P, R; P', R'; t) = \langle P, R | \exp[-(L_{e'e} - \Gamma)t] | P', R' \rangle. \quad (33)$$

If the e and e' state potentials are harmonic, and have the same frequency ($\omega_A = \omega_B$), we can evaluate the Green's function analytically. The result can be expressed as

$$\begin{aligned} G_{e'e}(P, R; P', R'; t) = & \frac{1}{(2\pi\hbar)^2} \int dx \int dx' \exp\left[\frac{i(Px + P'x')}{\hbar}\right] \\ & \times \exp\left[\frac{i}{\hbar} \Sigma_t(x, R, t; x', R'; 0)\right], \end{aligned} \quad (34)$$

where Σ_t is the high temperature ($\beta\hbar\omega_A \ll 1$) and the Ohmic dissipation [$\gamma(\omega) = \zeta$] limit of the functions Σ_t given in Appendix B of Ref. 8.⁴⁴

For general anharmonic potentials, we need to solve the equation of motion

$$\begin{aligned} \frac{\partial}{\partial t} G_{e'e}(P, R; P', R'; t) = & -(L_{e'e} - \Gamma) G_{e'e}(P, R; P', R'; t) \end{aligned} \quad (35)$$

with the initial condition

$$G_{e'e}(P, R; P', R'; 0) = \delta(P - P') \delta(R - R'). \quad (36)$$

In principle, once we obtain the Green's functions, we can solve the problem without considering explicitly the off-diagonal elements $W_{ee'}$. This formulation is, however, still not practical for molecular dynamics simulations since Eqs. (32) are integrodifferential equations and require W_{ee} or $W_{e'e'}$ at different times. We therefore approximate the equation of motion in the form

$$\begin{aligned}
\frac{\partial}{\partial t} W_{ee}(P,R;t) &= -(L_{ee} - \Gamma)W_{ee}(P,R;t) - \int dP' \int dR' \bar{G}_{e'e}(P,R;P',R')W_{ee}(P',R',t) \\
&\quad + \int dP' \int dR' \bar{G}_{e'e}^*(P,R;P',R')W_{e'e'}(P',R',t), \\
\frac{\partial}{\partial t} W_{e'e'}(P,R;t) &= -(L_{e'e'} - \Gamma)W_{e'e'}(P,R;t) + \int dP' \int dR' \bar{G}_{e'e}^*(P,R;P',R')W_{ee}(P',R',t) \\
&\quad - \int dP' \int dR' \bar{G}_{e'e}(P,R;P',R')W_{e'e'}(P',R',t),
\end{aligned} \tag{37}$$

where the time averaged Green's function is defined by

$$\bar{G}_{e'e}(P,R;P',R') \equiv \int_0^\infty d\tau G_{e'e}(P,R;P',R';\tau). \tag{38}$$

If the damping is strong, this approximation should work well, since G decays rapidly with time.³⁵⁻³⁷ Equation (37) suggests that not only the momentum, but also the position of the particle in the e state may change during the nonadiabatic transition. Tully and Preston proposed a molecular dynamics scheme for nonadiabatic transitions,³⁸ assuming that the position of the particle is the same before and the after the nonadiabatic transition. Equation (37) generalizes this procedure to include momentum changes as well. We can use the Green's function to determine the position and the momentum of the particle undergoing a nonadiabatic process. The particle is initially assumed to be in the e state. We can then calculate the dynamics of the particle using the following steps: (1) We use the Langevin equation which is equivalent to the classical Fokker-Planck equation

$$\ddot{R} + \zeta \dot{R} + \frac{d}{dR} U_{ee}(R) = f(t), \tag{39}$$

where the correlation of the noise is given by $\langle f(t')f(t) \rangle = \zeta \delta(t' - t)/\beta$. (2) While the particle is moving in the e state, its state changes from the position R' and the momentum P' in the e state to the position R and the momentum P in the e' state with hopping rate $\bar{G}_{e'e'}(P',R';P,R)$. The hopping process can be simulated using a Monte Carlo procedure. (3) Once the particle is in the e' state, we solve the corresponding Langevin equation in the e' state

$$\ddot{R} + \zeta \dot{R} + \frac{d}{dR} U_{e'e'}(R) = f(t). \tag{40}$$

(4) The hopping from e' to e can be calculated in a similar fashion. Once the particle returns to e , we then calculate its motion using Eq. (39). By repeating this procedure many times, we obtain the final distribution W_{ee} or $W_{e'e'}$.

One of the main problems in the simulation of nonadiabatic transitions in the gas phase is how to maintain conservation of energy. This has been traditionally a test for various approximations. In the presence of a bath that can induce

electronic dephasing as well as relaxation, conservation of energy is no longer a pressing issue since the system can exchange energy with the bath. We believe that constructing a computational algorithm for a few degrees of freedom in the gas phase is the most demanding and difficult objective, both conceptually and computationally. The separation of time scales which exists in the presence of fast dephasing in condensed phases simplifies the description enormously since it is equivalent to assuming that the coherences are in steady states with the populations. This is when a master equation (for populations only) is most useful.

In the limit of very fast dephasing, nuclear motions may be slow compared with the dephasing time and can be ignored. One can then use the classical Condon approximation in real space, and a fully classical description may hold. In the opposite extreme, an eigenstate representation may be more practical. It is for intermediate dephasing where the coordinate picture is useful yet we cannot quite make the static Condon approximation that the present scheme should become most adequate. This state of affairs is similar to the theoretical treatments of nonlinear optical spectroscopies^{8,42} which are formally identical to curve crossing problems where the electric field plays the role of the nonadiabatic coupling. In the absence of dephasing, spectra show sharp lines, a full quantum description is necessary, and reduced semiclassical descriptions usually fail (except for harmonic systems). In the other extreme of broad line shapes (fast dephasing), a static, fully classical, Condon description is appropriate. In the intermediate case, phenomena such as spectral diffusion and solvation effects may require a quantum formulation of the type presented here.

In conclusion, the multistate Fokker-Planck equation provides a powerful means for the study of nonadiabatic transitions in condensed phases. The present study had three main new points. First we generalized the conventional quantum Fokker-Planck equation to multistates system which can be applied to a system with anharmonic potentials and coordinate dependent nonadiabatic couplings. Second, we presented a rigorous procedure for calculating the pump-probe spectrum. Third, using the Green's functions of the multistate Fokker-Planck equation, we explored possible algorithms for molecular dynamics simulations. Our numerical results demonstrate the interplay of the nonadiabatic coupling and electronic dephasing processes in curve crossing.

ACKNOWLEDGMENTS

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APPENDIX A: THE MULTISTATES FOKKER-PLANCK EQUATION FOR A GAUSSIAN-MARKOVIAN BATH

We assume an Ohmic dissipation with the Lorentzian cutoff³¹

$$J(\omega) = \frac{M\zeta}{2\pi} \frac{\omega\gamma^2}{\gamma^2 + \omega^2} \quad (\text{A1})$$

In this case, one can obtain the equation of motion in the hierarchy form by generalizing procedure introduced by Tanimura and Wolynes.³² For the n th member of hierarchy W_{jk}^n , where j and k represent nonadiabatic states, the equation of motion is expressed as

$$\begin{aligned} \frac{\partial}{\partial t} W_{jk}^n(P, R; t) = & -\frac{P}{M} \frac{\partial}{\partial R} W_{jk}^n(P, R; t) - \frac{1}{\hbar} \int \frac{dP'}{2\pi\hbar} \sum_m [X_{jm}(P-P', R; t) W_{mk}^n(P', R; t) + X_{mk}^*(P-P', R) W_{jm}^n(P', R; t)] \\ & + \frac{\partial}{\partial P} W_{jk}^{n+1}(P, R; t) + n\zeta\gamma \left(P + \frac{M}{\beta} \frac{\partial}{\partial P} \right) W_{jk}^{n-1}(P, R; t). \end{aligned} \quad (\text{A2})$$

The hierarchy elements W_{jk}^n are defined by using the path integral. The equation of motion is derived by performing a time derivative of these hierarchy elements. Physically, one can think of this hierarchy of equations as dealing with a set of Wigner functions, modeling the states of the system with various numbers of phonons excited in the bath. We shall be interested only in the zeroth member of the hierarchy W_{jk}^0 which is identical to W_{jk} defined in Eq. (12). The other elements $n \neq 0$ are introduced for computational purposes. For deep hierarchy $N\gamma \gg \omega_c$, where ω_c is the characteristic frequency of the system such as the frequency of the harmonic potential, the above hierarchy can be terminated by

$$\begin{aligned} \frac{\partial}{\partial t} W_{jk}^N(P, R; t) = & -\frac{P}{M} \frac{\partial}{\partial R} W_{jk}^N(P, R; t) - \frac{1}{\hbar} \int \frac{dP'}{2\pi\hbar} \sum_m [X_{jm}(P-P', R; t) W_{mk}^N(P', R; t) + X_{mk}^*(P-P', R) W_{jm}^N(P', R; t)] \\ & + \Gamma W_{jk}^N(P, R; t) + N\zeta\gamma \left(P + \frac{M}{\beta} \frac{\partial}{\partial P} \right) W_{jk}^{N-1}(P, R; t). \end{aligned} \quad (\text{A3})$$

Using this hierarchical structure, we may deal with strong system-bath interactions. In the white noise limit $\gamma \gg \omega_c$, we may terminate the hierarchy of Eqs. (A2) and (A3) by setting $N=0$, obtaining Eq. (12). Since we have assumed $\beta\hbar\gamma \ll 1$, the temperature requirement of the Gaussian-Markovian case [Eqs. (A2) and (A3)] is less stringent than the Gaussian-white case [Eq. (18)].

APPENDIX B: A SEMICLASSICAL APPROXIMATION FOR THE MULTISTATE QUANTUM FOKKER-PLANCK EQUATION

By taking the classical $\hbar \rightarrow 0$ limit of Eq. (12), we obtain the multistate Fokker-Planck equation in the semiclassical form

$$\begin{aligned} \frac{\partial}{\partial t} W_{jk}(P, R; t) = & - \left\{ \frac{P}{M} \frac{\partial}{\partial R} - \frac{1}{2} \left[\frac{\partial U_{jj}(R)}{\partial R} + \frac{\partial U_{kk}(R)}{\partial R} \right] \frac{\partial}{\partial P} - \Gamma \right\} \\ & \times W_{jk}(P, R; t) - \frac{i}{\hbar} \sum_m [U_{jm}(R) W_{mk}(P, R; t) \\ & - U_{mk}(R) W_{jm}(P, R; t)]. \end{aligned} \quad (\text{B1})$$

This equation is exact if the potentials U_{jj} are the harmonic.

Note that a fully classical limit for the multistate system does not exist since the discrete electronic states are intrinsically quantum. Therefore, the present equation still contains the Planck constant.

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