Generalized Redfield Theory and Its Application to Transient Absorption Spectroscopies of Molecules in Condensed Phases

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We present a method of implementing the generalized Redfield theory on the calculation of femtosecond transient absorption spectrum of molecular systems in condensed phases. Numerical demonstration is carried out in a model Brownian molecular system involving two Morse potential surfaces. Intramolecular vibrational relaxation, its relation to the spectral density, its spectroscopic signature, and the temperature effect are analyzed.

I. INTRODUCTION

Molecular dynamics in dissipative media is the center of interest in quantum statistical mechanics. The key quantity is the reduced system density operator $\rho(t)$, whose time evolution can be symbolically described by the Liouville-von Neumann equation,

$$\dot{\rho} = -\frac{i}{\hbar}[H,\rho] - \mathcal{R}\rho \tag{1}$$

Unlike the Schrödinger equation, there are several nonequivalent forms of Liouville-von Neumann equation, resulting from different reduction or approximation schemes. Furthermore, in the presence of a time-dependent external field, the interplay between time-dependent coherent driving and dissipation may introduce a dramatic cooperative effect. It has been demonstrated in the case of quantum stochastic resonance in which the weak field response theory breaks down no matter how weak the periodic driving force is.[1-4] The combined effect of dissipation and external driving is most naturally incorporated in the Feynman-Vernon's path-integral formalism.[5] Here, in particular the development of iterative propagation schemes has opened the possibility to the exact treatment of the system-bath interaction in the non-Markovian regime.[6] An alternative approach to the theoretical formulation of the correlated effect of driving and dissipation is to establish equations of motion for the reduced density operator and a set of auxiliary dissipation operators.[7-10] The number of coupled operator equations is usually of the order of 50 for molecular systems at room temperature. Both the iterative path-integral formulation[6] and the coupled equations of motion approach[7-10] are computational expensive, especially when further implementations are made to nonlinear spectroscopies of real molecular systems.

Fortunately, in most femtosecond spectroscopic measurements, the external light field is either fast compared with the dissipation dynamics, or weak and operated far from the cooperative driving-dissipation regime. In this case, the cooperative driving-dissipation effect may be neglected, resulting in a simplified or field-independent dissipative superoperator $\mathcal{R}$ in the Liouville-von Neumann equation, eq 1. In this work, we shall apply a unified Redfield-Fokker-Planck prescription of the Liouville-von Neumann equation[11] to study transient absorption spectroscopies of a model molecular system in condensed phases. In Sec. II, we outline the unified Quantum Dissipation Theory (QDT) in which the field-independent dissipation superoperator $\mathcal{R}$ is expressed in terms of dissipative mode through which the system-bath interaction occurs. The key step is to introduce a so-called spectrum conjugation to the dissipative mode, thus the properties of detailed-balance and translational invariance are satisfied. Both the dissipative mode and its spectrum conjugation are ordinary operators of the reduced system. The final formulation of QDT relates further to the bath interaction spectral density, which also defines the dissipation rate. In Sec. III, the unified QDT is exploited to formulate further the transient absorption spectroscopies of a molecular system involving two adiabatic surfaces. Numerical application is made in Sec. IV for a one-dimensional two-Morse-surface molecular model involving energy relaxation. Finally, we summarize and conclude in Sec. V.

II. UNIFIED REDFIELD-FOKKER-PLANCK QUANTUM DISSIPATION THEORY

Consider a molecular system embedded in a dissipative medium (bath). The total system-bath Hamiltonian in a stochastic description assumes the form: $H_T = H + H_{SB}(t)$.

Here, H denotes the renormalized molecular Hamiltonian that is deterministic in nature, and $H_{SB}(t)$ describes the stochastic system-bath interaction and is assumed to be of the form

$$H_{SB}(t) = -\hbar Q F(t) \tag{2}$$

In this equation, Q is a Hermitian operator in the reduced system space, while $F(t)$ is a Hermitian operator in the stochastic bath space. In the following we shall term the reduced system operator Q as a *dissipative mode*. It determines the nature of dissipation such as relaxation and dephasing in either nuclear or electronic degrees of freedom. In general, the right-hand-side (r.h.s.) of eq 2 should include a summation over all types of dissipative modes. We shall be interested in the case in which all dissipation modes $\{Q_\alpha\}$ are statistically independent; that is that $\langle F_\alpha(t)F_{\alpha'}(\tau)\rangle \propto \delta_{\alpha\alpha'}$. In this case, the contribution from each dissipative mode to the final formulation of dissipative superoperator is additive: $\mathcal{R} = \sum_\alpha \mathcal{R}_\alpha$. For simplicity, we shall hereafter omit the subscript and focus on the contribution of an individual dissipative mode.

In the weak system-bath interaction regime, the effect of bath on the dynamics of reduced system completely describes the stationary force-force correlation function, or its Fourier transform.[12]

$$C(\omega) \equiv 2\,\mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\langle F(t)F(0)\rangle \tag{3}$$

Here, the zero-point energy of the reduced system is chosen such that $\langle F(t)\rangle = 0$. Note that F is an operator and its time correlation function is generally complex. Its spectrum $C(\omega) \geq 0$ is however positive and satisfies the detailed-balance relation.[12] In the widely used independent harmonic bath model, F represents a collective (macroscopic) bath mode.[12]

$$F = \sum_j c_j x_j \tag{4}$$

In eq 4, x_j is the dimensionless coordinate of the j^{th} microscopic harmonic bath mode with frequency ω_j. The spectral density for the system-bath interaction at a given dissipative mode is defined by[12]

$$J(\omega) \equiv \frac{\pi}{2}\sum_j |c_j|^2\delta(\omega - \omega_j); \qquad \omega \geq 0 \tag{5}$$

Physically, the spectral density of a harmonic bath, with $J(0) = 0$, is only defined in the positive frequency region. Its formal definition can however be extended, without loss of generality, to the negative frequency region via $J(-\omega) = -J(\omega)$. The bath interaction spectrum $C(\omega)$ (eq 3), together with its positivity and the detailed-balance properties, can thus be conveniently expressed in terms of the spectral density as follows.[12]

$$C(\omega) \equiv e^{\beta\omega/2}S(\omega) \equiv e^{\beta\omega/2}J(\omega)/\sinh(\beta\omega/2) \tag{6}$$

Here, $\beta \equiv \hbar/(k_BT)$ is the inverse temperature. $S(\omega)$ defined in eq 6 is the detailed-balance symmetrized bath spectrum; $S(-\omega) = S(\omega)$.

We have recently shown that the commonly used Redfield theory can be conveniently presented as[11]

$$\dot\rho(t) = -\frac{i}{\hbar}[H,\rho(t)] - \frac{1}{2}[Q, \tilde Q\rho(t) - \rho(t)\tilde Q^\dagger] \tag{7}$$

with

$$\tilde Q \equiv C(-\mathcal{L})Q \tag{8}$$

Here, the Liouvillian $\mathcal{L}$ is defined as the commutator action of the reduced system Hamiltonian.

$$\mathcal{L} \equiv \hbar^{-1}[H, \cdots] \tag{9}$$

Thus, $C(-\mathcal{L})$ in eq 8 is a superoperator defined by the spectrum function $C(-\omega)$ with its frequency variable being replaced by the Liouvillian operator. The Hilbert-space operator $\tilde Q$ defined in eq 8 can thus be called the *spectrum conjugation* to the dissipative mode Q. The equivalence between eq 7 and the commonly used Redfield theory[13,14] can be easily proved by using the H-eigenenergy representation.[11] We have also showed[11,15] that eq 7 recovers a well-established generalized quantum Fokker-Planck equation for Brownian oscillators.[16] In this sense, eq 7 may be considered as a unified Redfield-Fokker-Planck prescription of quantum dissipation theory (QDT).

To conclude this section, let us point out two important physical properties implied in eq 7: it is obviously Hermitian and traceless, $\mathrm{Tr}\dot\rho = 0$, or conservation the total population. One is the detailed-balance relation in which the reduced density operator evolves asymptotically toward the canonical equilibrium of $\rho_{eq} \propto e^{-\beta H}$. This property in eq 7 can be proved by showing the following identity:

$$\tilde Q e^{-\beta H} = e^{-\beta H}\tilde Q^\dagger \tag{10}$$

This is a sufficient condition for the canonical equilibrium reduced density operator to be the stationary solution to eq 7. The proof of eq 10 can be proceeded by using the first identity of eq 6 to recast the spectrum conjugation (eq 8) as

$$\tilde Q = e^{-\beta\mathcal{L}/2}[S(-\mathcal{L})Q] \equiv e^{-\beta H/2}[S(-\mathcal{L})Q]e^{\beta H/2} \tag{11}$$

The second identity of the above equation was made by using the definition of $\mathcal{L}$, eq 9. As $S(-\omega) = S(\omega)$ is a symmetric function, the quantity in the square bracket in eq 11 remains as Hermitian. Equation 10 can then be proved by the direct substitution of eq 11.

Another important property of eq 7 can be stated as follows.[15] Two dissipative modes Q and $Q' = Q + r$ that differ only by a trivial real c-number describe the same dissipative dynamics. This property, referred to as the dissipative mode invariance, can be mathematically proved by noting that for an arbitrary real c-number r, its spectrum conjugation (cf. eq 8), $\tilde{r} \equiv C(-\mathcal{L})r = C(0)r$, remains real. Thus, $\tilde{r}\rho(t) - \rho(t)\tilde{r}^{\dagger} = 0$, and the dissipation superoperator associating with $Q' = Q + r$ is identical to that with Q (cf. eq 7). For the dissipative mode Q that is linearly proportional to the coordinate of the reduced system, the above property becomes the conventional translational invariance.

Finally, we shall point out eq 7 in general is not of the Lindblad positive semigroup form.[17] However, as we mentioned earlier, if there are multiple dissipative modes, the second term in eq 7 should be replaced by the sum of their individual contribution. In this case, it is possible for certain systems that eq 7 with multiple dissipative modes becomes the Lindblad positive semigroup form.[15] However, as was shown by Lindblad,[18] the resulting semigroup and detailed-balance preserving Liouville-von Neumann equation would have to violate the translational-invariance.

III. APPLICATION TO OPTICAL NONLINEAR SPECTROSCOPIES

In this section, we shall show how the QDT, eq 7, can be used in formulating the resonant nonlinear optical spectroscopies such as transient absorption of a molecular system involving two adiabatic electronic states. We shall reemphasize that eq 7 is only applicable to the case in which the cooperative effect of dissipation and time-dependent external driving can be neglected (cf. Sec. I). In this case, we may replace the Hamiltonian in the first term of eq 7 with the total system-field Hamiltonian, while retaining the field-free Hamiltonian in the second term, or eq 8, for dissipation. For the numerical efficiency in the calculation of transient probe absorption spectroscopies, we shall be interested in implementing the QDT formulation in the electronic rotating-wave-approximation (RWA) framework. Furthermore, we shall not propagate the reduced density wave packet with the total system-pump-probe Hamiltonian as it should be specified at each individual delay time. We shall also abandon the third-order nonlinear response function formulation for 4WM-spectroscopies,[19] as it requires the density operator be propagated in a three-dimensional time-grid.

There are two other approaches to the formulation of transient spectroscopies. Both of them assume the probe field is weak, while the pump field can be arbitrary. One approach to the weak probe absorption is via the pump-dressed response function[20,21] that depends on the material system and the pump field, but not on the probe field. The transient absorption spectroscopies with the weak probe field of an arbitrary pulse shape and carrier frequency can be easily obtained via a two-fold temporal convolution between the pump-dressed response function and the probe field amplitude profiles.[20,21] The pump-dressed response function is two-dimensional in the time-grid. The involved Liouville-space wave packet propagation is required at the grip points that are of the same time-increment Δt, which is usually about 1 fs for molecular systems with the RWA, in both dimensions. This is the main disadvantage of the pump-dressed response formulation. In order to further reduce the number of the time-grid points at which the reduced density wave packet should be evaluated, we present in the following an alternative formalism of transient absorption based on the weak probe polarization.

Consider a resonant optical measurement in a two-surface molecular system whose adiabatic Hamiltonians are given by H_g and H_e. In the electronic RWA, the molecular Hamiltonian in the presence of a coherent pump excitation field is given by[22]

$$H(t) = H - D_{-}E_p^{*}(t)e^{i\Delta\Omega_p t} - D_{+}E_p(t)e^{-i\Delta\Omega_p t} \quad (12)$$

with

$$H = |g\rangle H_g \langle g| + |e\rangle \left(H_e + \Delta\omega_{eg}\right) \langle e| \quad (13)$$

$$D_{+} = \mu|e\rangle\langle g|; \qquad D_{-} = \mu|g\rangle\langle e| \quad (14)$$

Here, H denotes the field-free Hamiltonian of the reduced system, and $D_{\pm}$ the electronic transition dipole. In eq 12, $E_p(t)$ is the slowly varying envelop of the pump field. $\Delta\Omega_p \equiv \Omega_p - \omega_r$ is the difference between the pump carrier frequency Ω_p and a reference frequency ω_r for implementing the electronic RWA, such that $|\Delta\Omega_p|$ is of the order of vibrational frequency. $\Delta\omega_{eg} = \omega_{eg} - \omega_r$ in eq 13 is defined similarly for the shifted potential minimum difference. The reduced density operator under the influence of both pump excitation and dissipation is then governed by

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H(t), \rho(t)] - \mathcal{R}\rho(t) \quad (15)$$

Here, the dissipation superoperator $\mathcal{R}$ is defined in the second term of eq 7 with the field-free molecular Hamiltonian

H only. Obviously, the correlation between driving and dissipation is neglected. This approximation is expected to be valid when the pump field is weak and its time scale is short compared with that of dissipation.

We now turn to the transient absorption signal detected by a weak probe field with the slowing varying complex envelope of $E_T(t)$ and the carrier frequency of Ω_T. We denote also that $\Delta\Omega_T \equiv \Omega_T - \omega_r$. The calculation of this signal requires propagating the following non-Hermitian density operator in the RWA for each delay time t_d for the reasons that will be stated soon.

$$\begin{aligned}\delta\dot{\rho}_+(t;t_d) = &-\frac{i}{\hbar}[\delta H_+(t), \rho(t+t_d)] \\ &-\frac{i}{\hbar}[H(t+t_d), \delta\rho_+(t;t_d)] \\ &-\mathcal{R}\delta\rho_+(t;t_d)\end{aligned} \qquad (16)$$

Here, $\delta H_+(t)$ represents the interaction with the weak detection (probe) field $E_T(t)$ at its forward wavevector $\mathbf{k}_T$-direction. That is that

$$\delta H_+(t) = -D_+ E_T(t) e^{-i\Delta\Omega_T t} \qquad (17)$$

The transient probe absorption signal is then given by

$$S(t_d) = -2\,\mathrm{Im}\int_{-\infty}^{\infty} dt\, E_T^*(t) e^{i\Delta\Omega_T t}\mathrm{Tr}[D_-\delta\rho_+(t;t_d)] \qquad (18)$$

Equations 12-18 constitute the final formulation to evaluate the transient weak probe absorption signals. The implementation of this formulation is as follows. Firstly, eq 15 is propagated in the one-dimensional time-grid whose duration covers the range of interested delay time. The time t-propagation of eq 16, which contains the previously calculated $\rho(t+t_d)$ in its inhomogeneous term (i.e., the first term in eq 16), is then carried out for each specified delay time t_d as a parameter. As can be seen from eq 18, t-propagation of eq 16 is required only for the duration of probe pulse, and with the propagation time-step Δt being the same as that in eq 15. However, the delay time t_d as a parameter in eq 16 can be chosen flexibly and sparsely only on the important values in the final transient signal $S(t_d)$ (eq 18). The price paid here, in comparison with the pump-dressed response function formulation,[20,21] is that the propagation of eq 16 should be carried out by using a specific form of $E_T(t)$ and value of Ω_T for the probe.

To conclude this section, let us briefly state the construction of the above transient weak probe absorption formulation. Physically, the term with a trace in eq 18 is the weak probe polarization at its forward wavevector $\mathbf{k}_T$-direction. Eq 18 is thus the well-known formulation of weak probe absorption.[19] The total reduced density operator $\rho_{pp}(t;t_d)$ in the presence of both the pump and the t_d-delayed probe field satisfies then the same equation of motion as eq 15 with $H(t)$ being replaced by $H(t+t_d)+\delta H_+(t)$. In constructing the formulation in this section, the contributions of ρ_{pp} to the zeroth-order and the first-order in the weak probe interaction δH_+ were denoted by ρ and $\delta\rho_+$, respectively. Eqs 15 and 16 were then obtained by applying the standard first-order perturbation theory to the equation of motion for ρ_{pp}.

IV. MODEL CALCULATION AND DISCUSSIONS

In this section, we shall apply the general formulations presented in the previous sections to the transient absorption spectroscopies of a model one-dimensional two-surface molecular system embedded in a bath. Both the ground $V_g(R)$ and the excited $V_e(R)$ potential energy surfaces are chosen to be Morse and their parameters are given in Table 1. The transition frequency between the two potential minima is $\omega_{eg} = 15769$ cm^{-1}. The reduced mass is chosen to be $m = 32$ amu.

A single dissipative mode proportional to the vibrational coordinate $Q \propto R$ that is mainly responsible for vibrational relaxation is used in the following calculation. The spectral density (eq 5) is chosen to be of the Ohmic form:

$$J(\omega) = \eta\omega\exp(-|\omega/\omega_c|) \qquad (19)$$

The cut-off frequency is set to be $\omega_c = 1000$ cm^{-1}. Note that the harmonic frequencies of the ground and the excited states are 303 and 180 cm^{-1}, respectively. We now turn to the parameter η in eq 19. By examining eqs 6-8, we conclude that η is a dimensionless dissipation parameter if the dissipative mode Q is chosen to be dimensionless. As we are interested mainly in the excited state dynamics, the dimensionless vibrational relaxation mode is chosen as

$$Q = (m\omega_0'/\hbar)^{1/2}R \qquad (20)$$

Here, ω_0' denotes the harmonic frequency of the molecular system on the excited Morse potential V_e surface. We shall further denote

Table 1. Parameters of Morse Potential Surfaces: $V(R) = D_0[1-e^{-\alpha(R-R_0)}]^2$

	D_0 (cm^{-1})	α (Å^{-1})	R_0 (Å)
V_g	12550	1.871	2.80
V_e	4381	1.876	3.02

$$\gamma \equiv J(\omega_0') \tag{21}$$

For a given value of γ, the parameter η in eq 19 is also specified. Physically, γ is however a more favorable parameter than η is. It can be shown that γ defined by eq 21 would represent the vibrational energy relaxation rate if the excited surface was harmonic.[11] In the following calculation, the inverse rate is set to be $\gamma^{-1} = 265$ fs.

The pump field is a 10-fs transform-limited Gaussian pulse with the carrier frequency of $\Omega_p = 16912$ cm^{-1} that amounts to the center of the Franck-Condon transition from the initial ground thermal equilibrium wave packet. The probe field is a 50-fs transform-limited Gaussian with the carrier frequency of $\Omega_T = 11200$ cm^{-1}, which is located at the center of the Franck-Condon transition from the excited wave packet in the outer turning point region, assuming there is no vibrational relaxation (see Fig. 1). The transient dipole μ is set to be constant (Condon approximation) and the intensity of pump field is chosen to achieve about 20% of total population being excited onto the excited potential surface. The intensity of the probe is chosen in the weak (linear) response regime.

Equations 15 and 16 are propagated sequentially in the energy eigenstate representation. In this representation, $\tilde{Q}_{ab} = C(\omega_{ba})Q_{ab}$ (cf. eq 8).

Fig. 2 shows the relaxation dynamics of the mean excess energy $\Delta E(t)$ (upper panel) and the mean displacement $\Delta R(t) \equiv \bar{R}(t) - \bar{R}_{eq}$ (lower panel) of the wave packet $\rho_{ee}(t)$ being pumped onto the excited potential surface. The bath temperature is T = 300 K. The excited wave packet $\rho_{ee}(t)$ generated by the 10-fs pump field experiences not only the coherent oscillatory motion but also energy relaxation, toward the thermal equilibrium state on the excited surface. The peaks/valleys of $\Delta R(t)$ (lower panel) denote the outer/inner turning points of the dissipative wave packet on the excited potential surface. Note that the vibrational energy relaxation (upper panel) is not of a simple exponential form. The present model in which the vibrational coordinate is taken to be the dissipative mode corresponds to a Brownian oscillator. In the classical picture of a Brownian oscillator, the effective frictional force on the system is proportional to the momentum, which is zero at the turning points. As a result, the vibrational energy relaxation curve (the upper panel of Fig. 2) exhibits plateaus at the turning point regions. Due to the anharmonic, the plateaus at the outer turning point regions, at which ΔR (cf the lower panel) are maxima, last longer than those around the inner turning points.

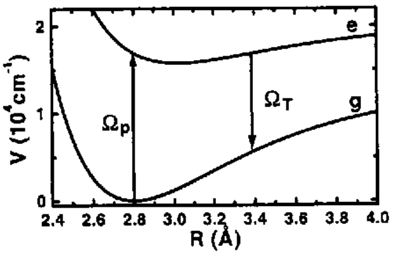

Fig. 1. Schematic diagram of pump-probe detection of molecular dynamics on the excited electronic surface.

As we mentioned earlier, the overall energy relaxation rate is given by the parameter γ (eq 21) that is independent of temperature. We have

$$\frac{\Delta E(t) - \Delta E_{eq}(T)}{\Delta E(0) - \Delta E_{eq}(T)} \approx e^{-\gamma t} \tag{22}$$

Here, $\Delta E_{eq}(T)$ is the thermal equilibrium energy of the wave packet on the excited electronic states at a given temperature.

Fig. 3 depicts the vibrational energy relaxation dynamics upon the same 10-fs pump excitation but at two specified temperatures. Included in this figure are also the simple exponential energy decay curves (dashed) assuming that eq 22 is an identity. Obviously, the parameter γ does represent the overall vibrational energy relaxation rate. Upon the excitation with the same pump field, the initial excess energy $\Delta E(0)$ at T = 100 K is lower than that at T = 300 K. This is due to the difference between the thermal equilibrium dis-

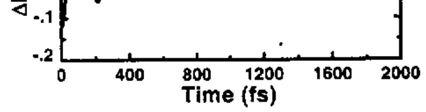

Fig. 2. Time evolution of the vibrational (excess) energy ΔE (upper panel) and the mean displacement $\Delta R \equiv \bar{R} - \bar{R}_{eq}$ (lower panel) of the wave packet being resonantly pumped by the 10-fs pulse onto the excited electronic surface. The overall energy relaxation rate is $\gamma^{-1} = 265$ fs.

tributions $\rho^g_{eq}(T)$ in the ground electronic state at two different temperatures prior to the pump excitation. On the other hand, the asymptotic excess energy $\Delta E(\infty) = \Delta E_{eq}(T)$ is the thermal equilibrium energy of $\rho^e_{eq}(T)$ in the excited electronic state.

Fig. 4 presents the transient absorption signals $S(t_d)$ with the same configuration of pump-probe pulse pair as specified earlier. The transient beating signal $S(t_d)$ at temperature T = 100 K is of higher strength in the first beat and weaker in others than each of those beats in the signal at temperature 300 K. This contrast feature can be understood from the thermal equilibrium distributions, the carrier frequencies of pump and probe pulses, and the underlying relaxation dynamics. Let us start with the initial thermal equilibrium density wave packet in the ground electronic state before the pump excitation. The initial thermal equilibrium distribution is more localized at T = 100 K than it is at 300 K, and therefore the former is more accessible than the latter by the resonant pumping processes. In fact, total populations being pumped onto the excited state surface are 22% at T = 100 K, and 20% at 300 K. The above picture also accounts for the relative heights of the first beats in the signals at the two temperatures shown in Fig. 4. If there was no dissipation, the quantum beats of the low temperature medium would remain stronger than those of the high temperature medium. The existence of vibrational relaxation leads the wave packet downward away from the probe detection window. Two factors contribute to the fact that the later signal beats stronger in T = 300 K than in 100 K. One is that the nonstationary excited wave packet in the case of T = 300 K is of higher mean excess energy than that in the lower temperature is (cf. Fig. 3). As a result, the former remains closer to the probe window than its low temperature counterpart. The second factor relates to the wave packet spreading (not shown) that increases the chance of the wave packet dynamics being observed at the fixed detection window.

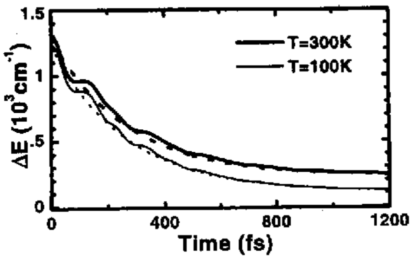

Fig. 3. Time evolution of the vibrational energy ΔE at two specified temperatures. Included in the dash curve is also the simple exponential decay (cf. eq 22) with the rate of γ^{-1} = 265 fs at each temperature.

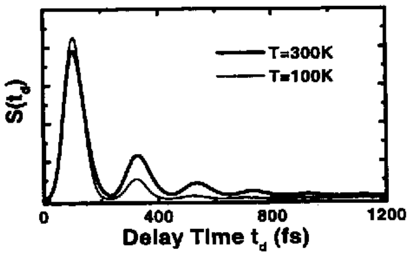

Fig. 4. Transient weak probe absorption signals (eqs 18 with 16) at two specified temperatures.

V. SUMMARY AND CONCLUSION

In summary, we presented a compact form of Redfield theory and further developed a methodology to implemented it to transient probe absorption spectroscopies. In the present formulation, quantum dissipation was presented in terms of bath interaction spectral density. Numerical demonstration was carried out in a model Brownian molecular system involving two Morse potential surfaces. Analyzed in detail were the intramolecular vibrational relaxation dynamics on the excited electronic surface, its spectroscopic signatures, and the temperature effect. Applications of the present formulation to molecular systems in the presence of electronic dephasing, vibrational relaxation and vibrational dephasing will be published elsewhere.

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Key Words

Quantum dissipation; Transient absorption; Vibrational relaxation.

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