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# Strong external field effects on electronic dephasing of molecular transitions in condensed media

M. Morillo

*Física Teórica, Universidad de Sevilla, Apartado de Correos 1065, Sevilla 41080, Spain
and Department of Chemistry and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824-1322*

R. I. Cukier

*Department of Chemistry and Center for Fundamental Materials Research, Michigan State University,
East Lansing, Michigan 48824-1322*

We discuss the effects of a strong external field on the optical transition between two electronic states of a solute immersed in a medium. The solute states may be weakly or quite strongly coupled to the medium. The electronic dephasing process is characterized via the power absorbed by the solute. The average absorbed power $\bar{\mathcal{P}}(t)$ for resonant, strong fields exhibits an oscillatory decay in time, reflecting the finite change in the population difference of the electronic states, and the dephasing arising from the coupling to the medium. The coefficients of $\bar{\mathcal{P}}(t)$ depend on the detuning from resonance as well as the coupling strength between the external field and the solute's transition dipole. Our method is nonperturbative in the external field strength and shows that the spectral line shapes can be systematically altered by the application of a strong external field. We also show that for strong but off-resonance fields, $\bar{\mathcal{P}}(t)$ returns to the linear response regime. © *1999 American Institute of Physics.* [S0021-9606(99)51816-3]

## I. INTRODUCTION

Optical spectroscopy of probe molecules (solutes) in condensed media (solvents) provides a wealth of information on the interaction between the solute and the solvent,[1–7] whether the solvent is a liquid,[8–10] a crystal,[3,11] a glass,[3,12] or a protein.[13,14] The broadening of the optical transition reflects the dephasing arising from the coupling of the solute to its many-degrees-of-freedom environment. Line shapes are particularly broad when the two states of the solute have quite different electronic structures, and there is substantial coupling of these differing charge distributions to the solvent. We shall refer to this dephasing mechanism as dissipation in the following, although it should be noted that it does not require nuclear motion. This is why the line shape for electronic dephasing can be quite broad.[2]

The original approaches to studying optical transitions were based on Linear Response Theory (LRT) (equivalently, Fermi's golden rule) and provide the material properties via the linear susceptibility. In the linear response regime there is a close connection between optical spectra (e.g., for inter-valence bands) and nonradiative (thermal) electron transfer rates,[15–17] as the information is contained in a spectral density (lineshape) that depends on the strength of the dissipation and the detuning of the transition frequency from the applied field frequency (the latter being zero for a thermal process). More recently, various forms of nonlinear spectroscopy have been developed. They are based on either perturbative expansions in the strength of the external field, involving nonlinear susceptibilities,[2,4,5] or on nonpertubative analysis of the density matrix.[18,19] We have recently studied the role of strong constant and time dependent external fields

on rates of thermal charge transfer reactions, at high[20,21] and low temperatures,[22] without relying on a perturbation expansion in the external field.

In a recent article,[23] we introduced a new nonperturbative approach to optical spectroscopy that relies on a strong, resonant external field to drive the system beyond the linear response regime. We shall refer to this spectroscopy as strong field spectroscopy (SFS). The coupling of the external field to the solute's transition dipole moment is sufficiently strong that it changes the solute's electronic-level population difference by a finite amount. The average power absorbed by the solute $\bar{\mathcal{P}}(t)$ is a function of time, and depends on the external field strength in a characteristic fashion. (The average is over the medium fluctuations.) This contrasts with a weak field, where the linear susceptibility is constant in time, and does not depend on the external field strength. We analyzed the time dependence of $\bar{\mathcal{P}}(t)$ for the case of weak coupling between the solute and the solvent, as it is amenable to an essentially analytic treatment. Weak coupling corresponds to the fast modulation regime introduced to linear spectroscopy by, e.g., Kubo.[24] It is defined in terms of the characteristic coupling strength $\Delta = \sqrt{2 E_r k_B T / \hbar^2}$, with $E_r$ the reorganization energy and $\tau_c$ the medium relaxation time. In the fast modulation regime $\Delta \tau_c < 1$. In this regime, simple expressions for the coefficients of the time dependent $\bar{\mathcal{P}}(t)$ could be obtained. These coefficients [cf. Eq. (28) below] are Lorentzian line shape functions with center frequencies shifted from the usual detuning between applied and transition frequencies by the strength of the external field solute coupling. The Lorentzian's widths reflect the strength of the dissipation appropriate to this fast modulation situation. The

dependence of these coefficients on the external field strength provides a potential method to manipulate the frequency regime for which the power absorbed will be maximal.

In this article, we develop our strong field, nonperturbative spectroscopy to be applicable to slow modulation, where $\Delta \tau_c > 1$. Examination of typical solute-solvent energetics indicates that the slow modulation regime is more likely to be obtained than the fast modulation regime in most condensed phase systems. We will show that while the resulting expression for $\bar{\mathcal{P}}(t)$ is numerically different than for fast modulation, the difference does not alter the conclusion that the power absorbed can be manipulated with strong external fields.

The above considerations pertain to resonant behavior, when the external field's frequency is tuned to induce maximum power absorption by the solute. Once off-resonance, the strong external field is not effective in inducing transitions in the solute. We will show how nonresonant SFS will then essentially return to the linear response regime.

The plan of the rest of this paper follows: In Sec. II we introduce a Hamiltonian appropriate to a two-state solute coupled to a solvent such that the solvent's equilibrium position may be significantly altered by the presence of the two solute charge distributions. A reduction to a stochastic set of equations of motion for the solute's density matrix is carried out, with the solvent providing a classical stochastic process as a high temperature approximation. In Sec. III we summarize our previous work on resonant SFS for fast modulation between the solute and solvent, and then analyze the nonresonant case to show how a form of linear response theory is obtained. The slow modulation case is discussed in Sec. IV. In Sec. V, we summarize our results and suggest future directions for this strong field spectroscopy.

## II. THE MODEL

A model Hamiltonian that can characterize electronic dephasing is:

$$\mathcal{H} = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( q_j - \frac{\gamma_j}{m_j \omega_j^2} \sigma_z \right)^2$$
$$- \frac{(\Delta G_0)}{2} \sigma_z + 2\hbar b(t) \sigma_x. \tag{1}$$

The solute has two electronic states denoted by the kets $|0\rangle$ and $|1\rangle$. The solvent is represented by independent harmonic oscillators whose origins depend substantially on the electronic state of the solute. These shifts reflect the differing interaction energies between the two charge distributions of the solute with the solvent. The $\sigma_i$ ($i = x, y, z$) are the Pauli spin operators. The external field-solute interaction energy is defined by $2\hbar b(t) = \langle 0|\hat{\mu}|1\rangle \cdot \mathbf{E}(t)$, where $\hat{\mu}$ is the solute's dipole moment operator and $\mathbf{E}(t)$ is the external field. The quantity $\Delta G_0$ is the standard free energy difference between reactants and products. The $m_j$'s and $\omega_j$'s are, respectively, the oscillator masses and frequencies, and the $\gamma_j$'s are the solute-solvent coupling constants. Notice that we are neglecting the tunnel splitting energy that could induce a ther-

mal electron transfer reaction, as we assume that it is much smaller than the term $2\hbar b(t)$ responsible for an optical transition.[15] (The formal similarity between optical spectroscopy for electronic dephasing and charge transfer reaction kinetics has often been exploited.[15,25,26,16]) Because the electronic dephasing is rapid on nuclear motion time scales, we neglect the effects of vibrational dephasing as well as vibrational population relaxation.

The reduction of Eq. (1) to a stochastic set of equations of motion can be carried out in a manner similar to the one we used to analyze charge transfer reactions.[27] Using the Heisenberg equation of motion for the operator $\mathcal{O}$,

$$i\hbar \dot{\mathcal{O}} = [\mathcal{O}, \mathcal{H}], \tag{2}$$

we obtain for the Pauli operators the equations

$$\dot{\sigma}_z(t) = 4b(t)\sigma_y(t),$$

$$\dot{\sigma}_y(t) = -4b(t)\sigma_z(t) - \frac{2}{\hbar} \sum_j \gamma_j q_j(t) \sigma_x(t)$$
$$- \frac{\Delta G_0}{\hbar} \sigma_x(t), \tag{3}$$

$$\dot{\sigma}_x(t) = \frac{2}{\hbar} \sum_j \gamma_j q_j(t) \sigma_y(t) + \frac{\Delta G_0}{\hbar} \sigma_y(t).$$

We will assume that the solute is initially in the ground electronic state $|0\rangle$ and that the temperature is high enough and the solvent frequencies low enough for the solvent degrees of freedom to be treated classically. Furthermore, we shall assume that the solvent *dynamics* is independent of the quantum state of the solute. This assumption will limit the applicability of our approach to solute-solvent couplings that are not too strong, as we shall discuss further below. The equations of motion for the solvent variables will be obtained from the Hamiltonian describing their interactions with the solute in its initial, ground state, namely,

$$\mathcal{H}_{\text{bath}}^0 = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( q_j - \frac{\gamma_j}{m_j \omega_j^2} \right)^2. \tag{4}$$

It then follows from Hamilton's equations that

$$\sum_j \gamma_j q_j(t) = \sum_j \gamma_j \left[ \left( q_j(0) - \frac{\gamma_h}{m_j \omega_j^2} \right) \cos \omega_j t + \frac{\gamma_j p_j(0)}{m_j \omega_j^2} \sin \omega_j t \right] + \sum_j \frac{\gamma_j^2}{m_j \omega_j^2}. \tag{5}$$

Note that the last term in the above expression is half the reorganization energy $E_r$. The reorganization energy is the difference between the solvent potential energy with the solute in state $|1\rangle$ and the solvent still in the equilibrium configuration for the state $|0\rangle$, and the equilibrium potential energy of the solvent with the solute in state $|1\rangle$. In other words, $E_r$ is

$$E_r = \mathcal{H}^0_{\text{bath}}\left(q_j = -\frac{\gamma_j}{m_j\omega_j^2}\right) - \mathcal{H}^0_{\text{bath}}\left(q_j = \frac{\gamma_j}{m_j\omega_j^2}\right)$$

$$= 2\sum_j \frac{\gamma_j^2}{m_j\omega_j^2}. \tag{6}$$

The equations of motion for the spin operators then can be written as

$$\dot{\sigma}_z(t) = 4b(t)\sigma_y(t),$$

$$\dot{\sigma}_y(t) = -4b(t)\sigma_z(t) - \frac{E_r + \Delta G_0}{\hbar}\sigma_x(t) - \eta(t)\sigma_x(t),$$
$$\tag{7}$$

$$\dot{\sigma}_x(t) = \frac{E_r + \Delta G_0}{\hbar}\sigma_y(t) + \eta(t)\sigma_y(t),$$

where

$$\eta(t) = \frac{2}{\hbar}\sum_j \gamma_j\left[\left(q_j(0) - \frac{\gamma_j}{m_j\omega_j^2}\right)\cos\omega_j t\right.$$
$$\left. + \frac{p_j(0)}{m_j\omega_j^2}\sin\omega_j t\right]. \tag{8}$$

In an optical transition, the solvent is initially at thermal equilibrium with respect to the initial electronic state. Thus an appropriate initial condition is given by the density operator

$$\rho_{\text{ini}} = \frac{1}{C}e^{-\beta\mathcal{H}^0_{\text{bath}}}|0\rangle\langle0|, \tag{9}$$

with $C$ the normalization constant. The average of Eq. (7) involves a trace over the spin(solute) and over the solvent variables. Defining $z(t) = \langle0|\sigma_z(t)|0\rangle$, $x(t) = \langle0|\sigma_x(t)|0\rangle$ and $y(t) = \langle0|\sigma_y(t)|0\rangle$, and carrying out the trace over the spin, provides the set of equations

$$\dot{z}(t) = 4b(t)y(t),$$

$$\dot{y}(t) = -4b(t)z(t) - (\omega_0 + \eta(t))x(t), \tag{10}$$

$$\dot{x}(t) = (\omega_0 + \eta(t))y(t),$$

where $\hbar\omega_0 = E_r + \Delta G^0$ is the energy difference in the optical transition. The function $\eta(t)$ depends upon the initial values of the solvent variables. The solvent variables are only known in terms of the probability law characterizing the conditional thermal equilibrium. The probability distribution of the solvent can be obtained by taking the trace over the spin operator in Eq. (9). Then, $\eta(t)$ is a Gaussian stochastic process with zero average and correlation function

$$\langle\eta(t)\eta(0)\rangle = K(t) = \frac{4k_BT}{\hbar^2}\sum_j \frac{\gamma_j^2}{m_j\omega_j^2}\cos\omega_j t, \tag{11}$$

where $\langle\cdots\rangle$ represents an average taken with the initial ensemble. The form of $K(t)$ depends upon the distribution of frequencies and coupling strengths $\gamma_j$. A useful model, corresponding to a Debye spectrum,[24,28,29] is

$$K(t) = \Delta^2 e^{-t/\tau_c}, \tag{12}$$

where $\Delta = \sqrt{2E_r k_B T/\hbar^2}$ characterizing the strength of the solute-solvent coupling, and $\tau_c$ characterizing the solvent's relaxation, as defined in Sec. I. This is the model that we will use here; more complex models can be introduced at the expense of a more numerically intensive calculation.

The equations of motion in Eq. (10) coincide with those obtained from the stochastic Hamiltonian,

$$\mathcal{H}_{\text{stoch}} = -\frac{\hbar}{2}(\omega_0 + \eta(t))\sigma_z + 2\hbar b(t)\sigma_x, \tag{13}$$

where the solvent dynamics is replaced by the classical stochastic process $\eta(t)$. This can be immediately seen by simply writing the density operator as a linear combination of Pauli operators

$$\sigma(t) = \tfrac{1}{2}[1 + x(t)\sigma_x + y(t)\sigma_y + z(t)\sigma_z]. \tag{14}$$

It is straightforward to verify that $z(t)$ represents the difference in population of the two electronic levels, while $x(t)$ is proportional to the electronic polarization. Inserting Eq. (14) into the Liouville equation results in the stochastic equations of motion for the time dependent coefficients $x(t)$, $y(t)$, $x(t)$. It should be pointed out that the above stochastic description relies on the consideration of the solvent variables as classical variables whose motion is not affected by the spin dynamics. Of course, the initial condition, where the solvent is equilibrated to the solute in state $|0\rangle$ is accounted for. The restriction to a solvent dynamics that is independent of the solute means that the reorganization energy cannot be too large. A quantitative measure of this restriction is that $E_r/\Delta\hbar < 1$.[30] Using the connection between $\Delta$ and $E_r$ given after Eq. (12) this means $\sqrt{E_r/2k_BT} < 1$ and limits reorganization energies to the scale of 100 cm$^{-1}$. For typical solvent relaxation times, $\tau_c$, there is still a wide range of parameter space where $\sqrt{E_r/2k_BT} < 1$ and the slow modulation condition of $\Delta\tau_c \gg 1$ is met. If $E_r$ is large compared to $\Delta$ then the buildup of quantum fluctuations during the dynamical evolution will be reflected in the solvent dynamics. There will be a complex coupling between the solvent and spin dynamics, and an analytic approach will be extremely challenging. We stress that the preceding connection between the mechanical Hamiltonian and the stochastic model is correct for small values of $b_0$, where the population $z(t)$ is hardly changing. It is when $z(t)$ is changing significantly and $E_r$ is large in the above sense that there can be a feedback from the solute to the solvent dynamics.

The instantaneous power absorbed by the solute from the external field is

$$\mathcal{P}(t) = \text{Tr}\,\rho(t)2\hbar\dot{b}(t)\sigma_x, \tag{15}$$

where the trace is over all the degrees of freedom. In the stochastic description, we insert $\sigma(t)$ as given by Eq. (14) into Eq. (15). Thus $\mathcal{P}(t)$ is a fluctuating quantity. Its average, $\bar{\mathcal{P}}(t)$, follows directly from Eqs. (14) and (15). Then,

$$\bar{\mathcal{P}}(t) = 2\hbar\dot{b}(t)\bar{x}(t), \tag{16}$$

where $\bar{x}(t)$ represents the stochastic average of $x(t)$. Thus our first task is to obtain appropriate expressions for the averages. This is done in the next section.

## III. EQUATIONS FOR THE AVERAGES

For weak external fields, appropriate to the linear response theory (LRT) regime, the distinction is made between fast and slow modulation on the basis of the quantity $\Delta \tau_c$ being small or large, respectively. These fast and slow modulation regimes lead to Lorentzian and Gaussian line shapes, respectively, as is well known in NMR and in optical line-broadening studies. The different regimes are accessible via a common formalism, as shown by, e.g., Kubo.[24] For strong external fields and fast modulation we previously developed equations of motion for the average values of $x(t)$, $y(t)$ and $z(t)$ based on a perturbation expansion in $\Delta \tau_c$.[23] This method was also used by us to study thermal charge transfer reactions in the presence of a strong external field[31] and by others to study aspects of optical transitions.[32] When the coupling is strong, it is not feasible to obtain equations of motion for the averages. Since we want to develop a common formalism for fast and slow modulation we now introduce another procedure to analyze both regimes. This method relies on a decoupling approximation that, as we shall see, leads to the same results as obtained by the perturbation in $\Delta \tau_c$ method. For slow modulation, we validate the results of the decoupling approximation by a numerical method.

It is convenient to define the variables $v_\pm = x \pm iy$ and rewrite Eq. (10) in terms of these new variables as

$$\dot{v}_+(t) = -i(\omega_0 + \eta)v_+(t) - i4b(t)z(t),$$

$$\dot{v}_-(t) = i(\omega_0 + \eta)v_-(t) + i4b(t)z(t), \qquad (17)$$

$$\dot{z}(t) = -i2b(t)(v_+(t) - v_-(t)).$$

Formal solution of the first two equations with the initial condition $v_\pm(0) = 0$ leads to the noise average

$$\bar{v}_+(t) = -i \int_0^t d\tau e^{-i\omega_0(t-\tau)} \overline{e^{-i\int_\tau^t ds\, \eta(s)} z(\tau)} 4b(\tau). \qquad (18)$$

We will assume that the stochastic process $z(\tau)$ within the integrand can be replaced by its noise average so that

$$\overline{e^{-i\int_\tau^t ds\, \eta(s)} z(\tau)} \approx \overline{e^{-i\int_\tau^t ds\, \eta(s)}} \bar{z}(\tau). \qquad (19)$$

This is the decoupling approximation noted above. Furthermore, as the stochastic process $\eta(t)$ is Gaussian, the average of the exponential can be expressed in terms of the second cumulant.[33] Then,

$$\bar{v}_+(t) = -i \int_0^t d\tau e^{-i\omega_0(t-\tau)} e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}}$$

$$\times \bar{z}(\tau) 4b(\tau). \qquad (20)$$

Taking into account that $x(t) = \mathrm{Re}\, v_+(t)$, the noise averaged power absorbed is

$$\bar{\mathcal{P}}(t) = -2\hbar \dot{b}(t)\left[ \int_0^t d\tau \sin \omega_0(t-\tau) \right.$$

$$\left. \times e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} \bar{z}(\tau) 4b(\tau) \right]. \qquad (21)$$

This expression relates the instantaneous average power of the solute with the noise averaged population difference. In

the limit of very weak fields one neglects the time evolution of $\bar{z}(\tau)$ by setting it equal to its initial value. Then the linear response theory result is recovered. Namely,

$$\bar{\mathcal{P}}_{\mathrm{LRT}}(t) = -2\hbar \dot{b}(t)\left[ \int_0^t d\tau \sin \omega_0(t-\tau) \right.$$

$$\left. \times e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} 4b(\tau) \right]. \qquad (22)$$

From Eqs. (17) with the initial conditions considered and the assumptions about averages of products mentioned above, it follows that

$$\bar{x}(t) = -\int_0^t d\tau \sin \omega_0(t-\tau)$$

$$\times e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} \bar{z}(\tau) 4b(\tau),$$

$$\bar{y}(t) = -\int_0^t d\tau \cos \omega_0(t-\tau)$$

$$\times e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} \bar{z}(\tau) 4b(\tau), \qquad (23)$$

$$\dot{\bar{z}}(t) = 4b(t)\bar{y}(t).$$

As noted above, we will consider that $\eta(t)$ is an Ornstein–Uhlenbeck process with correlation function given by Eq. (12). Then,

$$e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} = e^{-(\Delta\tau_c)^2[(t-\tau)/\tau_c + e^{-(t-\tau)/\tau_c} - 1]}. \qquad (24)$$

The averaged equations of motion in Eq. (23) are suitable to investigate the influence of strong external fields for the two limiting cases of fast and slow modulation, as we show in the following two sections.

## IV. FAST MODULATION

In the limit of short correlation time $\tau_c$ and/or small coupling strength $\Delta$, where $\Delta \tau_c \ll 1$, Eq. (24) can be approximated by

$$e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} \approx e^{-d(t-\tau)}, \qquad (25)$$

where $d = \Delta^2 \tau_c$ is assumed to be small compared with $\omega_0$. It measures the strength of the solute-solvent interaction giving rise to the dissipation. By taking time derivatives of Eq. (23), it is easy to check that the averages satisfy the equations of motion

$$\dot{\bar{x}}(t) = \omega_0 \bar{y}(t) - d\bar{x}(t),$$

$$\dot{\bar{y}}(t) = -\omega_0 \bar{x}(t) - d\bar{y}(t) - 4b(t)\bar{z}(t), \qquad (26)$$

$$\dot{\bar{z}}(t) = 4b(t)\bar{y}(t),$$

with initial conditions $\bar{x}(0) = \bar{y}(0) = 0$ and $\bar{z}(0) = 1$. These equations of motion are the same as those obtained by the perturbation theory.[23] Although Eqs. (26) can be readily integrated numerically, insight can be gained by carrying out an approximate analytical treatment. This case has been previously treated by us[23] for external sinusoidal fields $b(t) = b_0 \cos \Omega t$ with frequencies $\Omega$ that are close to the fre-

quency of the optical transition $\omega_0$. Here we will just quote the results. The population difference is given by

$$\bar{z}(t) = e^{-dt/2}\left(\cos \omega_1 t + \frac{d}{2\omega_1}\sin \omega_1 t\right), \qquad (27a)$$

where

$$\omega_1 = \sqrt{4b_0^2 - (d/2)^2}. \qquad (27b)$$

In obtaining Eq. (27a) we have assumed a sufficiently strong external field such that $b_0 > d/2$, leading to an underdamped oscillator behavior for $\bar{z}(t)$. Using this expression in Eq. (21), the power absorbed by the solute can be expressed as

$$\frac{\bar{\mathcal{P}}_{app}(t)}{(1/2)\hbar(2b_0)^2\Omega}$$

$$= 2e^{-dt/2}[C_0 \cos \omega_1 t + C_1 \sin \omega_1 t] + e^{-dt/2}$$

$$\times [C_2 \cos(2\Omega + \omega_1)t + C_3 \cos(2\Omega - \omega_1)t$$

$$+ C_4 \sin(2\Omega + \omega_1)t + C_5 \sin(2\Omega - \omega_1)t], \qquad (28)$$

where

$$C_0 = \frac{1}{4}[I(\delta_- - \omega_1) - I(\delta_+ + \omega_1) + I(\delta_- + \omega_1) - I(\delta_+ - \omega_1)]$$

$$-\frac{d}{2\omega_1}\frac{1}{4}[J(\delta_- + \omega_1) - J(\delta_- - \omega_1) - J(\delta_+ + \omega_1)$$

$$+ J(\delta_+ - \omega_1)],$$

$$C_1 = \frac{d}{2\omega_1}\frac{1}{4}[I(\delta_- - \omega_1) - I(\delta_+ + \omega_1) + I(\delta_- + \omega_1)$$

$$- I(\delta_+ - \omega_1)] + \frac{1}{4}[J(\delta_- + \omega_1) - J(\delta_- - \omega_1)$$

$$- J(\delta_+ + \omega_1) + J(\delta_+ - \omega_1)],$$

$$C_2 = -\frac{1}{2}\left[I(\delta_- - \omega_1) - I(\delta_+ + \omega_1) + \frac{d}{2\omega_1}J(\delta_- - \omega_1)\right.$$

$$\left. + \frac{d}{2\omega_1}J(\delta_+ + \omega_1)\right],$$

$$C_3 = -\frac{1}{2}\left[I(\delta_- + \omega_1) - I(\delta_+ - \omega_1) - \frac{d}{2\omega_1}J(\delta_- + \omega_1)\right.$$

$$\left. - \frac{d}{2\omega_1}J(\delta_+ - \omega_1)\right],$$

$$C_4 = \frac{1}{2}\left[J(\delta_- - \omega_1) + J(\delta_+ + \omega_1) - \frac{d}{2\omega_1}I(\delta_- - \omega_1)\right.$$

$$\left. + \frac{d}{2\omega_1}I(\delta_+ + \omega_1)\right],$$

$$C_5 = \frac{1}{2}\left[J(\delta_+ + \omega_1) + J(\delta_+ - \omega_1) + \frac{d}{2\omega_1}I(\delta_- + \omega_1)\right.$$

$$\left. - \frac{d}{2\omega_1}J(\delta_+ - \omega_1)\right],$$

where the $\delta_\pm = \omega_0 \pm \Omega$ are the detuning frequencies. The $I$'s and $J$'s appearing in the above expressions are defined in terms of the integrals

$$I(\nu) = \int_0^\infty dt\, e^{-dt/2}\cos(\nu t) = \frac{d/2}{(d/2)^2 + \nu^2},$$

$$J(\nu) = \int_0^\infty dt\, e^{-dt/2}\sin(\nu t) = \frac{\nu}{(d/2)^2 + \nu^2}. \qquad (29)$$

We refer to the $I$'s and $J$'s as the spectral densities; they are, respectively, the real and imaginary parts of the one-sided Fourier transform of the relaxation kernel $\exp(-dt/2)$, evaluated at the indicated frequencies.

In the fast modulation limit, the LRT result for the power follows directly from Eq. (22), which shows that $\bar{\mathcal{P}}_{LRT}(t)$ is a periodic function, and its cycle average

$$\langle\bar{\mathcal{P}}_{LRT}\rangle = \frac{\Omega}{2\pi}\int_0^{2\pi/\Omega} dt\, \bar{\mathcal{P}}_{LRT}(t) \qquad (30)$$

provides the conventional result

$$\langle\bar{\mathcal{P}}_{LRT}\rangle = \frac{1}{2}\hbar(2b_0)^2\Omega[I(\delta_-) - I(\delta_+)]. \qquad (31)$$

The system's (linear) susceptibility, $\langle\bar{\mathcal{P}}_{LRT}\rangle/\frac{1}{2}\hbar(2b_0)^2\Omega$, is independent of $b_0$, of course. The spectral density $I(\nu)$, cf. Eq. (29), is a Lorentzian with broadening given by the dissipation $d \equiv \Delta^2\tau_c$, reflecting the solute–solvent interaction.

The approximate result of Eq. (28) shows that a Fourier transform of $\bar{\mathcal{P}}(t)$ will lead to lines broadened by the dissipation, $d$, centered at the frequencies $\omega_1$ and $2\Omega \pm \omega_1$. The spectral densities are displaced by $\omega_1 \approx 2b_0$ [cf. Eq. (27a)] with respect to the weak field values [compare Eq. (31) with Eq. (28)], suggesting that the line shapes can be manipulated by the application of strong external fields.

Of interest is an indication of the duration of the external field required to obtain these strong field results. One might expect that the external field should be on for a time longer than the inverse of the dissipation, $1/d$, as this will insure that the field will be on during the lifetime of $\bar{z}(t)$, cf. Eq. (27a). To investigate this issue, we numerically solve Eq. (26) and construct $\bar{\mathcal{P}}(t)$ for an external field of the form

$$b(t) = b_0 \cos(\Omega t)e^{-t^2/2\tau^2}, \qquad (32)$$

where $\tau$ is a time characterizing the external field envelope. Results for $\bar{\mathcal{P}}(t)$ with $\tau = 100, 10,$ and $1$ are displayed in Fig. 1. The $\tau = 100$ value is essentially the same as that obtained for the field on for all time; a low frequency peak shifted from zero by $2b_0$ and a peak split by $2b_0$ around $2\omega_0$. The $\tau = 10$ plot shows that the shift from zero and the split peak are gone, indicating that the field is on for a time interval smaller than the inverse dissipation, and a basically linear response result is being obtained. For $\tau = 1$, note that the scale of the power absorbed is much smaller than for the larger $\tau$ values, as expected. Since the dissipation is an electronic dephasing effect, and this is quite fast in typical sol-
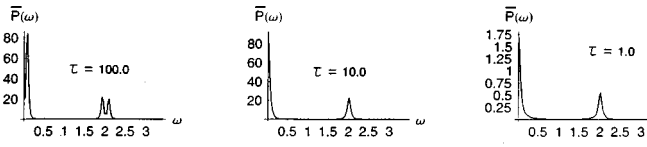
FIG. 1. Power spectrum, $\bar{\mathcal{P}}(\omega)$, of $\bar{\mathcal{P}}(t)$ for the indicated values of $\tau$, the width parameter for the duration of the external field, cf. Eq. (32), for $\omega_0 = 1.0$, $\Omega = 1.0$, and $d = 0.05$. Time is measured in units of $1/\omega_0$. As $\tau$ decreases, the strong external field effect vanishes and becomes appropriate to what would be obtained by linear response theory.

vents, the external field does not have to be on for very long in order to produce the full strong external field effect.

The analytic expression that we presented above is for resonant behavior, defined to be $\delta_- = 0(\Omega = \omega_0)$. Actually, resonance could be considered to be detunings $\delta_- \pm 2b_0 = 0$. To investigate this feature we plot in Fig. 2 a series of Fourier transforms of $\bar{\mathcal{P}}(t)$. The strong field effect discussed above is in evidence not only for $\delta_- = 0$, but also for fields that satisfy $\delta_- \pm 2b_0 = 0$. This result shows that there is a kind of linear response behavior in evidence, as the low-frequency behavior has a peak at zero frequency. Nevertheless, the strong field effect is still well in evidence. We also display results for detunings outside the resonance width to show how the linear response regime is regained, including the high-frequency behavior. The limit of the resonance behavior should be for detunings, now including the strong field effect of $2b_0$, that are outside the width, $1/d$. In fact, the displayed results for the nonresonant behavior are generated not by numerical solution of the equations of motion but rather from the following analytic approach.

Far from resonance one expects that the population difference $\bar{z}(t)$ changes slowly. This is the case when $\Omega - \omega_0 \pm 2b_0 \gg d$. For the purposes of this analysis, it is convenient to recast the averaged equations of motion [Eq. (26)] as
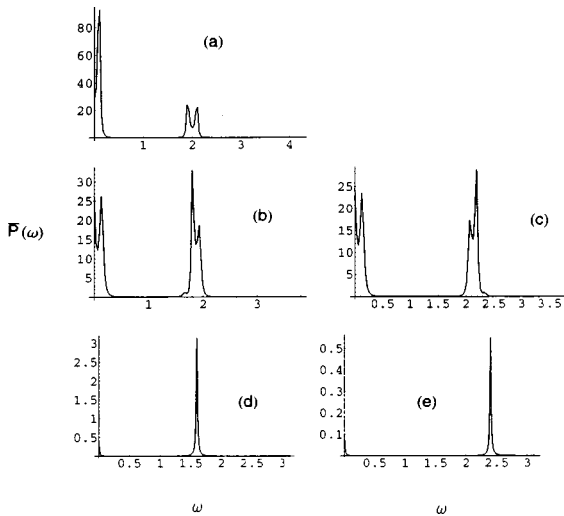


FIG. 2. Power spectrum, $\bar{\mathcal{P}}(\omega)$, of $\bar{\mathcal{P}}(t)$. (a) Resonant behavior is defined as $\omega_0 = \Omega = 1$. (b) and (c) Resonant behavior is defined as $\omega_0 - \Omega \pm 2b_0 = 0$, for $2b_0 = 0.05$, respectively. (d) and (e) The power spectrum away from resonance, with $2b_0 = 0.1$, respectively, that coincides with the result expected from linear response theory.

$$\ddot{x}(t) + 2\,d\dot{x}(t) + (\omega_0^2 + d^2)\bar{x}(t) = -4b_0\omega_0 \cos \Omega t \bar{z}(t),$$

$$\ddot{y}(t) + 2\,d\dot{y}(t) + (\omega_0^2 + d^2)\bar{y}(t)$$

$$= -\frac{d}{dt}(4b(t)\bar{z}(t)) - d4b(t)\bar{z}(t), \tag{33}$$

$$\dot{\bar{z}}(t) = 4b_0 \cos \Omega t \bar{y}(t).$$

We may neglect the first derivative of $\bar{z}(t)$ on the r.h.s. of the equation for $\bar{y}(t)$ in Eq. (33), as far from resonance $\bar{z}(t)$ varies slowly. The resulting equation is solved approximately by writing $\bar{y}(t) = y_1(t)\bar{z}(t)$ and neglecting transient effects. The result is

$$y_1(t) = \frac{4b_0\Omega}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]^{1/2}} \sin\left(\Omega t - \frac{\pi}{2} + \beta\right)$$

$$- \frac{4b_0 d}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]^{1/2}} \sin(\Omega t + \beta), \tag{34}$$

where

$$\cos \beta = \frac{2\,d\Omega}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]^{1/2}},$$

$$\sin \beta = \frac{\omega_0^2 - \Omega^2}{[(\omega_0^2 - \omega^2)^2 + 4\,d^2\Omega^2]^{1/2}}. \tag{35}$$

Using this approximate form for $\bar{y}(t)$ in the third equation in Eq. (33) produces

$$\dot{\bar{z}}(t) = \frac{(4b_0)^2}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]^{1/2}} [\cos^2 \Omega t(-\Omega \cos \beta$$

$$+ d \sin \beta) + \cos \Omega t \sin \Omega t (\Omega \sin \beta - d \cos \beta)]$$

$$\times \bar{z}(t). \tag{36}$$

This equation can be integrated to yield

$$\ln \bar{z}(t) = -\frac{(4b_0)^2}{2} \frac{d(\omega_0^2 + \Omega^2)}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]}\left(t + \frac{\sin 2\Omega t}{2\Omega}\right)$$

$$- \frac{(4b_0)^2}{4} \frac{\omega_0^2 - \Omega^2(1 + 2d^2)}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]}$$

$$\times (\cos 2\Omega t - 1). \tag{37}$$

The coefficients of the sinusoidal terms of $\ln \bar{z}(t)$ are small compared with the term linear in $t$. Thus, keeping just this term, we have

$$\bar{z}(t) \approx e^{-At}, \tag{38}$$

with

$$A = \frac{(4b_0)^2}{2} \frac{d(\omega_0^2 + \Omega^2)}{[(\omega_0^2 - \Omega^2)^2 + 4\,d^2\Omega^2]}. \tag{39}$$

Note that $A < d$. Thus the time decay of the population difference for off-resonance fields will be much slower than the decay for a field of the same strength and with a resonant frequency, as expected.

Now inserting the above approximate expression for the population difference into Eq. (23), and substituting this into the instantaneous power absorbed expression, Eq. (16), we obtain

$$\frac{\bar{\mathcal{P}}_{app}(t)}{(1/2)\hbar(2b_0)^2\Omega} = 4\sin\Omega t \int_0^\infty d\tau e^{-d\tau} \sin\omega_0\tau$$

$$\times \cos\Omega(t-\tau)\bar{z}(t-\tau)$$

$$= 4\sin\Omega t e^{-At} \int_0^\infty d\tau e^{-(d-A)\tau} \sin\omega_0\tau \cos\Omega(t-\tau)$$

$$= e^{-At}\{\sin(2\Omega t)[J(\omega_0-\Omega;d-A)+J(\omega_0+\Omega;d-A)]$$

$$+ (1-\cos(2\Omega t)[I(\omega_0-\Omega;d-A)$$

$$+ I(\omega_0+\Omega;d-A)]\}. \tag{40}$$

The spectral densities $I(\nu)$ and $J(\nu)$ are defined in Eq. (29). This result indicates that the solute absorbs power at zero frequency and at frequency $\omega \approx \Omega$. Then, if we average over a cycle of the external field, we find that, for off-resonance and strong fields, the net power absorbed is given by an expression that essentially coincides ($A \ll d$) with the one obtained from LRT, as in Eq. (31).

## V. SLOW MODULATION

We will now focus our analysis on the slow modulation regime defined by $\Delta\tau_c > 1$,[24] that is favored by increasing the solute-solvent coupling, i.e., larger $E_r$ values, or more slowly relaxing solvents with their longer $\tau_c$ values. For nonpolar or weakly polar solvents in simple or complex liquids, and for many glasses, where the coupling between the solute and solvent is via lattice deformations (phonons), the slow modulation regime is the appropriate one. Linear response analysis leads to a Gaussian line shape function for absorption,[15]

$$I_a(\Omega) = \frac{1}{\sqrt{2\pi}\Delta} \exp\left(-\frac{(\omega_0-\Omega)^2}{2\Delta^2}\right). \tag{41}$$

In the slow modulation regime,

$$e^{-\int_\tau^t ds_1 \int_\tau^{s_1} ds_2 \overline{\eta(s_1)\eta(s_2)}} \approx e^{-\Delta^2(t-\tau)^2/2} \tag{42}$$

is to be used in Eq. (23). Near resonance, the expression for $\bar{y}(t)$ can be simplified by neglecting the contribution of fast oscillations. By also taking into account the rapid decay of the integrand, we have

$$\bar{y}(t) = -2b_0\cos\Omega t \int_0^\infty d\tau e^{-\Delta^2\tau^2/2}\bar{z}(t-\tau). \tag{43}$$

Using this expression in the third equation of Eq. (23), we find

$$\dot{\bar{z}}(t) = -8b_0^2\cos^2\Omega t \int_0^\infty d\tau e^{-\Delta^2\tau^2/2}\bar{z}(t-\tau). \tag{44}$$

The solution of the last equation with the initial condition $z(0) = 1$ is to be inserted in the expression for the power absorbed. The resulting expression suggests that the main

contribution of the population difference comes from the average of $\bar{z}(t)$ over an external period. Then, we can replace the above equation by its cycle average as

$$\dot{\bar{z}}(t) = -(2b_0)^2 \int_0^\infty d\tau e^{-\Delta^2\tau^2/2}z(t-\tau). \tag{45}$$

In contrast to the fast modulation case, it is not possible to rewrite Eq. (45) as a damped oscillator. Nevertheless, the fact that in both cases there is a rapidly decaying kernel in the respective integral equations suggests that an approximate damped oscillator should be an appropriate solution. To verify that this is a viable procedure, we solve Eq. (45) by Laplace transformation techniques. Accounting for the initial condition, the Laplace transform is

$$\bar{\bar{z}}(s) = \frac{1}{s+\tilde{M}(s)}, \tag{46}$$

where

$$\tilde{M}(s) = (2b_0)^2 \int_0^\infty dt e^{-st}e^{-\Delta^2 t^2/2}$$

$$= (2b_0)^2 \frac{\sqrt{2\pi}}{2\Delta} e^{-s^2/2\Delta^2} \mathrm{erfc}\left(\frac{s}{\sqrt{2}\Delta}\right), \tag{47}$$

and erfc is the complementary error function. The inversion of this expression has to be done numerically. We have used available Fortran routines[34] to numerically evaluate the function $W(x) = e^{-x^2}\mathrm{erfc}(-ix)$ and perform the inverse Laplace transform of the previous expression.

The numerical results and the above analysis do suggest that an effective oscillator solution of Eq. (45) of the form

$$\bar{z}(t) = e^{-\lambda t}\left(\cos\Omega_1 t + \frac{\lambda}{\Omega_1}\sin\Omega_1 t\right) \tag{48}$$

provides a suitable approximation. The parameters $\lambda$, $\Omega_1$ can be determined by inserting Eq. (48) into (45). This leads to the algebraic equations

$$\Omega_1\,\mathrm{Re}\,G = \lambda\,\mathrm{Im}\,G,$$

$$\Omega_1 + \frac{\lambda^2}{\Omega_1} = (2b_0)^2\left(\mathrm{Im}\,G + \frac{\lambda}{\Omega_1}\mathrm{Re}\,G\right),$$

where[35]

$$G = \int_0^\infty dt e^{-(\Delta^2/2)t^2+\lambda t+i\Omega_1 t}$$

$$= \frac{1}{\Delta}\sqrt{\frac{\pi}{2}} e^{(\lambda+i\Omega_1)^2/2\Delta^2} \mathrm{erfc}\left(-\frac{(\lambda+i\Omega_1)}{\sqrt{2}\Delta}\right). \tag{49}$$

The parameters $\lambda$, $\Omega_1$ can then be obtained from the solutions of this system by a root finding technique for given values of $\Delta$ and $b_0$. In Fig. 3, we plot the evolution of $\bar{z}(t)$ as given by the numerical inversion of Eq. (46) and by our trial solution Eq. (48), for $\Delta = 0.15$, $b_0 = 0.15$, and for $\Delta = 0.15$, $b_0 = 0.07$. The simple form in Eq. (48) reproduces quite faithfully the numerical results. The behavior of $\bar{z}(t)$ is then essentially that of a damped oscillator with the devia-
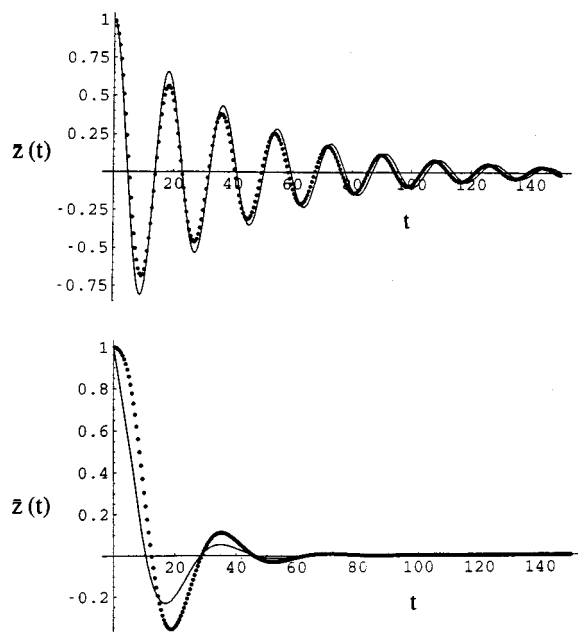
FIG. 3. The average population difference $\bar{z}(t)$ for slow modulation. The parameter values are for resonance, with $\omega_0 = \Omega = 1.0$, and for (a) $\Delta = 0.15$, $b_0 = 0.15$, and for (b) $\Delta = 0.15$, $b_0 = 0.07$. These results show that the effective oscillator solution in Eq. (48) agrees quite well with those from the numerical Laplace inversion of Eq. (46).

tions evident, as expected, at the shortest times. The damping depends on the ratio $\Delta/b_0$, while the frequency is proportional to $b_0$. Table I displays the dependence of $\lambda$ and $\Omega_1$ on $\Delta$ and $b_0$.

The formal similarity between the relaxation of the population difference as given by Eq. (48) in the slow modulation limit and that of Eq. (27a) in the fast modulation case, allows us to write an approximate expression for the noise averaged power absorbed that is formally identical to Eq. (28) with $d/2$ and $\omega_1$ replaced by $\lambda$ and $\Omega_1$, respectively. The coefficients $C_i$, $i=0,5$ will now be expressed in terms of spectral functions $I_1$ and $J_1$ that will differ from those in Eq. (29), as they reflect the Gaussian nature of the relaxation kernel. They are given by the real and imaginary part of the function $G$ defined in Eq. (49), namely,

$$I_1(\nu) = \mathrm{Re} \ \sqrt{\frac{\pi}{2}} \frac{1}{\Delta} e^{(\lambda + i\nu)^2/2\Delta^2} \mathrm{erfc}\left( -\frac{\lambda + i\nu}{\sqrt{2}\Delta} \right),$$
(50)

TABLE I. Values of $\lambda$ and $\Omega_1$ for $\Delta = 0.15$ and $\Delta = 0.3$.[a]

| $\Delta$ | $b_0$ | $\lambda$ | $\Omega_1$ |
|------|------|--------|--------|
| 0.15 | 0.07 | 0.0824 | 0.1750 |
| 0.15 | 0.10 | 0.0531 | 0.2492 |
| 0.15 | 0.15 | 0.0231 | 0.3476 |
| 0.15 | 0.20 | 0.0079 | 0.4379 |
| 0.15 | 0.25 | 0.0018 | 0.5284 |
| 0.3 | 0.10 | 0.2196 | 0.1999 |
| 0.3 | 0.15 | 0.1533 | 0.3783 |
| 0.3 | 0.20 | 0.1063 | 0.4985 |
| 0.3 | 0.25 | 0.0715 | 0.6008 |

[a]All quantities in units of $\omega_0$.



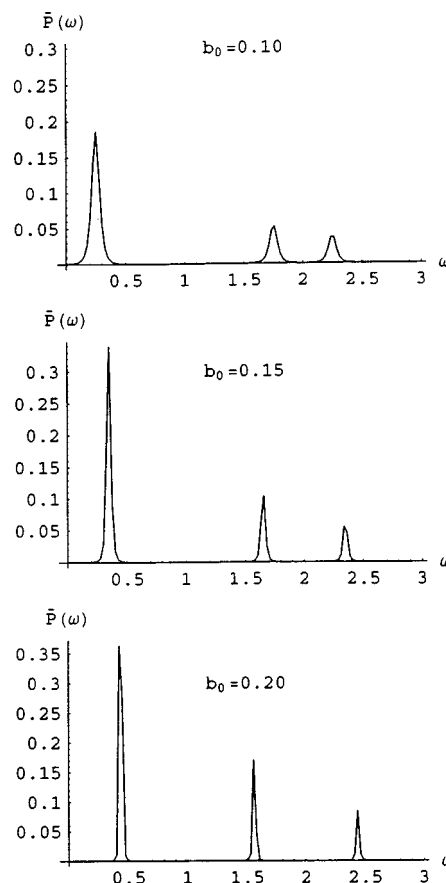FIG. 4. $\bar{\mathcal{P}}(\omega)$, the power spectrum of $\bar{\mathcal{P}}(t)$ in the slow modulation regime, for the parameters $\omega_0 = 1.0$, $\Omega = 1.0$, $\Delta = 0.15$, and the indicated $b_0$ values. The plot is qualitatively similar to the fast modulation result.

$$J_1(\nu) = \mathrm{Im} \ \sqrt{\frac{\pi}{2}} \frac{1}{\Delta} e^{(\lambda + i\nu)^2/2\Delta^2} \mathrm{erfc}\left( -\frac{\lambda + i\nu}{\sqrt{2}\Delta} \right).$$

In Fig. 4, we present $\bar{\mathcal{P}}(\omega)$, the power spectrum of $\bar{\mathcal{P}}(t)$, for the parameters $\omega_0 = 1.0$, $\Omega = 1.0$, $\Delta = 0.15$, for a number of $b_0$ values. Besides the low-frequency peak, we find two smaller peaks displaced by $2b_0$ with respect to the detuning, $\delta_-$. The plot is qualitatively similar to the one obtained in the fast modulation case. If the external field is reduced so that $b_0$ is smaller than the coupling strength $\Delta$, one goes back to the situation well described by LRT. Thus we have demonstrated that, as in the fast modulation case, we may manipulate $\bar{\mathcal{P}}(t)$ by the application of a strong external field.

The decoupling approximation used in Eq. (19) is of uncertain quality when applied to the slow modulation regime of this section. As a way of validating it, we return to the unaveraged equations of motion in Eqs. (10). These stochastic equations can be solved numerically by generating trajectories $x(t)$, $y(t)$, and $z(t)$ for different realizations of the noise, $\eta(t)$, and averaging over a suitable ensemble of initial conditions. We developed the methodology for carrying this out for the Ornstein–Uhlenbeck (OU) noise process in another context.[31] It can be adapted to the problem at hand. Briefly, the procedure to integrate the stochastic equations of motion is as follows. A fourth order Runge–Kutta integrator is used to advance the solutions of Eqs. (10) for
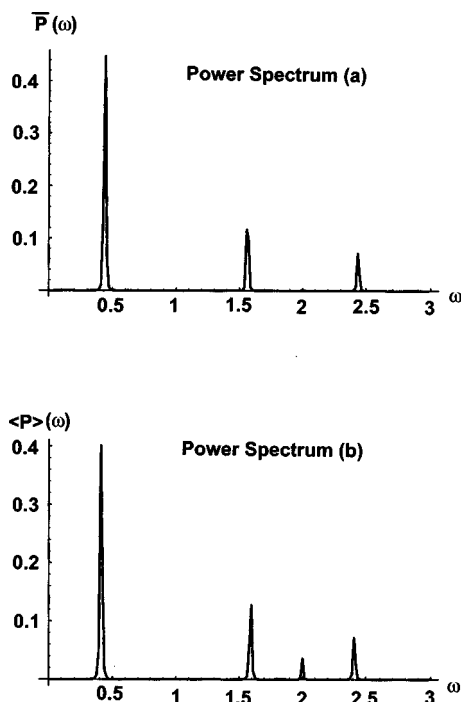
FIG. 6. A plot of $I_1(\nu)$ versus the detuning $\delta_-$, for $\omega_0 = 1.0$ and $\Delta = 0.15$, $b_0 = 0.15$. The shape resembles a Marcus plot of rate versus driving force.

FIG. 5. (a) $\bar{\mathcal{P}}(\omega)$, the power spectrum of $\bar{\mathcal{P}}(t)$ as obtained from the analytic method. (b) $\langle \mathcal{P} \rangle(\omega)$, the power spectrum of $\langle \mathcal{P} \rangle(t)$ as obtained by stochastic simulation. The parameters are $\omega_0 = 1.0$, $\Omega = 1.0$, $\Delta = 0.15$, $\omega_c = 1/\tau_c = 0.015$, and $b_0 = 0.20$.

each time step. A stochastic term is added at each step with its statistical properties described by the OU process. The OU process is generated by solving a Langevin equation with a delta-correlated noise term. This will ensure that the correlation function of $\eta(t)$ has the desired statistical properties given by Eq. (12). The procedure is carried out for a sufficient number of trajectories to yield the average behavior.

The result of such a stochastic simulation, along with the analytic result, is shown in Fig. 5 for the parameters $\omega_0 = 1.0$, $\Omega = 1.0$, $\Delta = 0.15$, $\omega_c = 1/\tau_c = 0.015$, and $b_0 = 0.20$. The agreement of the stochastic simulation [Fig. (5b)] with the analytic result [Fig. 5(a)] is quite good. Note that $b_0 = 0.20$ is a rather large external field, so the decoupling procedure is only of moderate accuracy. There are discernable differences in the widths of the lines, and the stochastic average does have an additional peak at twice the resonance frequency. We comment on the difference in widths in Sec. VI. The "extra" small peak at twice $\Omega$ can be traced to the analytic approaches' extension of the time integral to infinity in, e.g., Eq. (43). For strong damping, where the time integral rapidly converges, the additional peak should have small weight, as found in Fig. 5(b).

In optical spectroscopy (and in the related thermal electron transfer rate measurements), a "Marcus" plot[16]—a plot of the spectrum (rate constant) as a function of reaction free energy $\Delta G_0$—can be used as an aid in determining the reorganization energy, $E_r$. An analogous strategy is useful here. It is simplest to scan $\omega_0$ values for a fixed $b_0$ values. The $b_0$ value should satisfy $2b_0 > \Delta$ to make sure that the underdamped oscillator solution of Eq. (48) is appropriate. If we
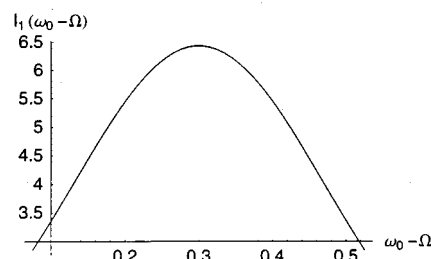
define $\omega_0^*$ by $\omega_0^* = \Omega - 2b_0$, and scan $\omega_0$ in the range $\omega_0^* - \lambda < \omega_0 < \omega_0^* + \lambda$, then the $\omega_0$ values will be within the resonant width, required to be in the strong field regime. Once the $\omega_0$ values are away from resonance, the linear response regime is regained, and this can be detected in terms of the conventional Gaussian result, cf. Eq. (41). Figure 6 provides a plot of the $I_1(\nu)$ function that contributes to the $C_i$ coefficients versus the detuning $\delta_-$. This plot, in fact, looks quite similar to a Marcus plot in having a peak at the $\omega_0^*$ frequency and falling off to either side of this frequency. The $I_1(\nu)$ factor is present in both the low-frequency, $\omega_1$, and high-frequency, $2\Omega \pm \omega_1$, terms that contribute to the slow modulation version of Eq. (28). Consequently, this Marcus behavior can be accessed in either frequency regime.

## VI. CONCLUDING REMARKS

In this paper, we showed how the use of a monochromatic strong, resonant external field can be used to investigate the electronic dephasing of a solute in a condensed medium. The strong field can drive $\bar{z}(t)$, the solute electronic level population difference, away from its initial value sufficiently to lead a significant time dependence of $\bar{P}(t)$, with $C_i$ coefficients that reflect the strength of the external field's coupling to the solute's transition dipole moment. In principle, measurement of the time dependence of the power absorbed for varying external field strengths could be used to manipulate where the resonant behavior occurs.

A result that follows from our analysis in Sec. III, and that we previously explored,[23] is an equation of motion approach to linear response theory. If the time dependence of $\bar{z}(t)$ is exponential, then the ratio $\bar{P}(t)/\bar{z}(t)$ will lead to the result of linear response theory. Usually, LRT is derived by a Golden Rule, initial rate calculation, in contrast to this dynamical method.

Once $\bar{z}(t)$'s decay is oscillatory, the strong field effects will be in evidence. While the fast modulation case lends itself to a more transparent analysis, we found that the slow modulation case does lead to qualitatively the same behavior. That is, the time dependence involves the same frequencies in both fast and slow modulation; just the coefficients change. Furthermore, we were able to demonstrate that a strong, but nonresonant, external field provides essentially the same result as linear response theory would predict.

Our method of derivation relies on the decoupling approximation introduced in Eq. (19). This approximation

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leads to the same results as the equation of motion method for fast modulation. The equation of motion method is a perturbation expansion in $\Delta\tau_c$.[32,33,31,23] For slow modulation, we are not aware of an analytic method that can justify the approximation. Therefore, we used a stochastic simulation method to carry out the OU noise average. The results essentially coincide with those obtained from the decoupling approximation. The difficulty with an analytic approach is the absence of a perturbation parameter. For a weak external field, where LRT is obtained, the decoupling approximation does lead to the well known optical or thermal charge transfer results.[27] In the LRT regime, the decoupling procedure can be justified by projection operator methods.[36] That the decoupling method is accurate provides an essentially analytic approach, with its attendent physical insight, into SFS. A close examination of the analytic and stochastic results does reveal that the irreversible electronic dephasing that leads to the widths of the lines in Figs. 5(a) and 5(b) are not quite the same. It is difficult to know whether this is a failure of the decoupling approximation, or the other approximations—the average over the high-frequency oscillations and the introduction of the effective oscillator—that we use to generate Fig. 5. Thus we plan to use the stochastic method to refine the results presented herein. Furthermore, once external fields that are nonsinusoidal are used, obtaining analytic results becomes quite difficult and, naturally, the stochastic averaging method can deal with any form of the external field.

The electronic dephasing studied here is a purely coherent process. That is, we assume that the time scale under study is shorter than the time scale for motion along the two electronic states' solvation coordinates. There is equilibrium in the solvation coordinate for both ground and excited electronic states. Recent work by Fainberg[19] develops a nonperturbative approach to nonlinear optical spectroscopy that considers nonequilibrium effects along these solvation coordinates. This contribution greatly generalizes studies of such nonequilibrium effects carried out in nonlinear optical spectroscopy that proceed by a perturbation expansion in powers of the external field strength.[2] The focus of these studies is on the population evolution along the solvation surfaces. Fainberg considers the use of short, intense pulses and provides expressions for the nonlinear polarization that reflect the dynamics along these surfaces. The short pulse restriction places this work in the regime of overdamped dynamics, where $b_0$ is smaller than the dissipation. In the SFS, the field is on for times long compared with the dissipation time, and the evolution of $\bar{z}(t)$ is underdamped, since $b_0$ is large compared to the dissipation. As just noted, we are restricted to just electronic coherence effects, and therefore do not consider evolution along the solvation surfaces. It would be of great interest to formulate our SFS in a fashion to be applicable to the regime where the effects of nonequilibrium solvation dynamics along the surfaces can be addressed.

The analysis we have carried out relies on the simplified stochastic Hamiltonian of Eq. (13). As outlined in Sec. II, once we are interested in $\bar{z}(t)$'s that do have a significant time dependence, and the reorganization energy is large in the sense that $E_r/\Delta\hbar>1$, the assumption of an "autono-

mous" solvent, that is, one whose dynamics is independent of the instantaneous solute state, is no longer tenable. The restriction to reorganization energies that satisfy $E_r/\Delta\hbar<1$ limits the applicability of this work to electronic dephasing in nonpolar and weakly polar solvents or to solutes whose charge rearrangement upon excitation is modest. In order to extend our work to polar solvents and larger changes in electronic structure upon optical excitation, we have developed new equations of motion that can account for the "nonautonomous" solvent behavior.[30] Here, the stochastic process that represents the solvent dynamics is explicitly coupled to the solute's state. While this coupling will probably preclude an analytic theory, the stochastic simulation method used above will permit us to extend SFS to the strong coupling regime.

The rapidity of electronic dephasing permits its approximate separation from the effects of vibrational dephasing and population relaxation. However, as vibrational dephasing and population relaxation are key pathways for longer time scale couplings to solutes, their effects should be included in this formulation of spectroscopy. Another direction for future study is the use of more sophisticated solvent fluctuation correlation functions, $K(t)$. Polar and nonpolar solvent correlation functions are known to be better characterized by multiple relaxation times, and they also have contributions from inertial motion. As the averaged equations of motion we have obtained are integro-differential equations, their solution for various forms of $K(t)$ should be amenable to numerical integration schemes.

## ACKNOWLEDGMENTS

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