External-field effects on molecular electronic transitions in charge-transfer systems

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We investigate strong-external-field effects on optical transitions between electronic states of charge-transfer systems in condensed media. We will use as a model a two-level system coupled to a dissipative medium driven by a strong, time-dependent external field. The external field induces transitions between the levels, and the dissipation, represented by a stochastic process, induces relaxation. The power absorbed by the system is characterized by spectral densities that not only depend on the detuning from resonance and the strength of the dissipation, as found for line shapes in linear spectroscopy, but also on the strength of the external field. Our treatment is nonperturbative in the strength of the external field, and leads to the conclusion that spectral line shapes can be manipulated by the application of sufficiently strong external fields. [S0163-1829(98)03712-6]

I. INTRODUCTION

The study of molecular electronic transitions in condensed media has provided a wealth of information on a molecular system's interaction with a medium.[1,2] When the coupling to the medium is strong, and there is a significant difference in electronic structure between the system's states, there may be a substantial broadening of the electronic transition. A prime example is that of optical electron transfer in polar media.[3] Linear spectroscopic methods, based on linear-response theory (LRT) (equivalently, Fermi's golden rule) provide information via the linear susceptibility. In linear spectroscopy, there is a close connection between optical spectra (e.g., for intervalence bands) and nonradiative (thermal) electron transfer rates.[4–6] In both, the information is contained in a spectral density (line shape) that depends on the strength of the dissipation and the detuning of the transition frequency from the 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,[2,7,8] or on nonpertubative analysis of the density matrix by numerical methods.[9] We have recently studied the role of strong constant and time-dependent external fields on rates of thermal charge transfer reactions, at high[10,11] and low temperatures,[12] without relying on a perturbation expansion in the external field.

In this paper we will use a nonperturbative approach to study strong external field effects on radiative electronic transitions. The focus will be on the time development of the power absorbed from the external field. By restricting the calculation to a two-state system, and by representing the system-medium interaction (the dissipation) by a classical stochastic process, we will arrive at a simple view of the effect of the strong external field on the system and its interaction with the medium. The strong external field changes the level populations by a finite amount, so that one does not obtain, as in LRT, a constant cycle-averaged power absorbed, $\langle \overline{P} \rangle$. Instead, $\langle \overline{P} \rangle$ will depend on time in a characteristic fashion. Furthermore, spectral densities will appear that are different from those found in LRT, as they depend on the external field strength, in addition to the detuning and the dissipation. The nonperturbative treatment leads to an (approximate) analytic expression for the dependence of the power absorbed on the external field strength. The spectral densities that appear in the analytic expression are Lorentzians whose line centers are linear functions of the external field strength. This result suggests the possibility of using external fields of varying strengths to access the spectral densities in frequency ranges that would not be accessible in the linear-response regime.

The plan of the rest of this paper is as follows. In Sec. II we will describe the Hamiltonian appropriate to a two-level system coupled to a stochastic bath and driven by an external field. The equations of motion that follow from this Hamiltonian are averaged over the stochastic process and solved approximately. In Sec. III we compare the numerical solution of the averaged equations of motion with the analytic solutions, and analyze the effect of a strong driving field.

II. DERIVATION OF THE AVERAGED POWER ABSORBED

The Hamiltonian we use,

$$\mathcal{H} = -\frac{\hbar}{2}[\omega_0 + \eta(t)]\sigma_z + 2\hbar b(t)\sigma_x, \tag{1}$$

describes a system with two electronic states $|0\rangle$ and $|1\rangle$, interacting with a classical external field and a medium. σ_i, with $i = x$, y, and z, are the Pauli spin operators. The exter-

nal field-system interaction energy is defined by $2\hbar b(t) = \langle 0|\hat{\boldsymbol{\mu}}|1\rangle \cdot \boldsymbol{E}(t)$, where $\hat{\boldsymbol{\mu}}$ is the system dipole moment operator and $\boldsymbol{E}(t)$ is the external field. The medium dynamics is described here by a classical stochastic process $\eta(t)$ that simulates the medium's fluctuations around its (differing) equilibrium positions in the $|0\rangle$ and $|1\rangle$ electronic states. The displacement of the medium's equilibrium position in response to the differing charge distributions of the $|0\rangle$ and $|1\rangle$ electronic system states incorporates the strong coupling typical of charge-polar medium interactions. The stochastic Hamiltonian of Eq. (1) can be obtained from a spin-boson Hamiltonian when two conditions are met.[10] First, the temperature must be sufficiently high to permit a classical treatment of the medium degrees of freedom. This is often the case for electronic transitions of solute molecules in polar solvents, where the coupling is to long-range collective modes (e.g., the solvent's orientational polarization).[5] Second, we require that $b_0\tau_c$ is small, where τ_c is the correlation time of the medium fluctuations and b_0 is the magnitude of the external field-system coupling $b(t)$. If this condition is not satisfied, a classical stochastic model for the medium dynamics would not be appropriate, and more sophisticated techniques would have to be used.[12]

The classical stochastic process equivalent to the one arising from a spin-boson Hamiltonian, with the bath initially equilibrated to the ground electronic state, is Gaussian. Its average over the medium fluctuations is the reorganization energy E_r, which measures the energetic cost of reequilibrating the medium to state $|1\rangle$ if it was initially equilibrated to state $|0\rangle$. Thus $E_r = G^{\mathrm{neq}}(|1\rangle) - G^{\mathrm{eq}}(|1\rangle)$, where the first term is the free energy of state $|1\rangle$ interacting with the medium equilibrated to state $|0\rangle$ (hence a nonequilibrium free energy), and the second is the free energy with the medium equilibrated to state $|1\rangle$. For convenience, we have included the average value of the stochastic process in the definition of $\hbar\omega_0$, so that the mean value $\overline{\eta(t)}$ is zero. The quantity $\hbar\omega_0$ then is the energy gap between the *solvated* electronic states, with the medium degrees of freedom kept fixed at their equilibrium configuration in the $|0\rangle$ electronic state, as we now show. With our definition of $\eta(t)$ as the fluctuation from equilibrium, $\hbar\omega_0 = \Delta G^0 + E_r$, where ΔG^0 is the standard free-energy difference between the $|1\rangle$ and $|0\rangle$ states, $\Delta G^0 = G^{\mathrm{eq}}(|1\rangle) - G^{\mathrm{eq}}(|0\rangle)$. Using the definition of E_r above, $\hbar\omega_0 = G^{\mathrm{neq}}(|0\rangle) - G^{\mathrm{eq}}(|0\rangle)$, which is the vertical excitation energy including the solvation contribution.

The evolution of the system can be obtained from the density matrix equation of motion

$$i\hbar \frac{\partial \rho}{\partial t} = [H(t), \rho(t)]. \tag{2}$$

Expressing the density matrix $\rho(t)$ as

$$\rho(t) = \tfrac{1}{2}[1 + x(t)\sigma_x + y(t)\sigma_y + z(t)\sigma_z], \tag{3}$$

and using Eqs. (1)–(3), results in the following stochastic equations of motion for the time dependent coefficients $x(t)$, $y(t)$, and $z(t)$

$$\dot{x}(t) = [\omega_0 + \eta(t)]y(t), \tag{4}$$

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

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

The instantaneous power absorbed by the system from the external field is given by

$$\mathcal{P}(t) = \mathrm{Tr}\rho(t) 2\hbar \dot{b}(t)\sigma_x. \tag{5}$$

In the stochastic description, $\mathcal{P}(t)$ is a fluctuating quantity. Its average $\overline{\mathcal{P}(t)}$ follows directly from Eqs. (3) and (5). Thus

$$\overline{\mathcal{P}(t)} = 2\hbar \dot{b}(t)\overline{x(t)}, \tag{6}$$

where $\overline{x(t)}$ represents the stochastic average of $x(t)$. In this paper, we will consider that $\eta(t)$ is an Ornstein-Uhlenbeck stochastic process with correlation function $\overline{\eta(t)\eta(s)} = \Delta^2 \exp(-|t-s|/\tau_c)$, with $\Delta^2 = 2E_r k_B T/\hbar^2$.[13] The quantities Δ and τ_c are, respectively, the strength and correlation time of the stochastic process. The thermal ability of the solvent to produce fluctuations in the $|0\rangle$–$|1\rangle$ energy gap is characterized by Δ. The correlation time of the fluctuations in polar media scales with the dielectric relaxation time, τ_L.[13]

In general, a closed set of equations of motion for the averages can only be obtained from the stochastic set [Eq. (4)] under some suitable approximations. This is the case even for weak external fields—the system-medium interaction leads to stochastic equations of motion with multiplicative noise. When $\Delta\tau_c \ll 1$, the fluctuations can be treated as a perturbation of the systematic dynamics.[11,14] This will be a good approximation, as long as we contemplate external fields with strengths such that $\omega_0 \gg b_0$. But note that the applied field can be quite substantial so as to prevent us from considering a perturbation expansion in its strength. As the correlations decay rapidly for typical polar media, we anticipate obtaining time-local average equations of motion. By following methods we have developed for treating external field effects on similar stochastic equations of motion,[10] we obtain

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

$$\dot{\overline{y}}(t) = -\omega_0 \overline{x}(t) - d\overline{y}(t) - 4b(t)\overline{z}(t), \tag{7}$$

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

The effect of dissipation appears in the factor $d \equiv \Delta^2 \tau_c$. Although Eq. (7) can be readily integrated numerically, insight can be gained by carrying out an approximate analytical treatment. To this end, it is convenient to recast Eq. (7) as the following set of second order in time equations of motion:

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

$$\ddot{\overline{y}}(t)+2d\dot{\overline{y}}(t)+(\omega_0^2+d^2)\overline{y}(t)=-\frac{d}{dt}(4b(t)\overline{z}(t))-d\,4b(t)\overline{z}(t), \quad (8)$$

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

We have taken the applied field to be sinusoidal in time, so that $b(t)=b_0\cos\Omega t$, with a frequency $\Omega\approx\omega_0$. We now approximate the $\overline{y}(t)$ equation, assuming that $\Omega\gg d,\dot{\overline{z}}$, as

$$\ddot{\overline{y}}(t)+2d\dot{\overline{y}}(t)+(\omega_0^2+d^2)\overline{y}(t)=4b_0\Omega\sin\Omega t\overline{z}(t). \quad (9)$$

Neglecting the transient part of the solution of the above equation, and noting that the system is initially in the $|0\rangle$ state, so that $x(0)=y(0)=0$ and $z(0)=1$, lets us write a solution near resonance as

$$\overline{y}(t)\approx-\frac{2b_0\Omega}{\omega_0}\left[\int_0^t d\tau\, e^{-d(t-\tau)}\overline{z}(\tau)\right]\cos\Omega t. \quad (10)$$

Using this result in Eq. (8), and averaging the resulting expression over the fast Ω oscillations, we find that the average population difference between the electronic states, $\overline{z}(t)$, satisfies

$$\dot{\overline{z}}(t)=-4b_0^2\int_0^t d\tau\, e^{-d\tau}\overline{z}(t-\tau). \quad (11)$$

Taking a time derivative of this last equation, one can write a second-order differential equation for $\overline{z}(t)$ whose solution for the initial conditions $z(0)=1$, $\dot{z}(0)=0$ is

$$\overline{z}(t)=e^{-dt/2}\left(\cos\omega_1 t+\frac{d}{2\omega_1}\sin\omega_1 t\right), \quad (12)$$

where $\omega_1=\sqrt{4b_0^2-(d/2)^2}$. Here we have assumed that the external field strength is such that $b_0>d/2$. Thus the time behavior of the population difference induced by the external field is basically that of an underdamped harmonic oscillator. Using this result in the first of Eqs. (8), with the initial conditions $x(0)=\dot{x}(0)=0$, yields

$$\overline{x}(t)=-4b_0\int_0^t d\tau\, e^{-d\tau}\sin(\omega_0\tau)\cos[\Omega(t-\tau)]\overline{z}(t-\tau). \quad (13)$$

An approximate expression for the power absorbed is obtained from Eqs. (6) and (13) as

$$\overline{\mathcal{P}}_{\rm app}(t)=8\hbar b_0^2\Omega\left[\frac{1}{2}\sin 2\Omega t\int_0^\infty d\tau\, e^{-d\tau}\sin\omega_0\tau\times\cos\Omega\tau\overline{z}(t-\tau)+\frac{1-\cos 2\Omega t}{2}\times\int_0^\infty d\tau\, e^{-d\tau}\sin\omega_0\tau\sin\Omega\tau\overline{z}(t-\tau)\right]. \quad (14)$$

Using the above analytical expression, and Eq. (12), the power absorbed by the system can be expressed as

$$\frac{\overline{\mathcal{P}}_{\rm app}(t)}{(1/2)\hbar(2b_0)^2\Omega}=2e^{-dt/2}[C_0\cos\omega_1 t+C_1\sin\omega_1 t]+e^{-dt/2}[C_2\cos(2\Omega+\omega_1)t+C_3\cos(2\Omega-\omega_1)t+C_4\sin(2\Omega+\omega_1)t+C_5\sin(2\Omega-\omega_1)t], \quad (15)$$

where

$$C_0=\tfrac{1}{4}[I(\delta_--\omega_1)-I(\delta_++\omega_1)+I(\delta_-+\omega_1)-I(\delta_+-\omega_1)]-\frac{d}{2\omega_1}\frac{1}{4}[J(\delta_-+\omega_1)-J(\delta_--\omega_1)-J(\delta_++\omega_1)+J(\delta_+-\omega_1)],$$

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

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

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

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

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

Here $\delta_{\pm}=\omega_0\pm\Omega$ are the detuning frequencies and, as $b_0 \gg d/2$ for strong external fields, $\omega_1\approx 2b_0$. The I's and J's appearing in the above expressions are defined in terms of the integrals

$$I(\nu)=\int_0^\infty dt\ e^{-dt/2}\cos(\nu t)=\frac{d/2}{(d/2)^2+\nu^2},$$
$$J(\nu)=\int_0^\infty dt\ e^{-dt/2}\sin(\nu t)=\frac{\nu}{(d/2)^2+\nu^2}. \tag{16}$$

We shall refer to the I' 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.

III. ANALYSIS OF THE AVERAGED POWER ABSORBED

The derivation carried out in Sec. II provides a closed-form approximate solution $\overline{\mathcal{P}}_{\rm app}(t)$ for the average power absorbed of the system. Before analyzing the implications of this expression, and comparing it with the numerical solution of the averaged equations of motion, let us regain the linear response theory. If $\hbar b_0$ is small, then the population difference is changing slowly, i.e., we may set $\overline{z}(t)\approx 1$ in Eq. (13). The resulting $\overline{\mathcal{P}}_{\rm app}(t)$, which we will denote as $\overline{\mathcal{P}}_{\rm LRT}(t)$, is a periodic function of time, and its cycle average

$$\langle\overline{\mathcal{P}}_{\rm LRT}\rangle=\frac{\Omega}{2\pi}\int_0^{2\pi/\Omega}dt\ \overline{\mathcal{P}}_{\rm LRT}(t), \tag{17}$$

provides the conventional result

$$\langle\overline{\mathcal{P}}_{\rm LRT}\rangle=\tfrac{1}{2}\hbar(2b_0)^2\Omega[I(\delta_-)-I(\delta_+)]. \tag{18}$$

The system's (linear) susceptibility $\langle\overline{\mathcal{P}}_{\rm LRT}\rangle/1/2\hbar(2b_0)^2\Omega$ is independent of b_0, of course. The spectral density $I(\nu)$, [cf. Eq. (16)] is a Lorentzian with broadening given by the dissipation $d\equiv\Delta^2\tau_c$, reflecting the interaction of the system with the medium.

Another view of LRT follows from our equations of motion method. If the $\dot{\overline{z}}(t)$ equation in Eq. (11) is solved for small b_0 by assuming that $\overline{z}(t)$ is slowly varying, so that Eq. (11) becomes time local, then $\overline{z}(t)=\exp[-(2b_0)^2t/d]$. [An equivalent procedure is to solve the second order equation that led to Eq. (12), but now in the limit of extreme overdamping.] Furthermore, as the right hand side of Eq. (14) becomes proportional to $\overline{z}(t)$ for slowly varying $\overline{z}(t)$, the ratio $\langle\overline{\mathcal{P}}_{\rm LRT}\rangle/\overline{z}(t)$ yields the same result as setting $\overline{z}(t)\approx 1$. Thus the cycle average will still yield the LRT result given by Eq. (18). These analytic predictions are verified by numerically solving for $\overline{z}(t)$. Numerical integration of the system of equations in Eq. (8) is readily carried out. Figure 1 presents the numerical solutions for varying values of the external field strength, b_0. For $b_0=0.0005$, $\overline{z}(t)$ does not decay on the time scale of the plot. For $b_0=0.005$, the decay is exponential (after a transient), and is well described by the above overdamped decay. Thus, our results show that LRT is obtained even if there is a finite population change, when the equation of motion approach is used. (Usually, LRT is done by a golden rule approach that uses an initial decay rate methodology.) As long as the decay of $\overline{z}(t)$ is exponential, the linear-response regime will be appropriate.

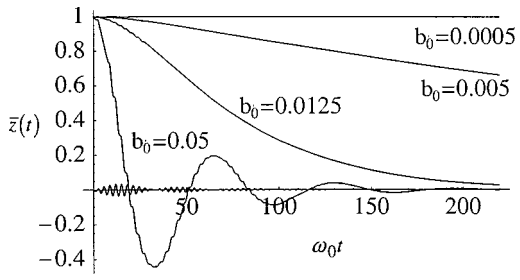

FIG. 1. Time behavior of $\overline{z}(t)$ for several values of the external field strength, as indicated on the plot, with $d=0.05$, $\omega_0=1.0$, and $\Omega=1.0$. Time is measured in units of $1/\omega_0$. The line with the small-amplitude oscillations is the difference between the numerical result and that obtained from Eq. (12) for $b_0=0.05$.

Turning to the case of stronger coupling, Fig. 1 displays a nonexponentially decaying $\overline{z}(t)$ for $b_0=0.0125$. Since $2b_0=d/2$, this is, according to the analytic approximation, a critically damped oscillator. For $b_0=0.05$ the decay is a damped oscillation, reflecting the inversion of the population difference, $\overline{z}(t)$, brought about by the applied field. This strong field result exhibits the damped oscillatory decay as obtained in Eq. (12). The other line in Fig. 1, with the small amplitude oscillations, is the difference between the numerical results and that obtained from Eq. (12), for $b_0=0.05$. Clearly, the analytic result given in Eq. (12) is an excellent approximation to that obtained by numerical solution of Eq. (8).

Once $\overline{z}(t)$ is accurately described, $\overline{\mathcal{P}}_{\rm app}(t)$ will be very close to the numerical result. This feature follows from Eqs. (6), (13) and (14), from which it is evident that the only approximation involved is that already made in obtaining $\overline{z}(t)$. Therefore, the expression in Eqs. (15) and (16) for the power absorbed is essentially the same as that obtained numerically.

There are a number of significant features of $\overline{\mathcal{P}}_{\rm app}(t)$ that arise for stronger fields. The susceptibility corresponding to $\overline{\mathcal{P}}_{\rm app}(t)$ now depends on the strength of the external field and, since our derivation is nonperturbative, includes the effect of the external field to all orders in its strength. Most significantly, operationally, the peaks of the spectral densities are now displaced by $2b_0$, with respect to the detunings $\delta_{\pm}$. In particular, the line-shape functions, for example an I that is close to resonance, and will therefore contribute the most to the power absorbed, have the form

$$I(\omega_0-\Omega-\omega_1)\approx I(\omega_0-\Omega-2b_0)$$
$$=\frac{d/2}{(d/2)^2+(\omega_0-\Omega-2b_0)^2}, \tag{19}$$

where we have noted that $\omega_1\approx 2b_0$ for $2b_0\gg d/2$. As we assume that we are close to resonance in the sense that $\omega_0-\Omega\approx 0$, Eq. (19) shows that the external field strength can produce a significant shift in the position of the resonance.

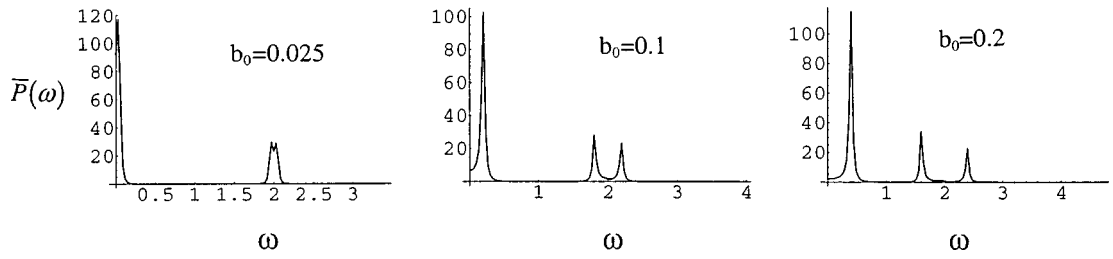

FIG. 2. Power spectrum $\overline{\mathcal{P}}(\omega)$ of $\overline{\mathcal{P}}(t)$ for the indicated b_0 values with $d=0.05$, $\omega_0=1.0$, and $\Omega=1.0$. The analytical $\overline{\mathcal{P}}_{\rm app}(t)$ [cf. Eq. (15)] shows that peaks should appear at the displayed frequencies. The amplitudes of the peaks are also quantitatively predicted by the analytic expression.

The spectral functions are time independent quantities that determine, in part, the time dependence of $\overline{\mathcal{P}}_{\rm app}(t)$. The time dependence of the average power absorbed arises from the finite population change in the system induced by the strong driving field. That the average power absorbed is time dependent is a feature that makes the strong-field result more involved than the LRT limit. However, the analysis can be simplified in several ways. For one, a cycle average of $\overline{\mathcal{P}}_{\rm app}(t)$ reduces the complexity of Eq. (15) considerably as only the C_0 and C_1 coefficient terms (those that only oscillate with ω_1) survive. The time dependence of $\langle\overline{\mathcal{P}}_{\rm app}(t)\rangle$, then, is a damped oscillation at only the one frequency, ω_1.

Another approach is to simply Fourier analyze the complete $\overline{\mathcal{P}}_{\rm app}(t)$. The approximate result of Eq. (15) shows that the frequencies ω_1 and $2\Omega\pm\omega_1$ appear, so a Fourier transform of $\overline{\mathcal{P}}_{\rm app}(t)$ will lead to lines broadened by the dissipation, d, centered at these frequencies. This is clearly seen in Fig. 2, where we display the (un-normalized) power spectrum of the numerically obtained $\overline{P}(t)$. The series of plots is for a fixed value of the dissipation and increasing b_0 values. The low-frequency peak shifts away from zero frequency, and the high-frequency peaks are split more as b_0 increases. The analytic expression in Eq. (15), when Fourier transformed, properly describes both the peak positions and amplitudes displayed in Fig. 2. Figure 3 provides the power spectrum for a larger value of dissipation than in Fig. 2, and shows the increasing broadening engendered by stronger dissipation.

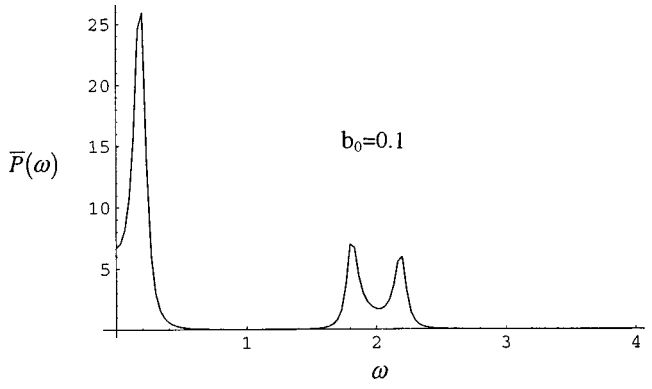

FIG. 3. Power spectrum $\overline{\mathcal{P}}(\omega)$ of $\overline{\mathcal{P}}(t)$ for $b_0=0.1$ with $d=0.1$, $\omega_0=1.0$, and $\Omega=1.0$. The analytical $\overline{\mathcal{P}}_{\rm app}(t)$ [cf. Eq. (15)] shows that the lines should be broadened more than for the smaller value of the dissipation, d, used to construct Fig. 2.

Increasing the value of b_0 for fixed values of the other parameters could be used as a means of generating sufficient data to fit to the analytic form of Eq. (15), and thereby obtaining the value of the dissipation, d. As $\omega_1\approx 2b_0$ and the applied frequency Ω must be much larger than b_0 (for the example in Fig. 2), the low-frequency peak and the high-frequency doublet of the power spectrum must be well separated. Their intensities are on the same scale, approximately. Thus, depending on the desired frequency domain of analysis, optical for Ω, the external field frequency, and roughly infrared for the low-frequency peak around b_0, either regime can be used to provide the same information.

IV. CONCLUDING REMARKS

In this work we have analyzed a model of a two-level system coupled to a dissipative medium and to an external field that induces transitions between the system states. The result presented in Eqs. (15) and (16) is a closed-form solution for $\overline{\mathcal{P}}_{\rm app}(t)$, the average power absorbed by the system, that does not rely on performing perturbation theory in the external field strength b_0. This approximate solution is in good agreement with that generated by numerical solution of the averaged equations of motion. It is remarkable that the entire nonlinear response effect can be so compactly expressed. It would be difficult to obtain this simple result by perturbation theory, as the perturbation theory would have to be carried out to infinite order.

We showed that the time-dependent power absorbed is determined by coefficients that are determined by spectral densities of a Lorentzian form. The centers of the Lorentzians are linear functions of b_0. Thus the spectral densities are centered on frequencies that can be controlled by the external field's strength. This observation suggests that line shapes could be manipulated to, e.g., be of greater intensity in a desired range of applied frequency Ω by the application of stronger external fields than those used in the linear-response regime.

It is also interesting that the use of strong external fields leads to the appearance of the I and J spectral densities, whereas only the I one appears in LRT. Of course, the same information is contained in either spectral density. Note that the coefficients of the low- and high-frequency terms in $\overline{P}(t)$ depend on the same I and J spectral densities, so a measurement in either frequency regime can be used to obtain the complete information.

The calculations presented here can be extended in sev-

eral directions. First, the line shapes obtained here are Lorentzian, due to the assumption of weak coupling $\Delta\tau_c \ll 1$. In polar media, the coupling tends to be stronger and, for the LRT regime, leads to Gaussian spectral densities.[4,5] We have analyzed[15] the technically more demanding strong-coupling case, and find that, again, the spectral density depends on the external field strength. Second, our stochastic Hamiltonian leads to equal population of the levels ($\bar{z} \to 0$) in the long-time limit. For not too strong external field strengths ($b_0 \ll \omega_0$), the long-time behavior should be well described by the Boltzmann distribution. Phenomenologically, this can be accounted for by interpreting $\bar{z}(t)$ as the deviation from its equilibrium value. This would not change the spectral densities I and J that would appear in the modified $\bar{\mathcal{P}}(t)$. Third, when the characteristic medium frequencies are large compared to the temperature, quantum medium effects on the spectral transitions should be evaluated. A tractable route /to these effects is via the spin-boson model, as we shall detail elsewhere.

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[1] J. L. Skinner and W. E. Moerner, J. Phys. Chem. **100**, 13251 (1996).
[2] S. Mukamel *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[3] N. S. Hush, Prog. Inorg. Chem. **8**, 391 (1967); N. Sutin, *ibid.* **30**, 441 (1983).
[4] R. Kubo and Y. Toyozawa, Prog. Theor. Phys. **13**, 160 (1955).
[5] R. A. Marcus, J. Phys. Chem. **93**, 3078 (1989).
[6] J. Ulstrup, *Charge Transfer Processes in Condensed Media* (Springer, Berlin, 1979).
[7] W. T. Pollard and R. A. Mathies, Annu. Rev. Phys. Chem. **43**, 497 (1992).
[8] G. R. Fleming and M. Cho, Annu. Rev. Phys. Chem. **47**, 109 (1996).
[9] W. Domcke and G. Stock, Adv. Chem. Phys. **100**, 1 (1997).
[10] M. Morillo and R. I. Cukier, J. Chem. Phys. **98**, 4548 (1993).
[11] R. I. Cukier and M. Morillo, Chem. Phys. **183**, 375 (1994).
[12] M. Morillo and R. I. Cukier, Phys. Rev. B **54**, 13 962 (1996).
[13] L. D. Zusman, Chem. Phys. **49**, 295 (1980).
[14] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992).
[15] M. Morillo and R. I. Cukier (unpublished).