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Influence of correlated stochastic perturbations on the nonlinear optical properties of a dimer

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The problem of correlated diagonal fluctuations is treated in the particular case of a dimer. Specifically, we analyze the influence of the correlation existing between the fluctuations on different sites. The local fluctuations induce a frequency modulation on the individual monomers. When these fluctuations are correlated, the internal dynamics of the dimer is altered. As a consequence, these intersite correlations give an additional contribution to the linear and nonlinear optical responses of the dimer. While this process has been discussed previously for δ-function-correlated Gaussian-Markovian processes, we consider here the non-δ-function-correlated case. The linear absorption spectrum and the third-order susceptibility in a degenerate-four-wave-mixing experiment are considered in order to emphasize the role of the correlated fluctuations in the linear and nonlinear regimes, respectively.

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I. INTRODUCTION

The theoretical descriptions of nonlinear optical responses of molecular compounds have been the object of numerous works these last few years [1–4]. Depending on the specific properties of the system under investigation, various approaches have been developed. They range from the local-field approximation commonly used in condensed phases [5–9] to the generalized master equation which has been applied successfully to a number of systems [10,11].

In most of the problems concerned with molecules embedded in liquid or solid phases, we are faced with the problem of partitioning the system off into guest molecules and surroundings. The description of the surrounding degrees of freedom can be very different, according to the specific features that one would like to emphasize. The choice of an appropriate description is mainly determined by the nature of the relevant part of the system, i.e., the one playing a fundamental role in the dynamical evolution. Sometimes, it can be a subset of degrees of freedom like in some problems of electronic [12], vibrational [13], or many other types of nonradiative relaxations [14]. In this case, the reduced density-matrix formalism [15] is well adapted to their descriptions. Other times, it can be populations, like in some problems of transport of quantum particles, such as electrons and excitons [1,16] in a surrounding medium. Then, a partition of the density matrix in diagonal and nondiagonal parts like the one proposed in the Mori-Zwanzig formalism [17] is suited best.

Of course, because of the complexity of the systems, at some level approximations must be made in the description, and this is always done to the detriment of the irrelevant parts. Very often however, this partition into relevant and irrelevant parts needs to be modified when physical parameters change in amplitude. This is particularly true in the study of the coherent motion of energy in a linear chain. As the temperature is raised, the coherent motion is disturbed by the influence of phonons, and for very high temperatures a hopping regime is established [18,19]. In these two limiting cases, the description of the relevant degrees of freedom does not rest upon the same physical quantities. Here, the coherences can be done away with in the high-temperature regime.

The limiting low- and high-temperature regimes can be conveniently described by either pure quantum theory or the Pauli master type of equation, respectively. However, a description capable of bridging the gap between these two limiting cases can only be done in the framework of the stochastic approach. This is the point of view taken in the interesting model proposed some years ago by Haken and co-workers [18,19], Reineker [20], and Rackovsky and Silbey [21]. It is based on the δ-function-correlated Gaussian-Markov processes, which account for the influence of the phonons and give rise to fluctuations of the site energies and transfer-matrix elements. This model has been extended quite recently to study the nonlinear optical properties of an aggregate [22]. However, these previous treatments involve an infinite temperature of the bath which can be acceptable for magnetic resonance experiments, but not when dealing with high-frequency molecular vibrations. At lower temperatures, the bath correlation times are expected to be finite, so that the assumption of δ-function-correlated Gaussian-Markov processes must be loosened. To this end, a number of authors have extended the descriptions of dynamical studies to the intermediate regime. They use either dichotomic [23–25] or Gaussian non-δ-function-correlated Markov processes [26–33]. The relations between these models have also been established [34].

Blumen and Silbey [35] studied the optical line shape of an exciton interacting with phonons using a Gaussian-Markov process with nonzero correlation time. But they truncated the cumulant expansion to the second order. This method was shown to be incorrect in the general case by Fox [36,37] and Rips and Capek [38] because all higher-order cumulants are nonvanishing; in fact, this expansion may not even converge. The second-order cumulant expansion is exact in the white-noise limit (zero-correlation time limit) [36,38] and in the vanishing excitonic bandwidth limit (zero static coupling) only [38].

Recently, Dubovsky and Mukamel [39] have analyzed the role of correlations between the local fluctuations on neighboring molecules. While this problem has been handled in the white-noise limit, we will be concerned here with the intermediate regime. For the sake of convenience, this study will be done on a simple dimer system. It has to be stressed that, until these last few years, the exact solution of the stochastic dimer problem was only known for the dichotomic Markov processes [24]. Then, quite recently, Chvosta [40] investigated the absorption line shape and the dynamics of a dimer with stochastic modulation of local energy at just one site by using the dichotomic Markov process and then reaching the Gaussian-Markov regime as a limiting case by summing over stochastic dichotomic Markov processes.

In Sec. II, we describe the dimer model used to study the influence of non-δ-function-correlated fluctuations. Then, in Secs. III and IV, the general formalism is introduced to describe the linear and the nonlinear optical responses. The absorption bandshape and the third-order optical susceptibiltity of a degenerate-four-wave-mixing experiment are introduced to observe these effects. Finally, in Sec. V, we present some numerical simulations and discuss the physical results.

II. DESCRIPTION OF THE DIMER

To study the influence of possible correlations between fluctuations of the transition energy of the individual molecules, we introduce a dimer model composed of two identical molecules interacting through a coupling term V. For the sake of convenience, each monomer is described by a two-level system with electronic gap $\hbar\omega_0$ and parallel transition dipole moments μ_0, as depicted in Fig. 1. The influence of the phonons acting on the dimer is accounted for by a local diagonal stochastic perturbation which induces a frequency modulation of the electronic transition of the individual molecules. While the case of independent diagonal fluctuations has generally been considered, we wish to address the specific problem of correlated fluctuations.

In the local basis set, the Hamiltonian of the dimer takes the form

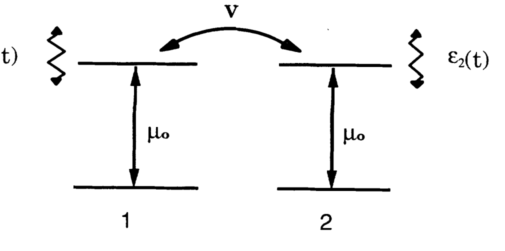

FIG. 1. Energy-level scheme of the dimer in the local basis set.

$$H_{\mathrm{dim}}(t)=H_0+\tilde{H}(t)\ , \tag{2.1}$$

where the zero-order Hamiltonian corresponds to

$$H_0=\hbar\omega_0\sum_{p=1}^{2}|p\rangle\langle p| +2\hbar\omega_0|B_i\rangle\langle B_i|+\hbar V[|1\rangle\langle 2|+|2\rangle\langle 1|]\ , \tag{2.2}$$

if $|B_i\rangle$ stands for the doubly excited state and $|p\rangle$ for the singly excited states on site p of the dimer. The stochastic part of the Hamiltonian is given by

$$\tilde{H}(t)=\sum_{p=1}^{2}\epsilon_p(t)|p\rangle\langle p|+[\epsilon_1(t)+\epsilon_2(t)]|B_i\rangle\langle B_i|\ . \tag{2.3}$$

This fluctuating contribution is assumed to be induced by a Gaussian-Markov process with zero mean value, characterized by single-site correlation functions

$$\langle\epsilon_1(t)\epsilon_1(t')\rangle=\langle\epsilon_2(t)\epsilon_2(t')\rangle=\hbar^2\Delta_0^2e^{-\gamma_0|t-t'|}\ , \tag{2.4}$$

as well as by intersite correlation functions

$$\langle\epsilon_1(t)\epsilon_2(t')\rangle=\langle\epsilon_2(t)\epsilon_1(t')\rangle=\hbar^2\Delta_1^2e^{-\gamma_1|t-t'|}\ . \tag{2.5}$$

This latter correlation function allows for the existence of a common origin of the random forces acting on the individual molecules. Above, we have introduced the notations Δ_i for the amplitudes of the fluctuations and γ_i^{-1} for their corresponding correlation times.

As usual, because of the coupling V, it is convenient to introduce the diagonalized states and their corresponding energies

$$\begin{aligned}|A_i\rangle&=\frac{1}{\sqrt{2}}[(-1)^i|1\rangle+|2\rangle]\ ,\\ \omega_i&=\omega_0+(-1)^iV,\quad i=1,2\ .\end{aligned} \tag{2.6}$$

Of course, the doubly excited state is invariant under this transformation. Therefore, in this new representation, the Hamiltonians take the forms

$$\begin{aligned}H_0&=\hbar\sum_{i=1}^{2}\omega_i|A_i\rangle\langle A_i|+2\hbar\omega_0|B_i\rangle\langle B_i|\ ,\\ \tilde{H}(t)&=\tfrac{1}{2}[\epsilon_1(t)+\epsilon_2(t)][|A_1\rangle\langle A_1|+|A_2\rangle\langle A_2|]\\ &\quad+\tfrac{1}{2}[-\epsilon_1(t)+\epsilon_2(t)][|A_2\rangle\langle A_1|+|A_1\rangle\langle A_2|]\\ &\quad+[\epsilon_1(t)+\epsilon_2(t)]|B_i\rangle\langle B_i|\ .\end{aligned} \tag{2.7}$$

The scheme of energy levels is shown in Fig. 2, and corresponds to a coupling V assumed to be real and negative. In absence of fluctuations, only the symmetric state $|A_2\rangle$ carries oscillator strength because of the transition dipole moment $\sqrt{2}\mu_0$. The states $|A_1\rangle$ and $|A_2\rangle$ are separated by an energy gap equal to $2V$. They are subjected to a nondiagonal fluctuating interaction $1/2[-\epsilon_1(t)+\epsilon_2(t)]$ which may mix them or induce transitions between them [22]. Through this nondiagonal stochastic coupling, part of the oscillator strength is transferred from level $|A_2\rangle$ to level $|A_1\rangle$. It is because of this nondiagonal fluctuation that $\tilde{H}(t)$ does not commute with the H_0 and that the usual cumulant expansion

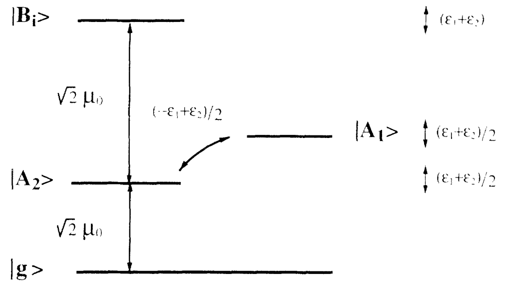

FIG. 2. Diagonal representation of the dimer restricted to the doubly excited states.

cannot yield the exact solution at the second order of the development. Indeed, Fox [36,37] and Rips and Capek [38] have shown that in such a situation all higher-order cumulants do not vanish.

In this work, in order to be able to carry out a meaningful evaluation of linear and nonlinear optical responses for finite correlation times between the stochastic variables, we will restrict ourselves to the strong-coupling limit [22,31] $V \gg \Delta_i$, so that we can neglect the residual stochastic interaction between these levels, as well as the residual oscillator strength that $|A_1\rangle$ borrows from $|A_2\rangle$. In this way, the internal dynamics of the dimer can be restricted to the one of a three-level system $\{|g\rangle, |A_2\rangle, |B_i\rangle\}$ subjected to diagonal fluctuations only and therefore solvable. However, it must be emphasized that we have to deal with a very specific three-level model for which the fluctuations of both excited-state energies are essentially identical (a feature that does not affect the linear response, but plays an important role in third-order optical processes) and depend on the initial intersite correlation in a transparent way.

Let us finally mention that the cumulant expansion up to the second order also yields the exact solution in the limit where the static coupling V vanishes [38], but in such a situation the intersite correlations will not affect the optical responses, which will remain those of two independent molecules.

A similar problem has been considered previously by Dubovsky and Mukamel in the white-noise limit [39]. Here, because the fluctuations are characterized by finite correlation times, the model is valid for any time scale of the system-bath dynamics.

III. STUDY OF THE LINEAR OPTICAL RESPONSE

Though there have been a number of earlier attempts to look at the linear response of a dimer [21,24,25,40,41], an extension of these approaches to nonlinear responses is far from trivial in the case of finite correlation times. It is the aim of this paper to investigate the effect of these finite correlation times as well as those of intersite correlation on the third-order response in the strong-coupling limit where such an extension is feasible. However, for the sake of convenience, it is appropriate to start with the evaluation of the optical line shape. The interest is twofold: first it will enable us to show how the calculations are carried out in the much simpler situation of linear response, and second, it will provide a reference for the algebraic expressions and numerical results of Sec. IV and facilitate the ensuing discussion. The Hamiltonian of the dimer interacting with the laser beam is given by

$$H(t) = H_{\text{dim}}(t) + H_{\text{int}}(t) , \tag{3.1}$$

where the radiation-field Hamiltonian takes the form

$$\begin{aligned} H_{\text{int}}(t) = {} & -\sqrt{2}\mu_0 \mathbf{d}\cdot\mathbf{E}(\mathbf{r},t) \\ & \times [\,|A_2\rangle\langle g| + |g\rangle\langle A_2| + |A_2\rangle\langle B_i| \\ & + |B_i\rangle\langle A_2|\,] . \end{aligned} \tag{3.2}$$

Here, $\mathbf{d}$ stands for the unit vector characterizing the orientation of the dipole moments $\boldsymbol{\mu}_0$. For a steady-state experiment, the electric field corresponds to

$$\mathbf{E}(\mathbf{r},t) = \boldsymbol{\epsilon} E_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{c.c.} , \tag{3.3}$$

where c.c. denotes the complex-conjugate part, and $\omega, \mathbf{k}, \boldsymbol{\epsilon}$ are the frequency, wave vector, and unit polarization vector, respectively.

The linear polarization of the dimer is obtained by first-order time-dependent perturbation theory [42] and can be expressed as the average value of the dipole moment operator

$$\mathbf{P}^{(1)}(\mathbf{r},t) = \text{Tr}[\langle \rho^{(1)}(\mathbf{r},t)\rangle \boldsymbol{\mu}] , \tag{3.4}$$

where the symbols Tr and $\langle\ \rangle$ stand for the trace and the stochastic average, respectively. The contribution to the first-order density matrix with respect to $H_{\text{int}}(t)$ is given by

$$\langle \rho^{(1)}(\mathbf{r},t)\rangle = -\frac{i}{\hbar}\int_{t_i}^{t} dt_1 \langle G(t-t_1) L_{\text{int}}(t_1) \rho(t_i)\rangle , \tag{3.5}$$

where $L_{\text{int}}(t_1)$ is the Liouvillian of the radiation-matter interaction $L_{\text{int}}(t_1) = [H_{\text{int}}(t_1), \ ]$ and $G(t-t_1)$ is defined by

$$\begin{aligned} G(t-t_1) = {} & e^{(-i/\hbar)L_S t} \left[\overleftarrow{T} \exp\left\{ -\frac{i}{\hbar}\int_{t_1}^{t} d\tau\, \tilde{L}_I(\tau) \right\} \right] \\ & \times e^{(i/\hbar)L_S t_1} . \end{aligned} \tag{3.6}$$

Here, $\overleftarrow{T}$ stands for the chronological operator and $\tilde{L}(t)$ for the Liouvillian corresponding to the stochastic part $\tilde{H}(t)$ of the dimer Hamiltonian. The Liouvillian L_S is given by

$$L_S = L_0 - i\hbar\Gamma , \tag{3.7}$$

where L_0 stands for the Liouvillian of the zero-order part H_0 and Γ for the damping Liouville operator. Notice that in Eq. (3.6) we have used the interaction picture

$$\tilde{L}_I(t) = e^{(i/\hbar)L_S t} \tilde{L}(t) e^{-(i/\hbar)L_S t} . \tag{3.8}$$

The additional notations,

$$\begin{aligned} L_{\text{int}}(t) &= -\mathbf{d}\cdot\mathbf{E}(\mathbf{r},t) L_\mu , \\ L_\mu &= \sqrt{2}\mu_0[(\,|A_2\rangle\langle g| + |g\rangle\langle A_2| \\ &\quad + |A_2\rangle\langle B_i| + |B_i\rangle\langle A_2|\,) ,\ ] , \end{aligned} \tag{3.9}$$

have also been introduced for convenience.

Taking advantage of the previous notation, the linear polarization reduces to

$$\mathbf{P}^{(1)}(\mathbf{r},t)=\mathbf{d}[\langle\rho^{(1)}_{gA_2}(\mathbf{r},t)\rangle\mu_{A_2g}+\langle\rho^{(1)}_{A_2g}(\mathbf{r},t)\rangle\mu_{gA_2}]\ . \tag{3.10}$$

The averaged first-order density matrix is deduced from Eq. (3.5), which can be developed into the form

$$\langle\rho^{(1)}_{gA_2}(\mathbf{r},t)\rangle=\frac{i}{\hbar}\mathbf{d}\cdot\boldsymbol{\epsilon}E_0\int_{t_i}^{t}dt_1 e^{-(i/\hbar)L_{SgA_2gA_2}(t-t_1)}\left\langle\overleftarrow{T}\exp\left\{-\frac{i}{\hbar}\int_{t_1}^{t}d\tau\,\tilde{L}_{IgA_2gA_2}(\tau)\right\}\right\rangle[e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t_1)}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t_1)}]L_{\mu gA_2gg}\ . \tag{3.11}$$

The matrix element $\tilde{L}_{IgA_2gA_2}(t)$ reads

$$\tilde{L}_{IgA_2gA_2}(t)=\tilde{L}_{gA_2gA_2}(t)=-\tfrac{1}{2}[\epsilon_1(t)+\epsilon_2(t)]\ . \tag{3.12}$$

Also, the corresponding matrix elements of L_S take the form

$$\begin{aligned}&L_{Sijij}=\hbar(\omega_i-\omega_j)-i\hbar\Gamma_{ijij}\ ,\\&\Gamma_{ijij}=\tfrac{1}{2}(\Gamma_{iiii}+\Gamma_{jjjj})+\Gamma^{(d)}_{ij}\ ,\quad i\neq j\ ,\end{aligned} \tag{3.13}$$

where $\hbar\omega_i$ and $\hbar\omega_j$ denote the energy of the states i and j respectively, Γ_{iiii} and Γ_{jjjj} their radiative decay constants, and $\Gamma^{(d)}_{ij}$ the pure dephasing.

We now have to evaluate the stochastic average. As was stated in Sec. II, we consider the strong coupling case $V \gg \Delta_i$, where we can neglect the stochastic coupling between the $|A_1\rangle$ and $|A_2\rangle$ states of the dimer. The evolution of the resulting three-level system is governed by the operators H_0 and $\tilde{H}(t)$, which are both diagonal, and furthermore, the Liouville operators L_S and $\tilde{L}(t)$ commute in the subspace of $\{|i\rangle\langle j|\}_{i\neq j}$ operators of interest here. Hence, the cumulants of higher order than 2 are strictly vanishing like for scalar Gaussian-Markovian stochastic variables. The first-order term does not contribute because of the statistical properties of the process $\langle\tilde{H}(t)\rangle=0$. Thus, we are led to

$$\begin{aligned}\left\langle\overleftarrow{T}\exp\left\{-\frac{i}{\hbar}\int_{t_1}^{t}d\tau\,\tilde{L}_{gA_2gA_2}(\tau)\right\}\right\rangle&=\exp\left\{\frac{1}{2}\left\langle\left[\frac{-i}{\hbar}\int_{t_1}^{t}d\tau\,\tilde{L}_{gA_2gA_2}(\tau)\right]^2\right\rangle\right\}\\&=\exp\left\{-\frac{1}{\hbar^2}\int_{t_1}^{t}dt'\int_{t_1}^{t'}dt''\langle\tilde{L}_{gA_2gA_2}(t')\tilde{L}_{gA_2gA_2}(t'')\rangle\right\}\\&=\exp\{-\tfrac{1}{2}f(t-t_1)\}\ ,\end{aligned} \tag{3.14}$$

where

$$f(t-t_1)=\sum_{i=0,1}\frac{\Delta_i^2}{\gamma_i^2}[e^{-\gamma_i(t-t_1)}+\gamma_i(t-t_1)-1]\ . \tag{3.15}$$

Inserting Eq. (3.14) into Eq. (3.11), and taking the limit $t_i \rightarrow -\infty$, we obtain the result

$$\begin{aligned}\langle\rho^{(1)}_{gA_2}(\mathbf{r},t)\rangle=&-\frac{i}{\hbar}\sqrt{2}\mu_0E_0\mathbf{d}\cdot\boldsymbol{\epsilon}\\&\times\int_{-\infty}^{t}dt_1e^{(i\omega_2-\Gamma_{gA_2gA_2})(t-t_1)}\\&\times\exp\{-\tfrac{1}{2}f(t-t_1)\}\\&\times[e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t_1)}+e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t_1)}]\ ,\end{aligned} \tag{3.16}$$

if the dimer is initially in its ground state.

Finally, the linear response of the system is obtained by inserting Eq. (3.16) into Eq. (3.10). Furthermore, the polarization can be expanded into the form

$$\mathbf{P}^{(1)}(\mathbf{r},t)=\mathbf{P}^{(1)}(\omega)e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+\mathbf{P}^{(1)}(-\omega)e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\ , \tag{3.17}$$

in order to define the linear optical susceptibility $\chi^{(1)}(\omega)$ by

$$\mathbf{P}^{(1)}(\omega)=\chi^{(1)}(\omega)\boldsymbol{\epsilon}E_0\ . \tag{3.18}$$

Hence, introducing the notation

$$\chi^{(1)}(\omega)=R^{(1)}(\omega)\mathbf{d}\otimes\mathbf{d}\ , \tag{3.19}$$

the final result can be cast into the familiar form

$$\begin{aligned}R^{(1)}(\omega)=&-\frac{2i}{\hbar}\mu_0^2\int_{-\infty}^{t}dt_1\exp\left\{-\left[\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}\right](t-t_1)\right\}\exp\left\{-\frac{\Delta_0^2}{2\gamma_0^2}(e^{-\gamma_0(t-t_1)}-1)-\frac{\Delta_1^2}{2\gamma_1^2}(e^{-\gamma_1(t-t_1)}-1)\right\}\\&\times[e^{[i(\omega_2+\omega)-\Gamma_{gA_2gA_2}](t-t_1)}-e^{[i(-\omega_2+\omega)-\Gamma_{gA_2gA_2}](t-t_1)}]\ .\end{aligned} \tag{3.20}$$

This expression of $R^{(1)}(\omega)$ carries all the information concerning the internal dynamics of the system. For instance, the absorption spectrum is directly related to the imaginary part of $R^{(1)}(\omega)$. One way to carry out the time integration in Eq. (3.20) is to take the series expansion of the exponential function $\exp\{-(\Delta_i^2/2\gamma_i^2)e^{-\gamma_i(t-t_1)}\}$. This leads to

$$R^{(1)}(\omega)=-\frac{2i}{\hbar}\mu_0^2 e^{[\Delta_0^2/2\gamma_0^2+\Delta_1^2/2\gamma_1^2]}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{1}{n!m!}\left[-\frac{\Delta_0^2}{2\gamma_0^2}\right]^n\left[-\frac{\Delta_1^2}{2\gamma_1^2}\right]^m$$
$$\times\left[\frac{1}{-i\omega_2-i\omega+\Gamma_{gA_2gA_2}+\dfrac{\Delta_0^2}{2\gamma_0}+\dfrac{\Delta_1^2}{2\gamma_1}+n\gamma_0+m\gamma_1}-\frac{1}{i\omega_2-i\omega+\Gamma_{gA_2gA_2}+\dfrac{\Delta_0^2}{2\gamma_0}+\dfrac{\Delta_1^2}{2\gamma_1}+n\gamma_0+m\gamma_1}\right] . \tag{3.21}$$

Notice that for $n=m=0$, the above energy denominators are those leading to the usual Markovian line shape. The farther away from the Markovian limit that the parameters put the system, the more terms have to be summed over before the series converges.

IV. NONLINEAR OPTICAL RESPONSE

In this section, we will be concerned with the determination of the nonlinear response of the dimer. Our emphasis will be mainly on the third-order hyperpolarizability $\chi^{(3)}(\omega_s;\omega_\alpha,\omega_\beta,\omega_\nu)$, which characterizes any optical four-wave mixing [6]. For our purpose, three stationary laser beams are required to determine the nonlinear response by a steady-state experiment. Therefore, the total electric field is just a linear combination of fields, similar to the one used in the study of the linear response.

To obtain the expression of the third-order hyperpolarizability, we need to evaluate the third-order contribution of the polarization

$$\mathbf{P}^{(3)}(\mathbf{r},t)=\mathrm{Tr}[\langle\rho^{(3)}(\mathbf{r},t)\rangle\boldsymbol{\mu}] , \tag{4.1}$$

where the third-order contribution to the averaged density matrix can be expressed as

$$\langle\rho^{(3)}(\mathbf{r},t)\rangle=\frac{i}{\hbar^3}\int_{t_i}^{t}dt_1\int_{t_i}^{t_1}dt_2\int_{t_i}^{t_2}dt_3\langle G(t-t_1)L_{\mathrm{int}}(t_1)G(t_1-t_2)L_{\mathrm{int}}(t_2)G(t_2-t_3)L_{\mathrm{int}}(t_3)\rangle\rho(t_i) . \tag{4.2}$$

It is assumed that the dimer is initially in its ground state. It must be mentioned that the factorization assumption cannot be applied here, as would be the case in the white-noise limit or zero-correlation time limit [9,22]. In other words, as a consequence of the finite correlation times, the statistical average has to be taken over the product of propagators $\langle GL_{\mathrm{int}}GL_{\mathrm{int}}GL_{\mathrm{int}}\rangle$ and cannot be broken down to a product of averaged propagators $\langle G\rangle L_{\mathrm{int}}\langle G\rangle L_{\mathrm{int}}\langle G\rangle L_{\mathrm{int}}$. In the evaluation of this statistical average there resides the complexity of calculating nonlinear responses, whereas the knowledge of $\langle G\rangle$ by itself is sufficient for linear responses. By inspection of Eq. (4.2) we see that we need the following matrix elements of the propagator

$$G_{ijij}(t-t')=e^{-[i(\omega_i-\omega_j)+\Gamma_{ijij}](t-t')}\times\left\{\overleftarrow{T}\exp\left[-\frac{i}{\hbar}\int_{t'}^{t}d\tau\,\tilde{L}_{ijij}(\tau)\right]\right\} , \quad i\neq j , \tag{4.3}$$

and

$$G_{gggg}(t-t')=1 ,$$
$$G_{ggA_2A_2}(t-t')=1-e^{-\Gamma_{A_2A_2A_2A_2}(t-t')} , \tag{4.4}$$
$$G_{A_2A_2A_2A_2}(t-t')=e^{-\Gamma_{A_2A_2A_2A_2}(t-t')} .$$

From Eq. (4.1) we see that we have to evaluate the matrix elements of the third-order averaged density matrix $\langle\rho_{gA_2}^{(3)}(\mathbf{r},t)\rangle$ and $\langle\rho_{A_2B_i}^{(3)}(\mathbf{r},t)\rangle$ and their complex conjugate. These matrix elements involve a statistical average over double and triple time-ordered exponentials. Indeed, assuming that the system is initially in its ground state, coherences and/or excited-state populations are created by the interaction L_{int} with the external optical fields. The third-order coherences of interest here are brought about by processes involving three steps. First, we always create a first-order coherence between the ground state and the $|A_2\rangle$ level. Then, we may either create an excited-state population in level $|A_2\rangle$ or built up coherences between $|g\rangle$ and $|B_i\rangle$. A last interaction generates the third-order coherences between $|g\rangle$ and $|A_2\rangle$, $|A_2\rangle$, and $|B_i\rangle$, from which the induced polarization follows. Thus, considering Eqs. (4.2)–(4.4), we end up with a product of two or three time-ordered exponentials.

As an example, we will treat the case of a triple product contributing to $\rho^{(3)}_{gA_2}(\mathbf{r},t)$:

$$\begin{aligned}M(t,t_1,t_2,t_3)=&\Big\langle \left\{\overleftarrow{T}\exp\left[-\frac{i}{\hbar}\int_{t_1}^{t}dt'\tilde{L}_{gA_2gA_2}(t')\right]\right\}\\ &\times\left\{\overleftarrow{T}\exp\left[-\frac{i}{\hbar}\int_{t_2}^{t_1}dt'\tilde{L}_{gB_igB_i}(t')\right]\right\}\left\{\overleftarrow{T}\exp\left[-\frac{i}{\hbar}\int_{t_3}^{t_2}dt'\tilde{L}_{gA_2gA_2}(t')\right]\right\}\Big\rangle\\ &=\exp\left\{\frac{1}{2}\left\langle\left[-\frac{i}{\hbar}\int_{t_1}^{t}dt'\tilde{L}_{gA_2gA_2}(t')-\frac{i}{\hbar}\int_{t_2}^{t_1}dt'\tilde{L}_{gB_igB_i}(t')-\frac{i}{\hbar}\int_{t_3}^{t_2}dt'\tilde{L}_{gA_2gA_2}(t')\right]^2\right\rangle\right\}\,,\end{aligned}\tag{4.5}$$

with the usual restriction $t>t_1>t_2>t_3$. Notice that, though this expression has been obtained by breaking the operators up into their matrix elements, we cannot apply the cumulant expansion up to second order only without considering either the strong-coupling limit or taking $V=0$. Indeed, since the calculation proceeds along the same lines as in Sec. III, it involves the passage from $\tilde{L}(t)$ to $\tilde{L}_I(t)$ in the interaction picture. It is therefore essential that $\tilde{L}(t)$ commutes with L_S in the considered subspace. Hence

$$\begin{aligned}M(t,t_1,t_2,t_3)=&\exp\left\{-\frac{1}{\hbar^2}\int_{t_1}^{t}\int_{t_1}^{t'}dt'dt''\langle\tilde{L}_{gA_2gA_2}(t')\tilde{L}_{gA_2gA_2}(t'')\rangle\right\}\exp\left\{-\frac{1}{\hbar^2}\int_{t_2}^{t_1}\int_{t_2}^{t'}dt'dt''\langle\tilde{L}_{gB_igB_i}(t')\tilde{L}_{gB_igB_i}(t'')\rangle\right\}\\ &\times\exp\left\{-\frac{1}{\hbar^2}\int_{t_3}^{t_2}\int_{t_3}^{t'}dt'dt''\langle\tilde{L}_{gA_2gA_2}(t')\tilde{L}_{gA_2gA_2}(t'')\rangle\right\}\\ &\times\exp\left\{-\frac{1}{\hbar^2}\int_{t_1}^{t}\int_{t_2}^{t_1}dt'dt''\langle\tilde{L}_{gA_2gA_2}(t')\tilde{L}_{gB_igB_i}(t'')\rangle\right\}\\ &\times\exp\left\{-\frac{1}{\hbar^2}\int_{t_1}^{t}\int_{t_3}^{t_2}dt'dt''\langle\tilde{L}_{gA_2gA_2}(t')\tilde{L}_{gA_2gA_2}(t'')\rangle\right\}\\ &\times\exp\left\{-\frac{1}{\hbar^2}\int_{t_2}^{t_1}\int_{t_3}^{t_2}dt'dt''\langle\tilde{L}_{gB_igB_i}(t')\tilde{L}_{gA_2gA_2}(t'')\rangle\right\}\,.\end{aligned}\tag{4.6}$$

Performing the double-time integration, we get

$$M(t,t_1,t_2,t_3)=\exp[-\tfrac{1}{2}f(t-t_1)-\tfrac{1}{2}f(t_2-t_3)-2f(t_1-t_2)]\exp[-\tfrac{1}{2}g(t,t_1,t_2,t_3)-g(t,t_1,t_1,t_2)-g(t_1,t_2,t_2,t_3)]\,,\tag{4.7}$$

where the functions f and g are defined by the expressions

$$\begin{aligned}f(t_m-t_n)&=\sum_{i=0,1}\frac{\Delta_i^2}{\gamma_i^2}[e^{-\gamma_i(t_m-t_n)}+\gamma_i(t_m-t_n)-1]\,,\\ g(t_m,t_n,t_p,t_q)&=-\sum_{i=0,1}\frac{\Delta_i^2}{\gamma_i^2}[e^{-\gamma_it_m}-e^{-\gamma_it_n}][e^{\gamma_it_p}-e^{\gamma_it_q}]\,.\end{aligned}\tag{4.8}$$

The two following products,

$$N_\pm(t,t_1,t_2,t_3)=\exp\{-\tfrac{1}{2}[f(t-t_1)+f(t_2-t_3)\pm g(t,t_1,t_2,t_3)]\}\,,\tag{4.9}$$

appear also in the complete expression of the averaged density-matrix element $\langle\rho^{(3)}_{gA_2}(\mathbf{r},t)\rangle$, which can now be written into the form

$$\begin{aligned}\langle\rho^{(3)}_{gA_2}(\mathbf{r},t)\rangle=&\frac{i}{\hbar^3}\sum_{j=\alpha,\beta,\nu}\sum_{j'=\alpha,\beta,\nu}\sum_{j''=\alpha,\beta,\nu}(\sqrt{2}\mu_0)^3(\mathbf{d}\cdot\boldsymbol{\epsilon}_j)(\mathbf{d}\cdot\boldsymbol{\epsilon}_{j'})\\&\times(\mathbf{d}\cdot\boldsymbol{\epsilon}_{j''})\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\{E_je^{i[\mathbf{k}_j\cdot\mathbf{r}-\omega_jt_1]}+\text{c.c.}\}\\&\times\{E_{j'}e^{i[\mathbf{k}_{j'}\cdot\mathbf{r}-\omega_{j'}t_2)]}+\text{c.c}\}\{E_{j''}e^{i[\mathbf{k}_{j''}\cdot\mathbf{r}-\omega_{j''}t_3]}+\text{c.c.}\}\\&\times e^{(i\omega_2-\Gamma_{gA_2gA_2})(t-t_1)}(2e^{-\Gamma_{A_2A_2A_2A_2}(t_1-t_2)}\{N_+(t,t_1,t_2,t_3)\exp[(i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)]\\&\qquad+N_-(t,t_1,t_2,t_3)\exp[(-i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)]\}\\&\qquad+e^{(2i\omega_0-\Gamma_{gB_igB_i})(t_1-t_2)}M(t,t_1,t_2,t_3)\exp[(i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)])\ . \end{aligned}\tag{4.10}$$

In the same way, one can establish the expression of $\langle\rho^{(3)}_{A_2B_i}(\mathbf{r},t)\rangle$.

Finally, the nonlinear response of the system is obtained by inserting Eq. (4.10) into Eq. (4.1). As is done in the linear regime, we introduce the formal development of the polarization in terms of its Fourier components

$$\mathbf{P}^{(3)}(\mathbf{r},t)=\sum_n[\mathbf{P}^{(3)}_n(\omega_n)e^{i(\mathbf{k}_n\cdot\mathbf{r}-\omega_nt)}+\text{c.c.}]\ ,\tag{4.11}$$

where all the combinations

$$\begin{aligned}&\mathbf{k}_n=\pm\mathbf{k}_j\pm\mathbf{k}_{j'}\pm\mathbf{k}_{j''}\\&\omega_n=\pm\omega_j\pm\omega_{j'}\pm\omega_{j''}\ ,\end{aligned}\tag{4.12}$$

are present, and the indices j, j', and j'' range over α, β, and ν, the optical field indices. Depending on the geometry of the experiment under investigation, a particular combination must be selected. As an example, if we consider the combination $\mathbf{k}_n=\mathbf{k}_\alpha+\mathbf{k}_\beta+\mathbf{k}_\nu$ with $\omega_n=\omega_\alpha+\omega_\beta+\omega_\nu$, we obtain the expression

$$\mathbf{P}^{(3)}_n(\omega_n)=\chi^{(3)}(\omega_n;\omega_\alpha,\omega_\beta,\omega_\nu)\vdots\boldsymbol{\epsilon}_\alpha E_\alpha\boldsymbol{\epsilon}_\beta E_\beta\boldsymbol{\epsilon}_\nu E_\nu\ ,\tag{4.13}$$

where the third-order optical susceptibility takes the form

$$\begin{aligned}&\chi^{(3)}(\omega_n;\omega_\alpha,\omega_\beta,\omega_\nu)\\&\quad=\sum_{\text{perm}}R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)\mathbf{d}\otimes\mathbf{d}\otimes\mathbf{d}\otimes\mathbf{d}\ .\end{aligned}\tag{4.14}$$

The symbol $\sum_{\text{perm}}$ stands for the sum over all the 3! permutations of the fields, because any ordering involving three different fields participates only once. The final result reads

$$\begin{aligned}R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)=&\frac{i}{\hbar^3}(\sqrt{2}\mu_0)^4\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3e^{i\omega_\nu(t-t_1)}e^{i\omega_\beta(t-t_2)}e^{i\omega_\alpha(t-t_3)}\\&\times(\{2e^{(i\omega_2-\Gamma_{gA_2gA_2})(t-t_1)}-e^{[i(-\omega_2+\omega_{B_i})-\Gamma_{A_2B_iA_2B_i}](t-t_1)}\}\\&\times e^{-\Gamma_{A_2A_2A_2A_2}(t_1-t_2)}\{N_+(t,t_1,t_2,t_3)\exp[(i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)]\\&\qquad+N_-(t,t_1,t_2,t_3)\exp[(-i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)]\}\\&\qquad+\{e^{(i\omega_2-\Gamma_{gA_2gA_2})(t-t_1)}-e^{[i(-\omega_2+\omega_{B_i})-\Gamma_{A_2B_iA_2B_i}](t-t_1)}\}\\&\times\{e^{(2i\omega_0-\Gamma_{gB_igB_i})(t_1-t_2)}M(t,t_1,t_2,t_3)\exp[(i\omega_2-\Gamma_{gA_2gA_2})(t_2-t_3)]\}-\text{c.c.})\ .\end{aligned}\tag{4.15}$$

Performing the series expansion for the exponential functions in Eq. (4.15) and then the time integrations, the third-order optical response $R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)$ can be written into the form

$$R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)=\frac{i}{\hbar^3}(\sqrt{2}\mu_0)^4e^{\Delta_0^2/\gamma_0^2+\Delta_1^2/\gamma_1^2}\sum_{\mathcal{N}=0}^{\infty}\frac{1}{m!n!p!q!r!s!m'!n'!p'!q'!r'!s'!}\sum_{\upsilon=1}^{6}R^{(3)}_\upsilon(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)\ ,\tag{4.16}$$

where, for the sake of simplicity, we have introduced the notation $\mathcal{N}\equiv\{m,n,p,q,r,s,m',n',p',r',s'\}$ for the set of summation indices. The various contributions are given in Appendix A. At this stage, we have all the information required to discuss the nonlinear response of the dimer. Because of the complexity of these previous results, this discussion will be done better from the numerical simulations of $R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)$.

V. NUMERICAL CALCULATIONS AND DISCUSSIONS

In the present section, we first investigate the influence of the intersite correlations existing between the fluctuations on different sites on the optical-absorption line shapes of a dimer. Next, the nonlinear optical response and more precisely the third-order hyperpolarizability will be studied.

It has to be mentioned that usually the amplitude modulation Δ_0 is larger than the amplitude of the intersite correlation function Δ_1, and the same is true for the correlation times, so that $\gamma_0^{-1}>\gamma_1^{-1}$. All along, we have chosen $V=-1000$ cm^{-1} and $\omega_0=20\,000$ cm^{-1}. Also, the relaxation parameters stemming from the radiative lifetime are of the order of the nanosecond time scale, and correspond to 10^{-3} cm^{-1}. In fact, they are negligible compared to the stochastic parameters.

We first consider, in the vicinity of the monoexcitonic resonance $\omega_2=\omega_0+V$, the frequency dependence of the imaginary part of $R^{(1)}(\omega)$ given by Eq. (3.21), and noted $\mathrm{Im}\{R^{(1)}(\omega)\}$. In Fig. 3 we have drawn these variations with and without intersite correlations. The values of the parameters Δ_0 and γ_0 are taken from the work of Nibbering *et al.* [43] on molecules of resorufin dissolved in dimethyl sulfoxide at room temperature. However, because these values correspond to fluctuations in the intermediate regime, they will be useful to analyze the influence of the correlated fluctuations on dimers as well. In this picture, the peak heights of the curves are normalized to unity to compare their respective linewidths. We observe that the intersite correlations broaden the absorption spectrum to a sizable extent.

In the particular case of identical correlation times, $\gamma_0^{-1}=\gamma_1^{-1}$, the full width at half maximum (FWHM) increases by 60% compared to the noncorrelated case for the numerical values chosen in the simulation. This increase arises from terms of the type

$$\left\langle\left[\frac{\epsilon_1(t)+\epsilon_2(t)}{2}\right]\left[\frac{\epsilon_1(t')+\epsilon_2(t')}{2}\right]\right\rangle =\frac{\hbar^2}{2}\left[\Delta_0^2e^{-\gamma_0|t-t'|}+\Delta_1^2e^{-\gamma_1|t-t'|}\right], \quad (5.1)$$

involved in the second-order cumulant expansion. In our model, frequency modulations and intersite correlation effects are always additive.

Notice that the absorption spectrum of the dimer can exhibit two different peaks in the case where Δ_i is comparable to the coupling V. In that case, the state $|A_1\rangle$ borrows some oscillator strength from the state $|A_2\rangle$. This process is not negligible when $\Delta_i\simeq V$. In our calculation, because we have $\Delta_i\ll V$, we observe only one peak.

In Fig. 4, the FWHM of $|\mathrm{Im}\{R^{(1)}(\omega)\}|$ is plotted versus Δ_0, for different values of γ_1 for the case $\gamma_1\geq\gamma_0$. With γ_0 being held fixed at 144 cm^{-1}, the one-site fluctuation corresponds to the intermediate regime for the range of values of Δ_0. In addition, the amplitude of the intersite correlation function Δ_1 is chosen to be equal to 80 cm^{-1} because it must be equivalent or smaller than Δ_0. As expected, the FWHM is an increasing function of Δ_0. Besides, we note that for small values of Δ_0 the influence of γ_1 is more pronounced. This is due to the fact that for large values of Δ_0, the one-site modulation governs the dynamical evolution. However, in the fast modulation limit, the frequency modulation becomes dominant and the influence of γ_1 is negligible. Next, in

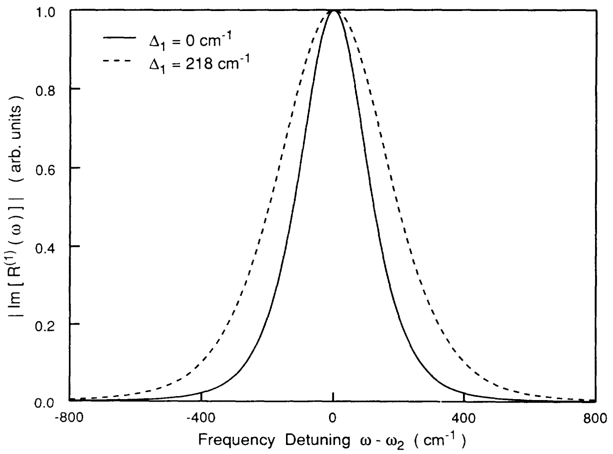

FIG. 3. We represent the variations of the absorption spectra $|\mathrm{Im}\{R^{(1)}(\omega)\}|$ as a function of $(\omega-\omega_2)$. The peak heights are normalized. The cases of correlated and noncorrelated fluctuations are pictured. The values of the parameters are $\Delta_0=218$ cm^{-1}, $\gamma_0=144$ cm^{-1}, and $\gamma_1=144$ cm^{-1}.

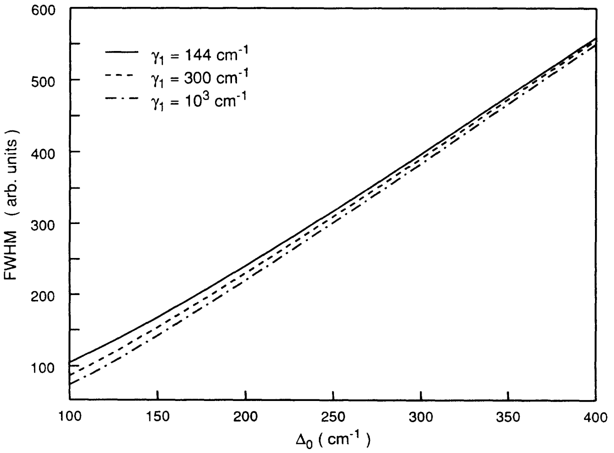

FIG. 4. Dependence of the FWHM of the absorption spectra on the amplitude Δ_0, in the intermediate modulation regime. The cases of various correlation times γ_1^{-1} are sketched. The values of the parameters are $\Delta_1=80$ cm^{-1} and $\gamma_0=144$ cm^{-1}.

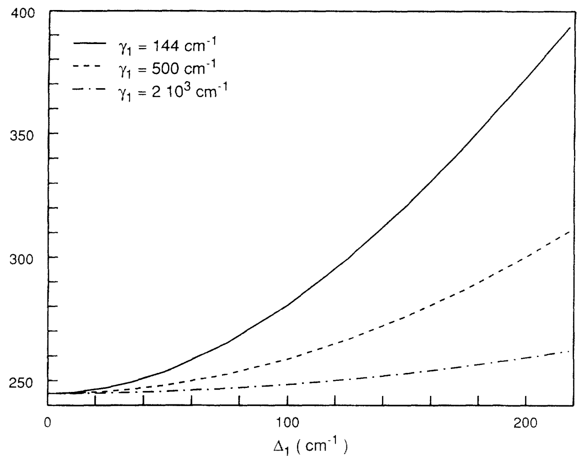

FIG. 5. We represent the FWHM of the absorption spectrum $|\mathrm{Im}\{R^{(1)}(\omega)\}|$ vs Δ_1 for different correlation times γ_1^{-1}. The parameters of the fluctuations are $\Delta_0 = 218$ cm^{-1} and $\gamma_0 = 144$ cm^{-1}.

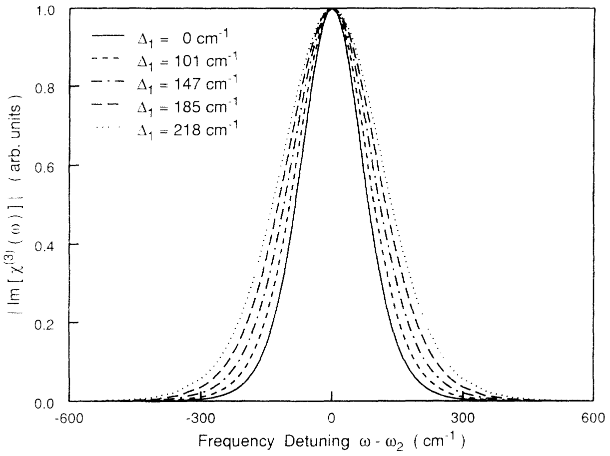

FIG. 6. We represent the frequency dependence of $|\mathrm{Im}\{\chi^{(3)}(\omega;\omega,\omega,-\omega)\}|$ for different values of $(\Delta_0^2+\Delta_1^2)$. The calculation has been done for $\gamma_0=\gamma_1=144$ cm^{-1} and $\Delta_0=218$ cm^{-1}. As in Fig. 3, the peak heights are normalized.

Fig. 5, we study in the intermediate regime of the modulation frequency the influence of the intersite correlation parameter Δ_1 on the FWHM of the absorption bandshape. The numerical simulations have been done for different γ_1. We observe that the influence of γ_1 is more pronounced on the FWHM of the line shape absorption for large values of Δ_1.

We now come to the discussion concerning the influence of the intersite correlations on the nonlinear optical response of the dimer. To do so, a simple degenerate-four-wave mixing experiment will be considered. The quantity of interest will be $\chi^{(3)}(\omega;\omega,\omega,-\omega)$. To simplify, we omit the tensorial notation and reduce its expression to

$$\chi^{(3)}(\omega;\omega,\omega,-\omega)=R^{(3)}(\omega,0,\omega)+R^{(3)}(\omega,0,-\omega) +R^{(3)}(\omega,2\omega,\omega)\ , \tag{5.2}$$

because only these three different terms contribute.

In the following, it will be convenient for the numerical simulations to consider the particular case of identical correlation times $\gamma_0^{-1}=\gamma_1^{-1}$. Notice that it is advantageous to go back to expression (4.15) rather than use the general form given in Appendix A, since there will only be 6 indices to sum over instead of 12. Each of the first two terms on the right-hand side of Eq. (5.2) is made of the six contributions listed in Appendix A. However, only $R_2^{(3)}$ and $R_3^{(3)}$ contribute noticeably for a near resonance experiment. The contribution of the third term on the right-hand side of Eq. (5.2) is negligible because it is strongly nonresonant. Here, for the series expansion to converge reasonably fast, Δ_0^2 and Δ_1^2 cannot exceed a few γ_0^2.

In Fig. 6, we represent $|\mathrm{Im}\{\chi^{(3)}(\omega;\omega,\omega,-\omega)\}|$ versus the detuning parameter $\Delta\omega=\omega-\omega_2$ with γ_0 and Δ_0 being held fixed. The various situations ranging from the limit where there is no intersite correlation at all to the fully correlated case are obtained by letting Δ_1 vary from 0 to Δ_0. We note that by increasing Δ_1, the nonlinear part of the absorption is broadened by about the same relative amount as the linear response. Obviously, because of the strong static coupling, these local and intersite effects are additive, as was the case for the linear absorption. Notice that when the intersite correlation time γ_1^{-1} is shorter than γ_0^{-1}, the additive effect will be weaker.

In the intermediate regime between fast and slow modulation, the line shapes are no longer of the Lorentzian type; however, their exact shapes may be to difficult to determine and distinguish experimentally. If this is the case, then we are left with the full width at half maximum as the main feature to reproduce from a theoretical model. Finally, it turns out that the situation where there is no intersite correlation cannot be differentiated from any other, and any experimental fit reduces to a two-parameter theory only.

VI. CONCLUSION

In this work, we have investigated the linear and nonlinear optical absorption of a dimer whose static coupling is stronger than the stochastic nondiagonal coupling. We have analyzed the role of the intersite correlation. We have shown that both linear and nonlinear regimes exhibit additive effects with respect to their corresponding absorptions, as long as we are in the strong-coupling case. It will be interesting in the following to consider the case of the stronger stochastic couplings. In such a situation, the nondiagonal stochastic coupling must be taken into account rigorously. This, in turn, implies a complete redefinition of the cumulant expansion, which is no longer valid in this case.

APPENDIX A

We have introduced the notation $\mathcal{N}\equiv\{m,n,p,q,r,s,m'n',p',q',r',s'\}$ for the set of the twelve summation indices. The third-order optical susceptibility takes the form

$$R^{(3)}(\omega_\alpha+\omega_\beta+\omega_\nu,\omega_\alpha+\omega_\beta,\omega_\alpha)=\frac{i}{\hbar^3}(\sqrt{2}\mu_0)^4 e^{\Delta_0^2/\gamma_0^2+\Delta_1^2/\gamma_1^2}\sum_{\mathcal{N}=0}^{\infty}\frac{1}{m!n!p!q!r!s!m'!n'!p'!q'!r'!s'!}\sum_{v=1}^{6}R_v^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)\;. \tag{A1}$$

In the following, the notation $\overline{ijkl}$ has been adopted for $(i+j+k+l)$. The various functions of Eq. (A1) are given by

$$\begin{aligned}
R_1^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)=C_1(\mathcal{N})\sum_{\eta=\pm1}\eta\Bigg\{&\left[-i(\eta\omega_2+\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times\left[-i(2\eta\omega_0+\omega_\alpha+\omega_\beta)+\Gamma_{gB_i}+2\frac{\Delta_0^2}{\gamma_0}+2\frac{\Delta_1^2}{\gamma_1}+\overline{mnqr}\gamma_0+\overline{m'n'q'r'}\gamma_1\right]^{-1}\\
&\times\left[-i(\eta\omega_2+\omega_\alpha+\omega_\beta+\omega_\nu)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mrs}\gamma_0+\overline{m'r's'}\gamma_1\right]^{-1}\Bigg\}\;,\\
R_2^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)=2C_2(\mathcal{N})\sum_{n=\pm1}\eta\Bigg\{&\left[-i(\eta\omega_2+\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times\left[-i(\omega_\alpha+\omega_\beta)+\Gamma_{A_2A_2}+\overline{npqr}\gamma_0+\overline{n'p'q'r'}\gamma_1\right]^{-1}\\
&\times\left[-i(\eta\omega_2+\omega_\alpha+\omega_\beta+\omega_\nu)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{nqs}\gamma_0+\overline{n'q's'}\gamma_1\right]^{-1}\Bigg\}\;,\\
R_3^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)=2C_3(\mathcal{N})\sum_{\eta=\pm1}\eta\Bigg\{&\left[i(\eta\omega_2-\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times[-i(\omega_\alpha+\omega_\beta)+\Gamma_{A_2A_2}+\overline{npqr}\gamma_0+\overline{n'p'q'r'}\gamma_1]^{-1}\\
&\times\left[-i(\eta\omega_2+\omega_\alpha+\omega_\beta+\omega_\nu)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{nqs}\gamma_0+\overline{n'q's'}\gamma_1\right]^{-1}\Bigg\}\;,\\
R_4^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)&\\
=-C_1(\mathcal{N})\sum_{\eta=\pm1}\eta\Bigg\{&\left[-i(\eta\omega_2+\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times\left[-i(2\eta\omega_0+\omega_\alpha+\omega_\beta)+\Gamma_{gB_i}+2\frac{\Delta_0^2}{\gamma_0}+2\frac{\Delta_1^2}{\gamma_1}+\overline{mnqr}\gamma_0+\overline{m'n'q'r'}\gamma_1\right]^{-1}\\
&\times\left[i(\eta\omega_2-\eta\omega_{B_i}-\omega_\alpha-\omega_\beta-\omega_\nu)+\Gamma_{A_2B_i}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mrs}\gamma_0+\overline{m'r's'}\gamma_1\right]^{-1}\Bigg\}\;,\\
R_5^{(3)}(\mathcal{N});\omega_\alpha,\omega_\beta,\omega_\nu)&\\
=-C_2(\mathcal{N})\sum_{\eta=\pm1}\eta\Bigg\{&\left[-i(\eta\omega_2+\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times\left[-i(\omega_\alpha+\omega_\beta)+\Gamma_{A_2A_2}+\overline{npqr}\gamma_0+\overline{n'p'q'r'}\gamma_1\right]^{-1}\\
&\times\left[i(\eta\omega_2-\eta\omega_{B_i}-\omega_\alpha-\omega_\beta-\omega_\nu)+\Gamma_{A_2B_i}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{nqs}\gamma_0+\overline{n'q's'}\gamma_1\right]^{-1}\Bigg\}\;,\\
R_6^{(3)}(\mathcal{N};\omega_\alpha,\omega_\beta,\omega_\nu)=-C_3(\mathcal{N})\sum_{\eta=\pm1}\eta\Bigg\{&\left[i(\eta\omega_2-\omega_\alpha)+\Gamma_{gA_2}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{mnp}\gamma_0+\overline{m'n'p'}\gamma_1\right]^{-1}\\
&\times\left[-i(\omega_\alpha+\omega_\beta)+\Gamma_{A_2A_2}+\overline{npqr}\gamma_0+\overline{n'p'q'r'}\gamma_1\right]^{-1}\\
&\times\left[i(\eta\omega_2-\eta\omega_{B_i}-\omega_\alpha-\omega_\beta-\omega_\nu)+\Gamma_{A_2B_i}+\frac{\Delta_0^2}{2\gamma_0}+\frac{\Delta_1^2}{2\gamma_1}+\overline{nqs}\gamma_0+\overline{n'q's'}\gamma_1\right]^{-1}\Bigg\}\;,
\end{aligned} \tag{A2}$$

where C_1, C_2, and C_3 are defined by

$$\begin{aligned} C_1(\mathcal{N}) &= \left[-\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{mnqr}} \left[-\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{m'n'q'r'}} \left[\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{ps}} \left[\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{p's'}} , \\ C_2(\mathcal{N}) &= \left[-\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{mnrs}} \left[-\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{m'n'r's'}} \left[\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{pq}} \left[\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{p'q'}} , \\ C_3(\mathcal{N}) &= \left[-\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{mpqs}} \left[-\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{m'p'q's'}} \left[\frac{\Delta_0^2}{2\gamma_0^2}\right]^{\overline{nr}} \left[\frac{\Delta_1^2}{2\gamma_1^2}\right]^{\overline{n'r'}} . \end{aligned} \tag{A3}$$

Notice that the decay constants have been shortened to

$$\Gamma_{ijij} = \Gamma_{ij} , \quad i \neq j , \quad \Gamma_{iiii} = \Gamma_{ii} . \tag{A4}$$

[1] J. Knoester and S. Mukamel, Phys. Rep. **205**, 1 (1991).

[2] K. Duppen, F. de Haan, E. T. J. Nibbering, and D. A. Wiersma, Phys. Rev. A **47**, 5120 (1993).

[3] E. T. J. Nibbering, thesis, University of Groningen, 1993.

[4] B. D. Fainberg, Opt. Spektrosk. **60**, 120 (1986)]; [Opt. Spectrosc. (USSR) **60**, 74 (1986)]; **68**, 525 (1990) [**68**, 305 (1990)].

[5] C. Flytzanis, in *Quantum Electronics VI,* edited by H. Rabin and C. L. Tang (Academic, New York, 1975).

[6] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).

[7] S. Mukamel, Z. Deng, and J. Grad, J. Opt. Soc. Am B **5**, 804 (1988).

[8] J. Knoester and S. Mukamel, J. Opt. Soc. Am. B **6**, 643 (1988).

[9] J. Knoester and S. Mukamel, Phys. Rev. A **39**, 1899 (1989).

[10] V. M. Kenkre, in *Energy Transfer Processes in Condensed Matter,* edited by B. Di Bartolo (Plenum, New York, 1984).

[11] B. Fain, *Theory of Rate Processes in Condensed Media* (Springer-Verlag, Berlin, 1980).

[12] J. Jortner, S. A. Rice, and R. M. Hochstrasser, Adv. Photochem. **7**, 149 (1969).

[13] A. Nitzan, S. Mukamel, and J. Jortner, J. Chem. Phys. **63**, 200 (1975).

[14] W. E. Howard and E. W. Schlag, in *Radiationless Transitions,* edited by S. H. Lin (Academic, New York, 1980), p. 81.

[15] W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973), Chap. 6.

[16] F. C. Spano and S. Mukamel, Phys. Rev. Lett. **66**, 1197 (1991).

[17] R. Zwanzig, Physica **30**, 1109 (1964).

[18] H. Haken and P. Reineker, Z. Phys. **249**, 253 (1972).

[19] H. Haken and G. Strobl, Z. Phys. **262**, 135 (1973).

[20] P. Reineker, Z. Naturforsch. Teil A **282** (1974).

[21] S. Rackovsky and R. Silbey, Mol. Phys. **25**, 61 (1973).

[22] A. S. Cordan, A. Boeglin, and A. A. Villaeys, Phys. Rev. A **47**, 5041 (1993).

[23] I. Sato and F. Shibata, Physica A **135**, 139 (1986).

[24] B. Kaiser, A. M. Jayannavar, and P. Reineker, J. Lumin. **43**, 73 (1989).

[25] V. Krauss and P. Reineker, Phys. Rev. A **43**, 4182 (1991).

[26] T. Takagahara, E. Hanamura, and R. Kubo, J. Phys. Soc. Jpn. **44**, 728 (1978).

[27] S. Mukamel, Chem. Phys. **37**, 33 (1979).

[28] I. Sato and F. Shibata, Physica A **128**, 551 (1984).

[29] I. Sato and F. Shibata, Physica A **135**, 388 (1986).

[30] K. Faid and R. F. Fox, Phys. Rev. A **34**, 4286 (1986).

[31] F. C. Spano and S. Mukamel, Phys. Rev. A **40**, 5783 (1989).

[32] A. A. Villaeys, A. Boeglin, and S. H. Lin, Phys. Rev. A **44**, 4660 (1991).

[33] A. A. Villaeys and A. Boeglin, Phys. Rev. A **44**, 4671 (1991).

[34] K. Maruyama and F. Shibata, Physica A **149**, 447 (1988).

[35] A. Blumen and R. Silbey, J. Chem. Phys. **69**, 3589 (1978).

[36] R. F. Fox, J. Math. Phys. **15**, 1479 (1974).

[37] R. F. Fox, J. Math. Phys. **20**, 2467 (1979).

[38] I. B. Rips and V. Capek, Phys. Status Solidi B **100**, 451 (1980).

[39] O. Dubovsky and S. Mukamel, J. Chem. Phys. **95**, 7828 (1991).

[40] P. Chvosta, Physica A **178**, 168 (1991).

[41] C. Aslangul, Phys. Rev. B **10**, 4364 (1974).

[42] S. H. Lin, R. G. Alden, R. Islampour, H. Ma, and A. A. Villaeys, *Density Matrix Methods and Femtosecond Processes* (World Scientific, Singapore, 1991).

[43] E. T. J. Nibbering, D. A. Wiersma, and K. Duppen, Phys. Rev. Lett. **66**, 2464 (1991).