PHYSICAL REVIEW A VOLUME 43, NUMBER 9 1 MAY 1991

Non-Markovian effects on optical absorption

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(Received 10 September 1990)

In this paper, we shall report the investigation of the non-Markovian effects of the dynamical process on optical absorption. It will be shown that in steady-state experiments the non-Markovian effects cannot be probed. The non-Markovian effects on the transient pump-probe experiment are treated, and a couple of typical memory functions have been used to obtain the transient band-shape functions. Finally, probe-pulse duration effects on the absorption are considered.

I. INTRODUCTION

In the past decade, experimental and theoretical studies of femtosecond (fs) processes have received considerable attention. They have been very useful in understanding the dynamics of molecules in solution, induced by optical excitation.[1–4] The ultrafast optical dephasing, observed experimentally, takes place on a time scale that corresponds to the correlation time of the interaction with the surrounding bath. Therefore the Markov approximation, often used in the theoretical treatments of fs processes, is no longer valid.

In fact, the validity and limitation of this approximation has begun to be quantitatively studied. Theoretical descriptions have introduced the fast- and slow-modulation limits depending on the relative time scales involved. While doped crystals and semiconductors are usually well described within the fast modulation limit, in solutions it may happen that the dynamics of the bath occurs on the same time scale as the dynamics of the molecule. Then, the slow modulation limit is warranted and the corresponding relaxation is non-Markovian. The case of non-Markovian relaxation processes has been considered in great detail by Mukamel.[5] Depending on the scheme of reduction of the cumulant expansion used to obtain the evolution operator, different types of master equations have been established. They correspond to different statistical properties for the bath. In addition, both schemes termed partial- (POP) and chronological- (COP) ordering prescriptions, reduce to the same Markovian equation in the fast modulation limit.

Quite recently, Nibbering, Duppen, and Wiersma[6] have performed experiments to demonstrate that resonance light scattering can be an interesting alternative to femtosecond transient spectroscopy. By taking advantage of the theory developed by Mukamel, they have analyzed their experimental results in $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ pure electronic transitions of azulene in isopentane and cyclohexane. In this manner, they were able to make a reliable analysis of the line shapes of these transitions. Also, they have fitted their results with the predictions of POP and COP line shapes. They conclude that the solution dynamics of azulene falls in the intermediate modulation regime. However, they were unable to decide which type of master equation was adequate to interpret their experimental results.

From the previous discussions, it appears pertinent to get more information about the bath memory function. Therefore, an important question to be answered is whether steady-state and transient experiments are capable of revealing the non-Markovian effects. Furthermore, it will be of interest to understand the dependence of the absorption band shape on the shape of the various memory functions. In this paper, we will be mainly concerned with these two questions. We will clearly show that steady-state experiments cannot be used to study the non-Markovian effects, and hence consider the case of the optical absorption in a pump-probe experiment.[7] In addition, we will show the possibility of differentiating between various memory functions in the non-Markovian regime, as well as the dependence of the non-Markovian effects on the transient optical absorption,[8,9] especially on optical band shapes.[8,9] For convenience, we choose two-level or pseudo-two-level systems for studying these questions.

The paper is organized as follows. In Sec. II, we present the general evolution of a system undergoing non-Markovian relaxation processes, initially excited by a fs light pulse. Sections III and IV are devoted to the evaluation of the band-shape functions in the steady-state and transient regimes. Then, two different types of memory functions are introduced in Sec. V. Finally, in Sec. VI the probe-pulse duration effects are analyzed.

II. GENERAL THEORY

For a system embedded in a heat bath, the Liouville equation for the density matrix of the system is given by

$$\frac{d\rho(t)}{dt} = -iL_0\rho(t) - iL_1(t)\rho(t) - \int_0^t d\tau\, M(\tau)\rho(t-\tau) , \tag{2.1}$$

where L_0 represents the Liouville operator of the system, $L_1(t)$ denotes the Liouville operator for the interaction $V(t)$ between the system and the radiation field, and $M(\tau)$ is the memory kernel for the dynamics of the system. For simplicity, we shall assume that only two levels need to be considered, as shown in Fig. 1. Notice that

$$\frac{d\rho_{nn}(t)}{dt} = -\frac{i}{\hbar}[V_{nm}(t)\rho_{mn}(t) - \rho_{nm}(t)V_{mn}(t)] - \int_0^t d\tau [M_{nn}^{nn}(\tau)\rho_{nn}(t-\tau) - M_{nn}^{mm}(\tau)\rho_{mm}(t-\tau)] , \tag{2.2}$$

and that

$$\frac{d\rho_{mn}(t)}{dt} = -i\omega_{mn}\rho_{mn}(t) - \frac{i}{\hbar}V_{mn}(t)[\rho_{nn}(t) - \rho_{mm}(t)] - \int_0^t d\tau\, M_{mn}^{mn}(\tau)\rho_{mn}(t-\tau) , \tag{2.3}$$

where, for example,

$$V_{mn}(t) = -(\boldsymbol{\mu}_{mn}\cdot \mathbf{E}_0)(e^{i\omega t} + e^{-i\omega t}) . \tag{2.4}$$

Here, $\boldsymbol{\mu}_{mn}$ denotes the transition dipole moment.

Introducing the rotating frame, and using the rotating-wave approximation (RWA), we define

$$\rho_{mn}(t) = e^{-i\omega t}\sigma_{mn}(t) , \tag{2.5}$$

while the population is kept the same, $\rho_{nn}(t) = \sigma_{nn}(t)$. Then, Eq. (2.4) becomes

$$\frac{d\sigma_{mn}(t)}{dt} = -i(\omega_{mn} - \omega)\sigma_{mn}(t) - \frac{i}{\hbar}V_{mn}[\sigma_{nn}(t) - \sigma_{mm}(t)] - \int_0^t d\tau\, M'^{mn}_{mn}(\tau)\sigma_{mn}(t-\tau) , \tag{2.6}$$

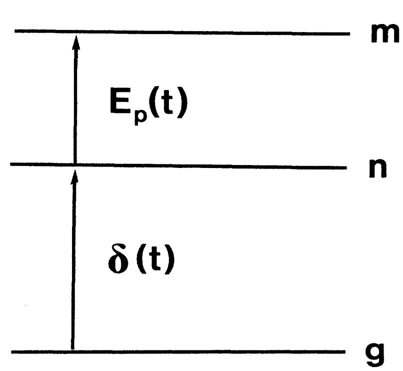

FIG. 1. Scheme of levels used in our study. The pump pulse is described by a δ pulse and $E_p(t)$ is the electric field of the probe pulse.

where the notations

$$V_{mn} = -\boldsymbol{\mu}_{mn}\cdot \mathbf{E}_0 \tag{2.7}$$

and

$$M'^{mn}_{mn}(t) = M^{mn}_{mn}(t)e^{i\omega t} \tag{2.8}$$

have been introduced. It follows that

$$\frac{d\sigma_{nn}(t)}{dt} = \frac{2}{\hbar}\mathrm{Im}[V_{nm}\sigma_{mn}(t)] - \int_0^t d\tau [M_{nn}^{nn}(\tau)\sigma_{nn}(t-\tau) + M_{nn}^{mm}(\tau)\sigma_{mm}(t-\tau)] , \tag{2.9}$$

where Im and Re stand for the imaginary and real parts of the quantity inside the brackets. Applying the Laplace transformation

$$\bar{\sigma}_{mn}(p) = \int_0^\infty dt\, e^{-pt}\sigma_{mn}(t) \tag{2.10}$$

to Eq. (2.6) yields

$$[p + i(\omega_{mn} - \omega) + \bar{M}'^{mn}_{mn}(p)]\bar{\sigma}_{mn}(0) = \sigma_{mn}(0) - \frac{i}{\hbar}V_{mn}[\bar{\sigma}_{nn}(p) - \bar{\sigma}_{mm}(p)] , \tag{2.11}$$

where $\bar{M}'^{mn}_{mn}(p)$, $\bar{\sigma}_{nn}(p)$, and $\bar{\sigma}_{mm}(p)$ represent the Laplace transforms of $\bar{M}'^{mn}_{mn}(t)$, $\sigma_{nn}(t)$, and $\sigma_{mm}(t)$, respectively. From Eq. (2.11), we find

$$\bar{\sigma}_{mn}(p) = \frac{\sigma_{mn}(0)}{p + i(\omega_{mn} - \omega) + \bar{M}'^{mn}_{mn}(p)} + \frac{(i/\hbar)V_{mn}[\bar{\sigma}_{mm}(p) - \bar{\sigma}_{nn}(p)]}{p + i(\omega_{mn} - \omega) + \bar{M}'^{mn}_{mn}(p)} . \tag{2.12}$$

Similarly, applying the Laplace transformation to Eq. (2.9) and substituting Eq. (2.12) into the resulting equation, we obtain

$$p\bar{\sigma}_{nn}(p) - \sigma_{nn}(0) = \bar{\beta}_{mn}(p) + \bar{W}_{mn}(p)[\bar{\sigma}_{mm}(p) - \bar{\sigma}_{nn}(p)] - \bar{M}^{nn}_{nn}(p)\bar{\sigma}_{nn}(p) - \bar{M}^{mm}_{nn}(p)\bar{\sigma}_{mm}(p) , \tag{2.13}$$

where

$$\bar{\beta}_{mn}(p) = \frac{2}{\hbar}\mathrm{Im}\left[\frac{V_{nm}\sigma_{mn}(0)}{p + i(\omega_{mn} - \omega) + \bar{M}'^{mn}_{mn}(p)}\right] \tag{2.14}$$

and

$$\bar{W}_{mn}(p) = \frac{2}{\hbar^2}\mathrm{Re}\left[\frac{|V_{mn}|^2}{p + i(\omega_{mn} - \omega) + \bar{M}'^{mn}_{mn}(p)}\right] . \tag{2.15}$$

Carrying out the inverse Laplace transformation of Eq. (2.13) yields

$$\frac{d\rho_{nn}(t)}{dt}=\beta_{mn}(t)+\int_0^t d\tau\{W_{mn}(\tau)[\rho_{mm}(t-\tau)-\rho_{nn}(t-\tau)]-M_{nn}^{nn}(\tau)\rho_{nn}(t-\tau)-M_{nn}^{mm}(\tau)\rho_{mm}(t-\tau)\}\ . \quad (2.16)$$

It should be noted that in the above treatment, the Markov approximation has not been introduced. In the following sections, we shall discuss the steady-state case and the transient case separately. As will be shown in Sec. III, for the steady-state case the non-Markovian effect does not appear, but it will appear in the transient case.

III. STEADY-STATE CASE

We shall consider the case where $\rho_{nn}(t)+\rho_{mm}(t)=1$. Notice that, for example, we have

$$p\bar{\rho}_{nn}(p)=p\int_0^\infty dt\, e^{-pt}\rho_{nn}(t)dt=\rho_{nn}(0)+\int_0^\infty dt\, e^{-pt}\frac{d\rho_{nn}(t)}{dt}\ . \quad (3.1)$$

Letting $p\to 0$, Eq. (3.1) becomes

$$\lim_{p\to 0}[p\bar{\rho}_{nn}(p)]=\rho_{nn}(0)+\int_0^\infty dt\frac{d\rho_{nn}(t)}{dt}=\rho_{nn}(\infty)\ . \quad (3.2)$$

Here, $\rho_{nn}(\infty)$ denotes the steady-state population. Using the relation

$$\bar{\rho}_{nn}(p)+\bar{\rho}_{mm}(p)=\frac{1}{p}\ , \quad (3.3)$$

we can solve for $\bar{\rho}_{nn}(p)$ from Eq. (2.13)

$$\bar{\rho}_{nn}(p)[p+2\bar{W}_{mn}(p)+\bar{M}_{nn}^{nn}(p)-\bar{M}_{nn}^{mm}(p)]=\rho_{nn}(0)+\bar{\beta}_{mn}(p)+\frac{1}{p}[\bar{W}_{mn}(p)-\bar{M}_{nn}^{mm}(p)]\ . \quad (3.4)$$

It follows that

$$\lim_{p\to 0}p\bar{\rho}_{nn}(p)=\rho_{nn}(\infty)=\frac{\bar{W}_{mn}(0)-\bar{M}_{nn}^{mm}(0)}{2\bar{W}_{mn}(0)+\bar{M}_{nn}^{nn}(0)-\bar{M}_{nn}^{mm}(0)}\ , \quad (3.5)$$

where

$$\bar{W}_{mn}(0)=\frac{2}{\hbar^2}\mathrm{Re}\left[\frac{|V_{mn}|^2}{i(\omega_{mn}-\omega)+\bar{M}_{mn}^{\prime mn}(0)}\right]\ . \quad (3.6)$$

The matrix element $\bar{M}_{mn}^{\prime mn}(0)$ corresponds to the dephasing constant, while $\bar{M}_{nn}^{nn}(0)$ and $-\bar{M}_{nn}^{mm}(0)$ represent the total decay rate of the state n and the rate constant for the transition $m\to n$, respectively.

From Eqs. (3.5) and (3.6), we can see that the non-Markovian effects disappear, and the band-shape function for the steady-state absorption is determined by

$$\alpha_{mn}(\omega)=\frac{\bar{W}_{mn}(0)}{2\bar{W}_{mn}(0)+\bar{M}_{nn}^{nn}(0)-\bar{M}_{nn}^{mm}(0)}\ . \quad (3.7)$$

IV. TRANSIENT CASE

In the ultrafast pumping-probe experiments,[10] one is concerned with the calculation of the susceptibility $\overleftrightarrow{\chi}(\omega)$, which is in turn related to the polarization $\mathbf{P}(t)$. The simplest situation corresponds to a δ pump pulse which prepares the system in some given state, while the probe beam is constantly applied. For the particular case of a purely monochromatic beam

$$\mathbf{E}(t)=\mathbf{E}(\omega)e^{-i\omega t}+\mathbf{E}(-\omega)e^{i\omega t}\ , \quad (4.1)$$

the general relation

$$\mathbf{P}(t)=\int_{-\infty}^{\infty}dt'\overleftrightarrow{\chi}(t-t')\cdot\mathbf{E}(t') \quad (4.2)$$

gives

$$\mathbf{P}(t)=\overleftrightarrow{\chi}(\omega)\cdot\mathbf{E}(\omega)e^{-i\omega t}+\overleftrightarrow{\chi}(-\omega)\cdot\mathbf{E}(-\omega)e^{i\omega t}\ , \quad (4.3)$$

where we have introduced the Fourier transform

$$\overleftrightarrow{\chi}(\omega)=\int_{-\infty}^{\infty}dt\,\overleftrightarrow{\chi}(t)e^{i\omega t}\ . \quad (4.4)$$

Therefore, from the evaluation of the polarization

$$\mathbf{P}(t)=\mathrm{Tr}[\rho(t)\boldsymbol{\mu}]\ , \quad (4.5)$$

the susceptibility is easily deduced. The symbol Tr stands for the trace over the system.

Here, we shall assume that the pumping laser excites the system from the ground state g to the excited state n, and the dynamics of the system in the n state is studied by the probing laser which induces the $n\to m$ transition. At time t after the pumping laser is removed, we have

$$\mathbf{P}(t)=\rho_{nm}(t)\boldsymbol{\mu}_{mn}+\rho_{mn}(t)\boldsymbol{\mu}_{nm}\ . \quad (4.6)$$

Carrying out the inverse Laplace transformation of $\bar{\sigma}_{mn}(p)$ given by Eq. (2.12) yields

$$\rho_{mn}(t)=e^{-i\omega t}L^{-1}\left[\frac{\rho_{mn}(0)}{p+i(\omega_{mn}-\omega)+\bar{M}_{mn}^{\prime mn}(p)}\right]-\frac{i}{\hbar}[\boldsymbol{\mu}_{mn}\cdot\mathbf{E}(\omega)e^{-i\omega t}]\times L^{-1}\left[\frac{\bar{\sigma}_{mm}(p)-\bar{\sigma}_{nn}(p)}{p+i(\omega_{mn}-\omega)+\bar{M}_{mn}^{\prime mn}(p)}\right]\ , \quad (4.7)$$

where L^{-1} denotes the operator for the inverse Laplace transformation. Substituting Eq. (4.7) into Eq. (4.6) and using the expression of the susceptibility valid for a monochromatic field (4.3), we obtain the susceptibility tensor as

$$\overleftrightarrow{\chi}(\omega)=\frac{i}{\hbar}(\boldsymbol{\mu}_{nm}\boldsymbol{\mu}_{mn})L^{-1}\left[\frac{\bar{\sigma}_{nn}(p)-\bar{\sigma}_{mm}(p)}{p+i(\omega_{mn}-\omega)+\bar{M}_{mn}^{\prime mn}(p)}\right]\ . \quad (4.8)$$

For a randomly oriented system, this last expression takes the simplified form

$$\chi(\omega)=\frac{i}{3\hbar}|\boldsymbol{\mu}_{nm}|^2 L^{-1}\left[\frac{\bar{\sigma}_{nn}(p)-\bar{\sigma}_{mm}(p)}{p+i(\omega_{mn}-\omega)+\bar{M}'^{mn}_{mn}(p)}\right]. \quad (4.9)$$

For optical absorption, one is concerned with the imaginary part of $\chi(\omega)$

$$\chi''(\omega)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{nm}|^2 \times\mathrm{Re}\left[L^{-1}\left[\frac{\bar{\sigma}_{nn}(p)-\bar{\sigma}_{mm}(p)}{p+i(\omega_{mn}-\omega)+\bar{M}'^{mn}_{mn}(p)}\right]\right], \quad (4.10)$$

which is easily deduced from the previous expression. This is a general and exact result within the RWA. It will be of interest, in the following, to introduce different types of memory functions.

V. APPLICATIONS TO DIFFERENT MEMORY FUNCTIONS

To show the application, we first consider the following example:[4]

$$M^{mn}_{mn}(t)=\gamma v^2 e^{-\gamma t}, \quad (5.1)$$

which corresponds to a non-Markovian process with correlation time γ^{-1}. Notice that the factor v^2 has the dimension of a frequency. Therefore, the Laplace transform of the corresponding modified $M'^{mn}_{mn}(t)$ operator takes the form

$$\bar{M}'^{mn}_{mn}(p)=\frac{\gamma v^2}{p+\gamma-i\omega}, \quad (5.2)$$

and enables a simple evaluation of the quantity

$$L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\bar{M}'^{mn}_{mn}(p)}\right] =L^{-1}\left[\frac{p+\gamma-i\omega}{(p-\lambda_1)(p-\lambda_2)}\right] =\frac{\lambda_1+\gamma-i\omega}{\lambda_1-\lambda_2}e^{\lambda_1 t}+\frac{\lambda_2+\gamma-i\omega}{\lambda_2-\lambda_1}e^{\lambda_2 t}, \quad (5.3)$$

where

$$\lambda_1=-\tfrac{1}{2}[\gamma+i(\omega_{mn}-2\omega)]+[\tfrac{1}{4}(\gamma-i\omega_{mn})^2-\gamma v^2]^{1/2},$$
$$\lambda_2=-\tfrac{1}{2}[\gamma+i(\omega_{mn}-2\omega)]-[\tfrac{1}{4}(\gamma-i\omega_{mn})^2-\gamma v^2]^{1/2}. \quad (5.4)$$

In this case, by using the convolution product, the imaginary part of $\chi(\omega)$ given by Eq. (4.9) becomes

$$\chi''(\omega)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{mn}|^2\mathrm{Re}\left[\int_0^t d\tau\left[\frac{\lambda_1+\gamma-i\omega}{\lambda_1-\lambda_2}e^{\lambda_1\tau}+\frac{\lambda_2+\gamma-i\omega}{\lambda_2-\lambda_1}e^{\lambda_2\tau}\right][\rho_{nn}(t-\tau)-\rho_{mm}(t-\tau)]\right]. \quad (5.5)$$

In the femtosecond pump-probe experiment, $\rho_{mm}(t)$ is usually negligible and we have the inequality

$$\rho_{mm}(t)\ll\rho_{nn}(t). \quad (5.6)$$

For this case, it is assumed that the dynamical behavior of the system is not affected by the element $M^{nn}_{mm}(\tau)$ associated to the transition $n\rightarrow m$. It is consequently given by the simple relaxation of the state n. Therefore, we approximate the time dependence by

$$\rho_{nn}(t)=e^{-\Gamma^{nn}_{nn}t}, \quad (5.7)$$

and the imaginary part of the susceptibility takes the form

$$\chi''(\omega)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{nm}|^2\mathrm{Re}\left[\frac{\lambda_2+\gamma-i\omega}{(\lambda_2-\lambda_1)(\lambda_2+\Gamma^{nn}_{nn})}(e^{\lambda_2 t}-e^{-\Gamma^{nn}_{nn}t})+\frac{\lambda_1+\gamma-i\omega}{(\lambda_1-\lambda_2)(\lambda_1+\Gamma^{nn}_{nn})}(e^{\lambda_1 t}-e^{-\Gamma^{nn}_{nn}t})\right]. \quad (5.8)$$

Taking into account the definition of the band-shape function $F(\omega)$

$$\chi''(\omega)=F(\omega)e^{-\Gamma^{nn}_{nn}t}, \quad (5.9)$$

we get

$$F(\omega)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{nm}|^2\mathrm{Re}\left[\frac{\lambda_2+\gamma-i\omega}{(\lambda_2-\lambda_1)(\lambda_2+\Gamma^{nn}_{nn})}(e^{(\lambda_2+\Gamma^{nn}_{nn}t)}-1)+\frac{\lambda_1+\gamma-i\omega}{(\lambda_1-\lambda_2)(\lambda_1+\Gamma^{nn}_{nn})}(e^{(\lambda_1+\Gamma^{nn}_{nn})t}-1)\right]. \quad (5.10)$$

In contrary with the previous case, now the band-shape function changes with time. However, when the conditions

$$\mathrm{Re}(\lambda_i+\Gamma^{nn}_{nn})<0,\quad i=1,2 \quad (5.11)$$

are satisfied, and for times long compared to the characteristic times of the system so that

$$e^{\mathrm{Re}[(\lambda_i+\Gamma_{nn}^{nn})t]} \ll 1, \quad i=1,2 \tag{5.12}$$

the band-shape function takes the explicit form

$$F(\omega)=\frac{1}{3\hbar}|\mu_{nm}|^2\frac{\gamma^2 v^2-\omega^2\Gamma_{nn}^{nn}-\Gamma_{nn}^{nn}(\gamma v^2+\Gamma_{nn}^{nn\,2}-2\gamma\Gamma_{nn}^{nn}+\gamma^2)}{[\gamma v^2+\omega(\omega_{mn}-\omega)+\Gamma_{nn}^{nn2}-\gamma\Gamma_{nn}^{nn}]^2+[\gamma(\omega_{mn}-\omega)-\Gamma_{nn}^{nn}(\omega_{mn}-2\omega)]^2} . \tag{5.13}$$

The expression obtained for $F(\omega)$ exhibits a line shape quite different from the usual Lorentzian curve. It shows a resonant variation in the vicinity of $\omega=\omega_{mn}$. In addition, because of the ω^2 dependence of the numerator, the absorption line shape must be asymmetric. In fact, for the values of physical interest here, the variations of the band-shape function near ω_{mn} showed in Figs. 2–5 do not emphasize a strong asymmetry. In Fig. 2, we consider the influence of the correlation time γ^{-1} on the frequency dependence of $F(\omega)$. For small values of γ, we get a narrow absorption spectrum with a linewidth of the order of Γ_{nn}^{nn}. With the increase of γ, the depletion of the upper excited state m broadens the resonance from Γ_{nn}^{nn} to $|(v_2-\Gamma_{nn}^{nn})|$ in the Markovian case. The reduction by Γ_{nn}^{nn} of the broadening v^2 expected in this limit is typical of two-level systems driven by stationary beams when the lower excited state is unstable. This narrowing phenomenon due to the linewidth of the lower excited state is well known and has been discussed previously.[11] In addition to the broadening, we observe a shift of the resonance. This frequency shift $\Delta\omega$ depends approximately on γ as

$$\Delta\omega=\frac{\gamma\omega_{mn}(v^2-\Gamma_{nn}^{nn})}{\omega_{mn}^2-\gamma^2} .$$

Therefore, the shift decreases for increasing values of γ. Figure 3 shows the same variations but for different values of v^2. Here, the linewidth is less affected because we are far from the Markovian regime. However, we observe a resonance shift which clearly results from the coupling of the system with the bath. Finally, in Fig. 4, the influence of the total decay rate of state n is analyzed. We note an obvious broadening of the resonance with the increase of Γ_{nn}^{nn} since the values of γ considered in the numerical simulation correspond to a strong non-Markovian case.

In the second example, we will consider a memory function containing a modulation term given by the expression[12]

$$M_{mn}^{\prime mn}(t)=\gamma v^2 e^{(-\gamma+i\omega)t}(1+a\cos\omega_{mn}t) . \tag{5.14}$$

Its Laplace transform takes the simple form

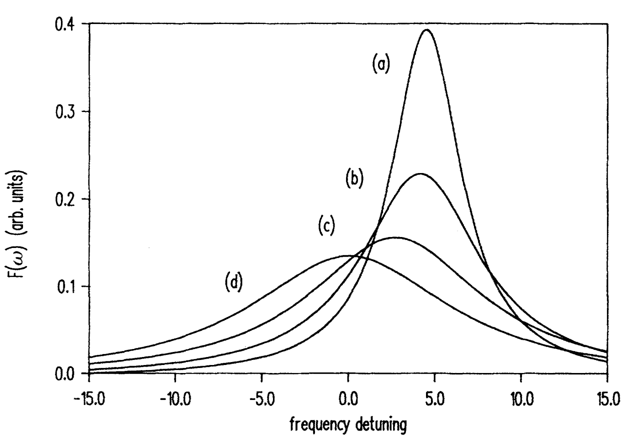

FIG. 2. We represent the variation of the band-shape function $F(\omega)$ with the frequency detuning $(\omega-\omega_{mn})$ for different correlation times γ^{-1}. The curves $(a-d)$ are obtained for increasing values of $\gamma=10^3$, 1.5×10^3, 3×10^3 and 10^5, respectively. The other values are $\omega_{mn}=10^3$, $\Gamma_{nn}^{nn}=2$, and $v=3$.

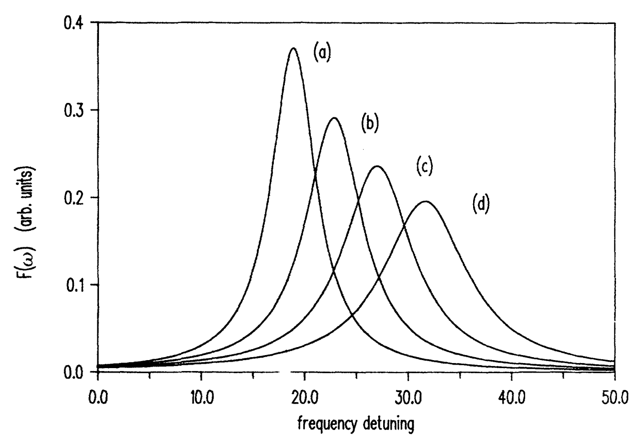

FIG. 3. Frequency-detuning dependence of the band-shape function $F(\omega)$ for various amplitudes $v=10$, 11, 12, and 13, respectively. The other values are $\omega_{mn}=10^3$, $\Gamma_{nn}^{nn}=1$, and $\gamma=2\times10^2$.

$$\overline{M}\,'^{mn}_{mn}(p)=\gamma v^2\left[\frac{1}{p+\gamma-i\omega}+\frac{a}{2}\left[\frac{1}{p+\gamma-i(\omega+\omega_{mn})}+\frac{1}{p+\gamma-i(\omega-\omega_{mn})}\right]\right] \tag{5.15}$$

and enables us to express the required inverse Laplace transform as

$$L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\right]=\frac{(\lambda_1+\mu_1)(\lambda_1+\mu_2)(\lambda_1+\mu_3)}{(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)}e^{\lambda_1 t}+\frac{(\lambda_2+\mu_1)(\lambda_2+\mu_2)(\lambda_2+\mu_3)}{(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)}e^{\lambda_2 t}$$
$$+\frac{(\lambda_3+\mu_1)(\lambda_3+\mu_2)(\lambda_3+\mu_3)}{(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)(\lambda_3-\lambda_4)}e^{\lambda_3 t}+\frac{(\lambda_4+\mu_1)(\lambda_4+\mu_2)(\lambda_4+\mu_3)}{(\lambda_4-\lambda_1)(\lambda_4-\lambda_2)(\lambda_4-\lambda_3)}e^{\lambda_4 t}\,. \tag{5.16}$$

In the previous expression, the quantities $(\lambda_1,\lambda_2,\lambda_3,\lambda_4)$ are the roots of the equation

$$(p+\mu_1)(p+\mu_2)(p+\mu_3)(p+\mu_4)+\gamma v^2(p+\mu_2)(p+\mu_3)+\frac{\gamma v^2 a}{2}[(p+\mu_1)(p+\mu_3)+(p+\mu_1)(p+\mu_2)]=0\,, \tag{5.17}$$

and the following notations have been introduced:

$$\begin{aligned}\mu_1&=\gamma-i\omega\,,\\ \mu_2&=\gamma-i\omega-i\omega_{mn}\,,\\ \mu_3&=\gamma-i\omega+i\omega_{mn}\,,\\ \mu_4&=-i\omega+i\omega_{mn}\,.\end{aligned} \tag{5.18}$$

The imaginary part of the susceptibility is now given by

$$\chi''(\omega)=\frac{1}{3\hbar}|\mu_{mn}|^2\mathrm{Re}\left[\int_0^t d\tau\, L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\right][\rho_{nn}(t-\tau)-\rho_{mm}(t-\tau)]\right]\,. \tag{5.19}$$

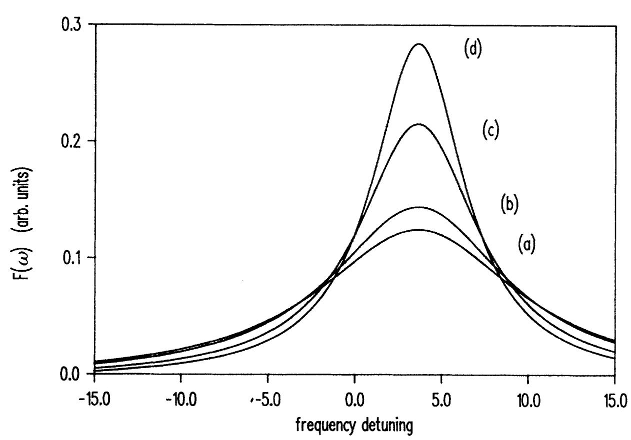

FIG. 4. Frequency-detuning dependence of the band-shape function $F(\omega)$ for different Γ^{nn}_{nn}. Again, the curves $(a-d)$ correspond to the values $\Gamma^{nn}_{nn}=0.1$, 1, 3, and 4, respectively. The other values are $\omega_{mn}=10^3$, $\gamma=2\times10^3$, and $v=3$.

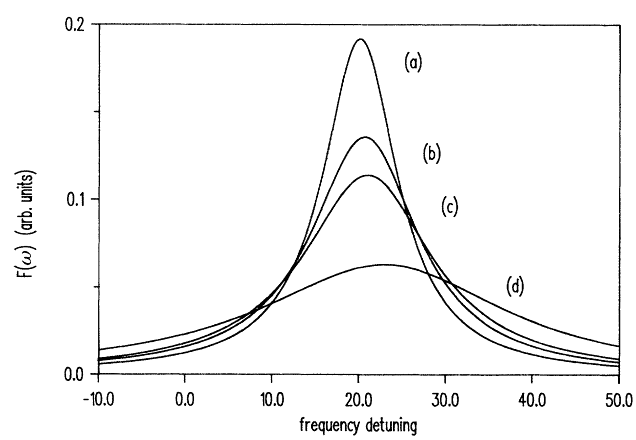

FIG. 5. Frequency-detuning dependence of the band-shape function $F(\omega)$ for different amplitudes of the modulation of the memory function. Here, the various curves $(a-d)$ correspond to the increasing values of $a=0.05$, 0.08, 0.1, and 0.2. The other parameters are $\omega_{mn}=10^3$, $\Gamma^{nn}_{nn}=1$, $v=2$, and $\gamma=140$.

Using the same assumption (5.6) and (5.7) introduced in the first example, we get

$$\chi''(\omega)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{mn}|^2\mathrm{Re}\left[\frac{(\lambda_1+\mu_1)(\lambda_1+\mu_2)(\lambda_1+\mu_3)}{(\lambda_1+\Gamma_{nn}^{nn})(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)}(e^{\lambda_1 t}-e^{\Gamma_{nn}^{nn}t}) + \frac{(\lambda_2+\mu_1)(\lambda_2+\mu_2)(\lambda_2+\mu_3)}{(\lambda_2+\Gamma_{nn}^{nn})(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)}(e^{\lambda_2 t}-e^{\Gamma_{nn}^{nn}t}) + \frac{(\lambda_3+\mu_1)(\lambda_3+\mu_2)(\lambda_3+\mu_3)}{(\lambda_3+\Gamma_{nn}^{nn})(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)(\lambda_3-\lambda_4)}(e^{\lambda_3 t}-e^{\Gamma_{nn}^{nn}t}) + \frac{(\lambda_4+\mu_1)(\lambda_4+\mu_2)(\lambda_4+\mu_3)}{(\lambda_4+\Gamma_{nn}^{nn})(\lambda_4-\lambda_1)(\lambda_4-\lambda_2)(\lambda_4-\lambda_3)}(e^{\lambda_4 t}-e^{\Gamma_{nn}^{nn}t})\right] \quad (5.20)$$

Again, from this expression, the band-shape function will be time dependent. For

$$\mathrm{Re}(\lambda_i+\Gamma_{nn}^{nn})<0, \quad i=1,4 \quad (5.21)$$

and times long enough, the exponential decaying terms can be neglected. Consequently, the band-shape function takes the final form

$$F(\omega)=-\frac{1}{3\hbar}|\boldsymbol{\mu}_{mn}|^2\mathrm{Re}\left[\frac{(\lambda_1+\mu_1)(\lambda_1+\mu_2)(\lambda_1+\mu_3)}{(\lambda_1+\Gamma_{nn}^{nn})(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)} + \frac{(\lambda_2+\mu_1)(\lambda_2+\mu_2)(\lambda_2+\mu_3)}{(\lambda_2+\Gamma_{nn}^{nn})(\lambda_2-\lambda_1)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)} + \frac{(\lambda_3+\mu_1)(\lambda_3+\mu_2)(\lambda_3+\mu_3)}{(\lambda_3+\Gamma_{nn}^{nn})(\lambda_3-\lambda_1)(\lambda_3-\lambda_2)(\lambda_3-\lambda_4)} + \frac{(\lambda_4+\mu_1)(\lambda_4+\mu_2)(\lambda_4+\mu_3)}{(\lambda_4+\Gamma_{nn}^{nn})(\lambda_4-\lambda_1)(\lambda_4-\lambda_2)(\lambda_4-\lambda_3)}\right]. \quad (5.22)$$

On Fig. 5, the frequency dependence of $F(\omega)$ is represented for different values of the modulation parameter a. When the modulation is very weak, we obtain the same curves previously described. For increasing values of a, the modulation gives rise to a broadening of the band-shape function. Of course, in this case it is not easy to relate this variation to the analytical dependence of the parameters.

VI. PROBE DURATION EFFECT

In the previous sections of this paper, it has been assumed that the probe field is constantly applied and gives rise to an interaction described by relation (2.4). However, in a real experiment, the probe beam is usually pulsed and its interaction with the material system takes the form

$$V_{mn}(t)=-\boldsymbol{\mu}_{mn}\cdot[\mathbf{E}(\omega)e^{-i\omega t}+\mathbf{E}(-\omega)e^{i\omega t}]A(t)\ , \quad (6.1)$$

where $A(t)$ represents the time-dependent amplitude of

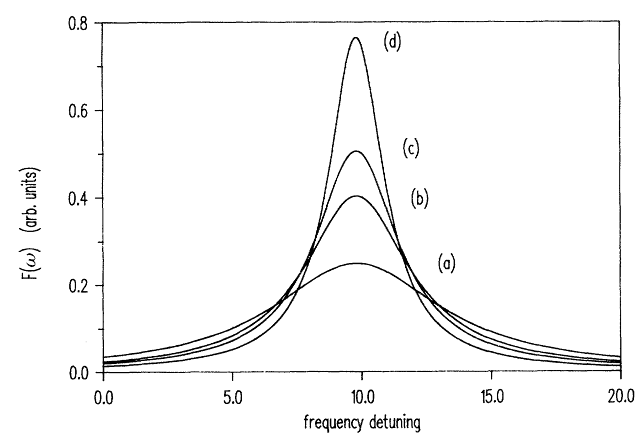

FIG. 6. Influence of the probe-pulse duration on the frequency dependence of the band-shape function. The various curves $(a-d)$ have been obtained for the values $T_p=0.5$, 0.8, 1, and 1.5, respectively. The other values are $\omega_{mn}=10^3$, $\Gamma_{nn}^{nn}=1$, $\gamma=10^2$, $v=10$, and $t=t_p$.

the probe field. Therefore, to account for the probe-duration effects,[13] the dynamics of the system must be evaluated again by including the new interaction given by relation (6.1). Now, the Laplace transform of Eq. (2.6) takes the form

$$[p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)]\overline{\sigma}_{mn}(p)=\sigma_{mn}(0)-\frac{i}{\hbar}V_{mn}\int_0^{\infty}dt\,e^{-pt}A(t)\times[\sigma_{nn}(t)-\sigma_{mm}(t)]\ , \qquad (6.2)$$

where $V_{mn}=-\boldsymbol{\mu}_{mn}\cdot\mathbf{E}(\omega)$ and the required nondiagonal density matrix elements are easily deduced

$$\overline{\sigma}_{mn}(p)=\frac{\sigma_{mn}(0)}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}+\frac{(i/\hbar)V_{mn}}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\times\int_0^{\infty}dt\,e^{-pt}A(t)[\sigma_{mm}(t)-\sigma_{nn}(t)]\ . \qquad (6.3)$$

Therefore, the time dependence of the density matrix results in the form

$$\rho_{mn}(t)=e^{-i\omega t}L^{-1}\left[\frac{\rho_{mn}(0)}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\right]-\frac{i}{\hbar}[\boldsymbol{\mu}_{mn}\cdot\mathbf{E}(\omega)e^{-i\omega t}]\times L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\int_0^{\infty}dt\,e^{-pt}A(t)[\sigma_{mm}(t)-\sigma_{nn}(t)]\right]\ . \qquad (6.4)$$

By following the same procedure previously developed for stationary beams, we deduce the corresponding susceptibility. Nevertheless, because of the pulsed nature of the probe beam, we require the generalized susceptibility formalism. It has been of considerable interest in the recent developments of the theory of real-time femtosecond experiments.[8–10,14] In the time-frequency representation of the generalized susceptibility, we have

$$\mathbf{P}(t)=\overleftrightarrow{\chi}(\omega,t)\mathbf{E}(\omega)e^{-i\omega t}+\overleftrightarrow{\chi}(-\omega,t)\mathbf{E}(-\omega)e^{i\omega t}\ . \qquad (6.5)$$

If we introduce the expression (6.4) of $\rho_{mn}(t)$ into the definition (4.6) of the polarization and identify with relation (6.5), we obtain the expression of the generalized susceptibility into the form

$$\overleftrightarrow{\chi}(\omega,t)=-\frac{i}{\hbar}\boldsymbol{\mu}_{nm}\boldsymbol{\mu}_{mn}L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\int_0^{\infty}dt\,e^{-pt}A(t)[\sigma_{mm}(t)-\sigma_{nn}(t)]\right]\ . \qquad (6.6)$$

In order to get an explicit expression of the generalized susceptibility, we introduce the simple form

$$A(t)=e^{-2|t-t_p|/T_p} \qquad (6.7)$$

for the probe field envelope. Here, t_p and T_p are the probing time and coherence time of the pulse. Therefore, for a randomly oriented system, we finally get for the imaginary part of the generalized susceptibility

$$\chi''(\omega,t)=\frac{1}{3\hbar}|\boldsymbol{\mu}_{mn}|^2\mathrm{Re}\left[L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\int_0^{\infty}dt\,e^{-pt}A(t)e^{-\Gamma^{nn}_{nn}t}\right]\right]\ , \qquad (6.8)$$

where the assumptions (5.6) and (5.7) have been introduced. The Laplace transform can be calculated by taking advantage of the convolution product. It gives

$$L^{-1}\left[\frac{1}{p+i(\omega_{mn}-\omega)+\overline{M}\,'^{mn}_{mn}(p)}\int_0^{\infty}dt\,e^{-pt}A(t)e^{-\Gamma^{nn}_{nn}t}\right]=\int_0^{t}d\tau\left[\frac{\lambda_1+\gamma-i\omega}{\lambda_1-\lambda_2}e^{\lambda_1 t}+\frac{\lambda_2+\gamma-i\omega}{\lambda_2-\lambda_1}e^{\lambda_2 t}\right]A(t-\tau)e^{-\Gamma^{nn}_{nn}(t-\tau)}\ , \qquad (6.9)$$

where we have introduced the Laplace transform previously evaluated and given by relations (5.3) and (5.4). At this stage, $\chi''(\omega,t)$ must be related to the band-shape function. In Sec. V we have described the absorption of energy per unit time Q in terms of the imaginary part of the susceptibility. This result, well known in classical physics,[15] is still valid for steady-state regimes in quantum cases.[16] Recently, it has been extended to non-steady-state regimes into the form[10]

$$Q=i\omega\chi''(\omega,t)|E(\omega)|^2A(t)\ , \qquad (6.10)$$

for isotropic systems. Therefore, it is still possible to define a band-shape function, as done previously in relation (5.9). From the analytical expression of $A(t)$ and looking, for the sake of simplicity, at time $t=t_p$, we get

$$\chi''(\omega,t)=\frac{1}{3\hbar}|\mu_{mn}|^2 e^{-\Gamma_{nn}^{nn}t_p}\mathrm{Re}\left[\int_0^{t_p}d\tau\left[\frac{\lambda_1+\gamma-i\omega}{\lambda_1-\lambda_2}e^{\lambda_1 t}+\frac{\lambda_2+\gamma-i\omega}{\lambda_2-\lambda_1}e^{\lambda_2 t}\right]\exp\left[\Gamma_{nn}^{nn}-\frac{2}{T_p}\right]\tau\right] . \tag{6.11}$$

Performing the time integration, we obtain for the absorption band shape the expression

$$F(\omega,t_p)=\frac{1}{3\hbar}|\mu_{nm}|^2\mathrm{Re}\left\{\frac{\lambda_2+\gamma-i\omega}{(\lambda_2-\lambda_1)\left[\lambda_2+\Gamma_{nn}^{nn}-\frac{2}{T_p}\right]}\left[\exp\left[\lambda_2+\Gamma_{nn}^{nn}-\frac{2}{T_p}\right]t_p-1\right]+\frac{\lambda_1+\gamma-i\omega}{(\lambda_1-\lambda_2)\left[\lambda_1+\Gamma_{nn}^{nn}-\frac{2}{T_p}\right]}\left[\exp\left[\lambda_1+\Gamma_{nn}^{nn}-\frac{2}{T_p}\right]t_p-1\right]\right\} , \tag{6.12}$$

which is quite similar to the one obtained in the transient case, but with a stationary probe beam. This situation is recovered here, in the limit $T_p=\rightarrow\infty$. Again, for times t_p long enough, the decaying exponential terms are negligible. Therefore, the influence of the probe-pulse duration is quite easy to understand in terms of its corresponding spectral distribution. It gives rise to a broadening of the absorption band shape which increases as the duration of the pulse decreases. This is what is observed in Fig. 6, where the cases of various pulse durations have been considered.

VII. CONCLUSION

In this work we have been concerned mainly with the dynamics of non-Markovian systems which are usually studied by pump-probe spectroscopy. In these experiments the excitation by an ultrashort laser pulse prepares the molecule in a given state, and the subsequent dynamics is tested by the absorption of the probe pulse. It has been established that no information can be obtained about the non-Markovian character of the system in the steady-state regime. However, in the transient case the non-Markovian behavior can be observed and a couple of memory functions have been introduced to analyze the influence of their characteristic parameters on the band-shape function. Finally, the effects of the probe-pulse duration have been studied and result on a simple broadening of the band-shape function. While this study has been only done for the simpler memory function, similar results can be expected in other situations.

ACKNOWLEDGMENTS

Arizona State University Center for the Study of Early Events in Photosynthesis is funded by the U.S. Department of Energy (U.S. DOE) Grant No. DE-FG02-88ER1969 as part of the U.S. Department of Agriculture–U.S. DOE–National Science Foundation (NSF) Plant Science Center Program. This work was supported in part by NSF.

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