

Influence of Non-Markovian Effects in Degenerate Four-Wave-Mixing Processes

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In this work, we analyze the influence of non-Markovian effects on a pulsed time-delayed four-wave-mixing experiment. By using a perturbative approach the density matrix equations are solved for a medium modeled by two-level systems and excited by short pulses. We show that the intensity of the diffracted light can be expressed as a simple function of the bath memory function. This demonstrates the interest of such an experiment to get information on the bath.

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Introduction.— In the last decade, femtosecond spectroscopy has received considerable attention and is today a powerful tool to study the optical dynamics of molecules in solution [1–5]. These experiments show that the loss of optical coherence can take place on a time scale that corresponds to the correlation time of the interaction with the surrounding bath. In this case, the Markov approximation often used in the theoretical treatment of femtosecond processes is no longer valid.

Theoretical descriptions have already been made to study the validity and limitation of this approximation. In particular, two types of master equations using different ordering prescriptions and known as POP and COP [6] have been used to calculate the non-Markovian line-shape function. These equations correspond to different statistical properties of the bath. Using this theoretical approach, Nibbering, Duppen, and Wiersma [7] proposed that resonance light scattering can be an alternative to femtosecond transient spectroscopy. But they were unable to decide which type of master equation was adequate to interpret their experimental results. Recently, theoretical studies [8] have been made to analyze the non-Markovian effects of the dynamical processes on optical absorption. They show that in the transient case, band-shape functions can be used to get information about the bath memory function. A couple of typical memory functions have been used to demonstrate this influence. In addition, in many approaches related to this problem, a number of analytical functions have been required to characterize the bath. These dependences are introduced either empirically or as resulting from microscopic models. For this reason, the physical results that have been established are dependent on the particular models.

It is the purpose of this work to show that information concerning the bath memory function can be obtained by analyzing the diffracted light obtained in a forward degenerate four-wave-mixing experiment [9]. These time-delayed four-wave-mixing techniques are a helpful tool to

study fast relaxation and dephasing processes [10,11]. We will show that the intensity of the diffracted light observed in such an experiment is proportional to a simple expression of the bath memory function. As a first step, we start with the equations of the density matrix obtained in the rotating-wave approximation and including a memory kernel for the dynamics of the system modeled by homogeneously broadened two-level systems excited by short pulses. Using perturbative techniques up to the third order we give a general expression of the third-order contributions to the coherences. As a second step, we apply this general result to the case of the forward degenerate four-wave-mixing experiment. In our theoretical approach no assumptions are introduced on the analytical form of the bath memory function. This point makes our results quite general with respect to the bath memory function and independent of its analytical form.

The feasibility of the proposed experiment is mainly restricted by the conditions on the pulse durations. We assume that they are shorter than any characteristic time of the medium and shorter than the correlation time of the bath memory function. This can only be achieved by using femtosecond sources. For instance, the correlation time of the bath for the $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ electronic transition of azulene in isopentane and cyclohexane are respectively 25 and 13 fs [7].

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

$$\frac{d\rho(t)}{dt} = -iL_0\rho(t) - iL_1(t)\rho(t) - \int_0^t M(\tau)\rho(t-\tau)d\tau, \quad (1)$$

where L_0 represents the Liouville operator of the system, L_1 the Liouville operator for the interaction $V(t)$ between the system and the radiation field, and $M(t)$ is the memory kernel for the dynamics of the system. The evolution of the density matrix elements can be expressed as

$$\frac{d\rho_{nn}(t)}{dt} = -\frac{i}{\hbar}[V_{nm}(t)\rho_{mn}(t) - \rho_{nm}(t)V_{mn}(t)] - \int_0^t d\tau [M_{nn}^{nn}(\tau)\rho_{nn}(t-\tau) - M_{nn}^{mm}(\tau)\rho_{mm}(t-\tau)], \quad (2)$$

$$\frac{d\rho_{nm}(t)}{dt} = -i\omega_{nm}\rho_{nm}(t) - \frac{i}{\hbar}V_{mn}(t)[\rho_{nn}(t) - \rho_{mm}(t)] - \int_0^t d\tau M_{nn}^{nm}(\tau)\rho_{nn}(t-\tau), \quad (3)$$

where ω_{mn} denotes the transition frequency between the states $|m\rangle$ and $|n\rangle$ and $V_{mn}(t)$ takes the form

$$V_{mn}(t) = -\boldsymbol{\mu}_{mn} \cdot \mathbf{E}(\mathbf{r}, t). \quad (4)$$

Here, $\boldsymbol{\mu}_{mn}$ is the transition dipole moment and $\mathbf{E}(\mathbf{r}, t)$ the total electromagnetic field. It can be written as

$$\mathbf{E}(\mathbf{r}, t) = \sum_a \left\{ \frac{1}{2} \mathcal{E}_a(t) \exp[i(\omega_a t - \mathbf{k}_a \cdot \mathbf{r})] + \text{c.c.} \right\}, \quad (5)$$

where c.c. stands for the complex conjugate part. For our purpose we shall assume that the system can be modeled by independent two-level systems which are in equilibrium at $t=0$. At the initial time, the system is in its ground state $|1\rangle$ so that $\rho_{11}(0)=1$. The excited state $|2\rangle$ is depleted and $\rho_{22}(0)=0$. In addition, with these initial conditions, there is no initial coherence in the medium and $\rho_{12}(0)=0$. Since $|1\rangle$ is assumed to be a ground state and assuming that the bath does not induce transitions from $|1\rangle$ to $|2\rangle$, we have the relations

$$M_{11}^{11}(t)=0, \quad M_{22}^{11}(t)=0. \quad (6)$$

To ensure the conservation of populations, it is necessary to have

$$M_{22}^{22}(t) = -M_{11}^{22}(t). \quad (7)$$

It is important to note that the time evolution of populations and coherences are not on the same time scale. The time evolution of the coherences is much faster than that of the populations. Therefore, to a first approximation, coherences will be more affected by the bath fluctuations and we can neglect their influence on the populations. Then we assume

$$M_{11}^{22}(t) = \Gamma_{11}^{22} \delta(t), \quad (8)$$

which corresponds to the Markovian case. Here, Γ_{11}^{22} is a constant which describes spontaneous emission and $\delta(t)$ is the Dirac's distribution. Bath fluctuations will be taken into account in the time evolution of the coherences by $M_{21}^{21}(t)$. In addition, if we consider femtosecond pulses and a medium absorbing in the visible range, ω_{21} is about 100 times the spectral width of the pulse. Therefore the rotating-wave approximation can be used and the general relations (2) and (3) can be written as

$$\frac{d\rho_{11}(t)}{dt} = -\frac{i}{\hbar} [\tilde{V}_{12}(t)\sigma_{21}(t) - \sigma_{12}(t)\tilde{V}_{21}(t)] + \Gamma_{11}^{22}\rho_{22}(t), \quad (9)$$

$$\frac{d\rho_{22}(t)}{dt} = -\frac{i}{\hbar} [\tilde{V}_{21}(t)\sigma_{12}(t) - \sigma_{21}(t)\tilde{V}_{12}(t)] - \Gamma_{11}^{22}\rho_{22}(t), \quad (10)$$

$$\frac{d\sigma_{21}(t)}{dt} = -\frac{i}{\hbar} \tilde{V}_{21}(t)[\rho_{11}(t) - \rho_{22}(t)] - \int_0^t d\tau \tilde{M}_{21}^{21}(\tau)\sigma_{21}(t-\tau), \quad (11)$$

with the definitions

$$\tilde{V}_{21}(t) = \tilde{V}_{12}^*(t) = -\boldsymbol{\mu}_{21} \cdot \frac{1}{2} \sum_a \mathbf{A}_a(t) \exp(i\Delta_a t) \exp(i\mathbf{k}_a \cdot \mathbf{r}), \quad (12)$$

$$\tilde{M}_{21}^{21}(t) = M_{21}^{21}(t) \exp(i\omega_{21}t), \quad \Delta_a = \omega_{21} - \omega_a. \quad (13)$$

Here, the notation $\sigma_{21}(t) = \rho_{21}(t) \exp(i\omega_{21}t)$ has been introduced. Equations (9)–(11) combined with the definitions (12) and (13) are solved by using a perturbative technique up to the third order. To the zeroth-order approximation we have

$$\frac{d\rho_{11}^{(0)}(t)}{dt} = \Gamma_{11}^{22}\rho_{22}^{(0)}(t) = -\frac{d\rho_{22}^{(0)}(t)}{dt}, \quad (14)$$

$$\frac{d\sigma_{21}^{(0)}(t)}{dt} = -\int_0^t d\tau \tilde{M}_{21}^{21}(\tau)\sigma_{21}(t-\tau). \quad (15)$$

These equations are readily solved by introducing the initial conditions. We obtain $\rho_{11}^{(0)}(t)=1$, $\rho_{22}^{(0)}(t)=0$, and $\rho_{12}^{(0)}(t)=0$. Using the zeroth-order solution previously determined, the dynamical equations to the first order take the form

$$\frac{d\rho_{11}^{(1)}(t)}{dt} = \Gamma_{11}^{22}\rho_{22}^{(1)}(t) = -\frac{d\rho_{22}^{(1)}(t)}{dt}, \quad (16)$$

$$\frac{d\sigma_{21}^{(1)}(t)}{dt} = -\frac{i}{\hbar} \tilde{V}_{21}(t) - \int_0^t d\tau \tilde{M}_{21}^{21}(\tau)\sigma_{21}^{(1)}(t-\tau). \quad (17)$$

At the initial time, there is no first-order correction. This implies that $\rho_{11}^{(1)}(t) = \rho_{22}^{(1)}(t) = 0$. Taking the Laplace transformation of Eq. (17), we get

$$\sigma_{21}^{(1)}(p) = -\frac{i}{\hbar} \frac{\tilde{V}_{21}(p)}{p + \tilde{M}_{21}^{21}(p)}. \quad (18)$$

Carrying out the inverse Laplace transformation of Eq. (18) yields

$$\sigma_{21}^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \tilde{V}_{21}(\tau)g(t-\tau)d\tau, \quad (19)$$

where $g(t)$ is the inverse Laplace transform of $1/[p + \tilde{M}_{21}^{21}(p)]$. Let us now assume that the variations of the pulse envelopes $A_a(t)$ are much faster than the time evolution of the system dynamics and much faster than the correlation time of the bath. We also assume that these pulses are centered at a positive time t_{pa} . By introducing the relation (12) into the expression (19), and using the definition of $\sigma_{21}(t)$, the first-order contribution to the

coherences can be expressed as

$$\rho_{21}^{(1)}(t) = \frac{i}{2\hbar} \sum_a \exp[-i\Delta_a(t-t_{p_a})] g(t-t_{p_a}) H(t-t_{p_a}) S_a \exp[-i(\omega_a t - \mathbf{k}_a \cdot \mathbf{r})], \quad (20)$$

where $S_a = \int_{-\infty}^{+\infty} [\boldsymbol{\mu}_{21} \cdot \mathbf{A}_a(\tau)] d\tau$ and $H(t)$ is the Heaviside function.

We are now concerned with the second-order contributions to populations and coherences. They can be written in the form

$$\rho_{11}^{(2)}(t) = -\rho_{22}^{(2)}(t), \quad (21)$$

$$\rho_{22}^{(2)}(t) = -\frac{i}{\hbar} \int_0^t [\tilde{V}_{21}(\tau) \sigma_{12}^{(1)}(\tau) - \sigma_{21}^{(1)}(\tau) \tilde{V}_{12}(\tau)] \exp[-\Gamma_{11}^{22}(t-\tau)] d\tau, \quad (22)$$

$$\sigma_{21}^{(2)}(t) = 0. \quad (23)$$

Introducing the first-order corrections previously determined, the contribution to the second-order populations takes the form

$$\begin{aligned} \rho_{22}^{(2)}(t) = & \frac{1}{4\hbar^2} \sum_{\alpha\beta} \{ g^*(t_{p_\beta} - t_{p_\alpha}) H(t_{p_\beta} - t_{p_\alpha}) H(t - t_{p_\beta}) \exp[-\Gamma_{11}^{22}(t - t_{p_\beta})] \\ & + g(t_{p_\alpha} - t_{p_\beta}) H(t_{p_\alpha} - t_{p_\beta}) H(t - t_{p_\alpha}) \exp[-\Gamma_{11}^{22}(t - t_{p_\alpha})] \} \\ & \times \exp(i\Delta_\beta t_{p_\beta}) \exp(-i\Delta_\alpha t_{p_\alpha}) S_\beta S_\alpha^* \exp[i(\mathbf{k}_\beta - \mathbf{k}_\alpha) \cdot \mathbf{r}]. \end{aligned} \quad (24)$$

We are now ready to evaluate the third-order contribution to the coherences. It results from the equation

$$\frac{d\sigma_{21}^{(3)}(t)}{dt} = -\frac{i}{\hbar} \tilde{V}_{21}(t) [\rho_{11}^{(2)}(t) - \rho_{22}^{(2)}(t)] - \int_0^t d\tau \tilde{M}_{21}^{21}(\tau) \sigma_{21}^{(3)}(t - \tau). \quad (25)$$

Finally, using the second-order contribution given by the relation (24) and the definition of $\sigma_{21}(t)$, the third-order contribution to the coherences takes the form

$$\begin{aligned} \rho_{21}^{(3)}(t) = & -\frac{i}{4\hbar^3} \sum_{\alpha\beta\gamma} \{ g^*(t_{p_\beta} - t_{p_\alpha}) H(t_{p_\beta} - t_{p_\alpha}) H(t - t_{p_\beta}) \exp[-\Gamma_{11}^{22}(t - t_{p_\beta})] \\ & + g(t_{p_\alpha} - t_{p_\beta}) H(t_{p_\alpha} - t_{p_\beta}) H(t - t_{p_\alpha}) \exp[-\Gamma_{11}^{22}(t - t_{p_\alpha})] \} \\ & \times g(t - t_{p_\gamma}) H(t - t_{p_\gamma}) S_\gamma S_\beta S_\alpha^* \exp[-i(\Delta_\gamma + \Delta_\beta - \Delta_\alpha)(t - t_{p_\gamma})] \\ & \times \exp[-i(\Delta_\beta - \Delta_\alpha)(t_{p_\gamma} - t_{p_\beta})] \exp[i\Delta_\alpha(t_{p_\beta} - t_{p_\alpha})] \exp\{i[(\omega_\gamma + \omega_\beta - \omega_\alpha)t - (\mathbf{k}_\gamma + \mathbf{k}_\beta - \mathbf{k}_\alpha) \cdot \mathbf{r}]\}. \end{aligned} \quad (26)$$

This expression enables us to determine the third-order nonlinear polarization of the medium which is given by the relation

$$\mathbf{P}^{(3)}(\mathbf{r}, t) = \mathcal{P}^{(3)}(\mathbf{r}, t) + \mathcal{P}^{(3)*}(\mathbf{r}, t) \quad (27)$$

with the notation

$$\mathcal{P}^{(3)}(\mathbf{r}, t) = \boldsymbol{\mu}_{12} \rho_{21}^{(3)}(\mathbf{r}, t). \quad (28)$$

Application to forward degenerate four-wave mixing.—Let us now apply these general results to a well-known forward-degenerate four-wave-mixing experiment illustrated in Fig. 1. The medium is excited by three pulses. The pump pulses propagate in the direction \mathbf{k}_1 and \mathbf{k}_2 and are delayed by τ . The probe pulse has a wave vector \mathbf{k}_3 and we note T the delay between pulses 2 and 3. We assume that the probe pulse arrives at least several pulse widths after pulses 1 and 2. The output light intensity in the direction $\mathbf{k}_4 = \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ is

$$I(\tau) \sim \int_{-\infty}^{+\infty} dt |\mathcal{P}_{\mathbf{k}_4}^{(3)}(\mathbf{r}, t, \tau)|^2, \quad (29)$$

where $\mathcal{P}_{\mathbf{k}_4}^{(3)}(\mathbf{r}, t, \tau)$ is the part of the third-order nonlinear polarization of the medium in the direction \mathbf{k}_4 and is defined by the relation (28). This quantity is straightforwardly obtained by selecting the terms in the direction $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ and $\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{k}_1$ in the expression (26). Neglecting τ with respect to T , which is assumed to be

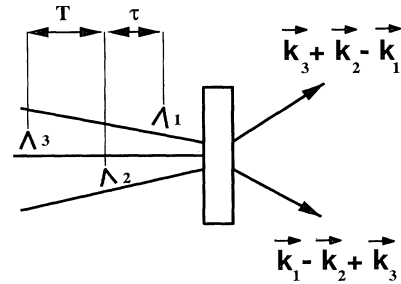


FIG. 1. Geometry for three-pulse time-delayed four-wave-mixing experiment.

positive, we obtain

$$|\mathcal{P}_{\mathbf{k}_4}^{(3)}(\mathbf{r}, t, \tau)|^2 = \begin{cases} \frac{|\mu_{12}|^2}{4\hbar^2} |S_3 S_2 S_1^*|^2 |g^*(\tau) e^{-\Gamma_{11}^2 \tau} g(t-t_{p_3}) H(t-t_{p_3})|^2, & \tau > 0, \\ \frac{|\mu_{12}|^2}{4\hbar^2} |S_3 S_2 S_1^*|^2 |g(-\tau) e^{-\Gamma_{11}^2 \tau} g(t-t_{p_3}) H(t-t_{p_3})|^2, & \tau < 0. \end{cases} \quad (30)$$

Introducing these relations in the expression (29), the output light intensity in the direction \mathbf{k}_4 takes the form

$$I(\tau) \sim |g(|\tau|)|^2. \quad (31)$$

This result can be understood as a generalization of the one obtained in the Markovian case. In this case, the memory function $M_{21}^2(t)$ can be written as

$$M_{21}^2(t) = \Gamma_{21} \delta(t). \quad (32)$$

Consequently, $g(t) = \exp(-\Gamma_{21}t)$ and $I(\tau)$ reduces to

$$I(\tau) \sim \exp(-2\Gamma_{21}|\tau|), \quad (33)$$

which is a well-known result.

In conclusion, we have analyzed the influence of non-Markovian effects in a three-pulse time-delayed four-wave-mixing experiment. We have shown that the intensity of the diffracted light can be expressed as a simple function of the bath memory function when the medium is excited by short pulses. Our calculation does not make assumptions about the analytical form of the memory kernel. For this reason, our result is quite general. The experimental determination of $|g(t)|$ is consequently an easy way to get information about $M_{21}^2(t)$. Therefore, this type of experiment must be an interesting approach to learn about the dynamics of the bath.

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