

Influence of neighboring levels in three-pulse photon-echo processes

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It is the purpose of the present paper to study the dynamics underlying a three-pulse photon-echo process performed on a vibronic system coupled to non-Markovian baths, when a neighboring level enters into the global dynamical evolution because of broadband excitation required in these experiments. Particular emphasis is on the energy gap between the vibronic levels, but also on the fluctuation amplitudes and correlation times of their corresponding thermal baths. The photon-echo signal appears to be very sensitive to the additional interfering contributions introduced by the neighboring vibronic level. It is shown that these contributions associated to the pathways involving different vibronic states are modulated by their corresponding energy gap. As a consequence, these contributions to the integrated photon-echo signal strongly decrease for large energy gaps. Also, an oscillating behavior is observed on the time dependence of the photon-echo signal resulting from the summation of the contributions provided by the individual vibronic levels. Moreover, the influence of the non-Markovian character of the baths, accountable for inhomogeneous broadening, affects the amplitude and the time dependence of the photon-echo signal, as well as its dependence with the delay time of the laser pulses. Of course, for longer times a Markovian dynamical evolution is recovered.

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I. INTRODUCTION

It is well established that dephasing processes have a determinant role in the dynamics underlying most of the nonlinear optical processes [1–7]. With the enormous strides made in recent years, enabling today a major control of optical and infrared laser fields, nonlinear optical spectroscopy methods based on multiple pulse coherent excitation offer interesting possibilities for a comprehensive study of the intricate electronic and nuclear motions taking place in large molecular systems [8,9]. These methods have proved to be quite selective for disentangling the time scales of molecular and collective dynamics of condensed phase. Among these approaches, photon-echo spectroscopy is probably the one that can deeply peer an ensemble average to extract microscopic information [10–17]. While in hole-burning and related spectroscopies, a highly selective excitation is achieved inside the inhomogeneous broadening, in photon-echo spectroscopy, due to the high time resolution, the broadband pulsed excitation covers the entire inhomogeneous distribution of states. However, by choosing a convenient sequence of pulsed excitations and appropriate phase-matching conditions, it is possible to generate a rephasing process which results in the suppression of the inhomogeneous broadening.

A general configuration in three-pulse photon-echo experiments is made of three short laser pulses with different wave vectors and frequencies. Then, the field radiated by the sample in one of the convenient phase-matched directions is detected in different ways. It can be either integrated over

time and analyzed as a function of the delay times between the first and second or second and third pulses or, in the time-gated condition, measured as a function of time after the interaction with the last pulse. While traditional two-photon pulse echo is well adapted to probing fast dynamics in inhomogeneously broadened systems, it is not really sensitive if a broad range of time scales comes into play. Then, multiple time variables are required in photon-echo experiments as it is the case in three-pulse photon-echo [11,18,19] or stimulated photon-echo [20,21].

With this goal in mind, a large number of theoretical descriptions have been dedicated to the analysis of the various forms of photon-echo spectroscopies. Among them, some are devoted to particular laser excitation structures and detection directions, and some to particular processes related to the internal structure of the molecular systems where the photon-echo process takes place. Concerning this last class of descriptions, basically two different types of structures are considered, either involving a small number of discrete levels [22] or made of two levels coupled to Markovian or non-Markovian baths. However, because quite often nonlinear optical processes involve nonresonant transitions, it is questionable to ask whether a neighboring level, which is not supposed to be involved in the photon-echo process under investigation, could influence the photon-echo signal qualitatively as well as quantitatively. It is the purpose of the present paper to describe the contributions of the additional interfering pathways entering in the global dynamical evolution resulting from the presence of this additional neighboring level.

It is our intent, in the present paper, to analyze the internal dynamics of a vibronic system coupled to non-Markovian baths, when a neighboring level enters into the global dynamical evolution because of broadband excitation required

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in these experiments. For obvious mathematical difficulties, this description implies the use of the impact limit approximation which, of course, overestimates the spectral overlap between the vibronic resonances and the spectral distribution of the laser pulses participating in the photon-echo experiment. However, as long as the experiment requires a well-defined time ordering of the three laser pulses, this assumption does not imply any loss of generality because these overlaps just enter as multiplicative constants in the description. Here, particular emphasis will be on the energy gap between the vibronic levels, but also on the fluctuation amplitudes and correlation times of the thermal baths.

The paper is organized as follows. In Sec. II, because most of the theoretical descriptions of nonlinear optical processes are based on perturbational expansions, we introduce the basic grounds required to describe the free dynamical evolution of the vibronic system whose Hamiltonian is made of a ground state and two excited vibronic states coupled to non-Markovian baths. Next, in Sec. III, we describe the general time evolution under multiple laser excitation underlying a general four-wave-mixing process. Then, in Secs. IV and V, we focus on the evaluation of the third-order polarization created during a general photon-echo process with a particular emphasis on the three-pulse photon-echo experiment according to the usual phase-matching conditions and time-ordering prescription of the fields specific for this experiment. Then, Sec. VI is dedicated to the evaluation of the bath correlation factors for the various pathways which enter into the global time evolution and correspond either to transitions involving a single excited vibronic state or to the interfering terms involving two different excited vibronic states. Finally, in Sec. VII, the photon-echo signal is evaluated in the case of homodyne detection and numerical simu-

lations illustrate the influence of the neighboring level according to different physical situations.

II. GENERAL DESCRIPTION OF THE MODEL HAMILTONIAN

The system we want to investigate is made of two vibronic states, say $|e_1\rangle$ and $|e_2\rangle$, interacting with a bath made of low-frequency modes. In the present work, the bath is described by a set of harmonic oscillators which can be of quantum or stochastic nature. The Hamiltonians of the vibronic system and of the bath are H_v and H_b , respectively. In the following, the interaction between the two vibronic states and their corresponding baths is described by W . Therefore, the zeroth-order Hamiltonian of the vibronic and bath parts, H_0 , is made of

$$H_0 = E_g|g\rangle\langle g| + E_{e_1}|e_1\rangle\langle e_1| + E_{e_2}|e_2\rangle\langle e_2| + \sum_k \hbar\omega_k \left(\mathbf{b}_k^\dagger \mathbf{b}_k + \frac{1}{2} \right), \quad (2.1)$$

where the notation $|g\rangle$ stands for the ground state of the total molecular and bath system, and $|e_1\rangle$ and $|e_2\rangle$ are two different excited vibronic states coupled to the baths through the interaction term W given by

$$W = \sum_k w^{(1)} \beta_k |e_1\rangle\langle e_1| (\mathbf{b}_k^\dagger + \mathbf{b}_k) + \sum_k w^{(2)} \beta_k |e_2\rangle\langle e_2| (\mathbf{b}_k^\dagger + \mathbf{b}_k) \quad (2.2)$$

if the coupling strengths are assumed to be factorized in molecular and bath parts. Then, a matricial representation of the system-bath Hamiltonian $H_{sb} = H_0 + W$ can be done into the form

$$H_{sb} = \begin{pmatrix} E_g + H_b & 0 & 0 \\ 0 & E_{e_1} + H_b + \sum_k w^{(1)} \beta_k (\mathbf{b}_k^\dagger + \mathbf{b}_k) & 0 \\ 0 & 0 & E_{e_2} + H_b + \sum_k w^{(2)} \beta_k (\mathbf{b}_k^\dagger + \mathbf{b}_k) \end{pmatrix}_{g, e_1, e_2} \quad (2.3)$$

in the zeroth-order representation. Finally, the last term $V(t)$ describes the usual interaction between the vibronic system and the three pulsed laser fields required for the photon-echo process. It corresponds to

$$V(t) = -\vec{\mu} \cdot \vec{E}_{\text{tot}}(\vec{r}, t). \quad (2.4)$$

Using the rotating wave approximation (RWA), the laser-molecule interaction Hamiltonian reduces to the expression

$$V_{mn}(t) = - \sum_{j=a,b,c} \vec{\mu}_{mn} \cdot [\vec{E}_j(\omega_j) e^{-i\omega_j t + i\vec{k}_j \cdot \vec{r}} \mathcal{H}(E_m - E_n) + \vec{E}_j(-\omega_j) e^{i\omega_j t - i\vec{k}_j \cdot \vec{r}} \mathcal{H}(E_n - E_m)] \mathcal{A}_j(t - T_j) \quad (2.5)$$

if the laser fields $\vec{E}_j$, with $j=a,b,c$, are applied on the $m \rightleftharpoons n$ transition. Here, $\mathcal{A}_j(t - T_j)$ stands for the pulse envelop of field j . As usual, $\vec{\mu}$ is the dipole moment operator and $\mathcal{H}(E)$ represents the Heaviside function.

The dynamical evolution of the total system is conveniently described by the Liouville equation of the total density matrix $\sigma(t)$. It takes the form

$$\frac{\partial \sigma(t)}{\partial t} = -\frac{i}{\hbar} [L_0 + L'_v(t)] \sigma(t) - \Gamma \sigma(t), \quad (2.6)$$

where L_0 stands for the zeroth-order Liouvillian and $L'_v(t)$ stands for the time-dependent interaction Liouvillian. Therefore, we have for the zeroth-order and total Liouvillians

$$L_0 = L_v + L_b + L'_w, \quad (2.7)$$

$$L = L_0 + L'_v(t).$$

Notice that the vibronic-bath interaction term, which is the source of the inhomogeneous broadening in the slow modulation limit obtained for a convenient choice of the bath correlation times and amplitude fluctuations defined in Appendix B, has been included in the zeroth-order Liouvillian. On the other hand, the interaction Liouvillian between the laser field and the total system will be treated perturbatively. In the previous relation, the various Liouvillians L_v , L_b , and L'_w are the Liouvillians associated to the vibronic Hamiltonian H_v , to the bath Hamiltonian H_b , and to the vibronic-bath interaction W , respectively. Also, L'_v is the interaction Liouvillian corresponding to the coupling between the vibronic system and the laser fields $V(t)$. Finally, Γ represents the damping Liouvillian. Also, it will be assumed, as usual, that the vibronic system and the bath are uncorrelated at the initial time t_0 . Consequently, their corresponding density matrices can be factorized, so that $\sigma(t_0) = \rho(t_0) \rho_b(t_0)$. When the molecule does not interact with the laser beam, the reduced density matrix of the vibronic part alone, denoted $\rho(t) = \text{Tr}_b[\sigma(t)]$, can be obtained from Eq. (2.6) into the form

$$\rho(t) = \langle e^{-(i/\hbar)L_v(t-t_0) - \Gamma(t-t_0) - (i/\hbar)(L_b + L'_w)(t-t_0)} \rangle_b \rho(t_0), \quad (2.8)$$

where t_0 stands for the initial time. This expression can be simplified using time-ordered exponential operator as [23]

$$\rho(t) = e^{-(i/\hbar)L_v(t-t_0) - \Gamma(t-t_0)} \left\langle e^{-(i/\hbar)L_b(t-t_0)} \times \exp_+ \left[-\frac{i}{\hbar} \int_0^{t-t_0} d\tau L'_w(\tau) \right] \right\rangle_b \rho(t_0), \quad (2.9)$$

with

$$L'_{w(I)}(\tau) = e^{(i/\hbar)L_b\tau} L'_w e^{-(i/\hbar)L_b\tau}, \quad (2.10)$$

because L'_w commutes with L_v and Γ . When performing the trace over the bath states, the factor $e^{-(i/\hbar)L_b(t-t_0)}$ can be omitted because the trace is not altered by a unitary transform, so that

$$\left\langle e^{-(i/\hbar)L_b(t-t_0)} \exp_+ \left[-\frac{i}{\hbar} \int_0^{t-t_0} d\tau L'_w(\tau) \right] \right\rangle_b = \text{Tr}_b \left\{ \rho_b(t) \exp_+ \left[-\frac{i}{\hbar} \int_0^{t-t_0} d\tau L'_{w(I)}(\tau) \right] \right\} \quad (2.11)$$

and the average can be expressed using the cumulant expansion. Also, we will assume, all along, that the bath remains at equilibrium during the course of the nonlinear optical process. In the previous expression, the symbol Tr_b stands for

the trace over the bath states and $\rho_b(t)$ is the density matrix of the bath. Therefore, the density matrix $\rho(t)$ takes the form

$$\rho(t) = e^{-(i/\hbar)L_v(t-t_0) - \Gamma(t-t_0)} \exp \left[-\frac{i}{\hbar} \int_0^{t-t_0} d\tau \langle L'_{w(I)}(\tau) \rangle_b - \frac{1}{\hbar^2} \int_0^{t-t_0} d\tau \int_0^\tau d\tau' \langle L'_{w(I)}(\tau) L'_{w(I)}(\tau') \rangle_b \right] \rho(t_0). \quad (2.12)$$

Due to the structure of the interaction between the vibronic system and the baths, $\langle L'_{w(I)}(\tau) \rangle_b = 0$ and we get, up to the second order of the bath-system interaction,

$$\rho(t) = e^{-(i/\hbar)L_v(t-t_0) - \Gamma(t-t_0)} \times \exp \left[-\frac{1}{\hbar^2} \int_0^{t-t_0} d\tau \int_0^\tau d\tau' \langle L'_{w(I)}(\tau) L'_{w(I)}(\tau') \rangle_b \right] \rho(t_0). \quad (2.13)$$

Then, we are left with the evaluation of the bath correlation function $\mathcal{C}(\tau, \tau') = \langle L'_{w(I)}(\tau) L'_{w(I)}(\tau') \rangle_b$ given by

$$C_{\text{bath}}(\tau, \tau') = \text{Tr}_b [e^{(i/\hbar)L_b\tau} L'_w e^{-(i/\hbar)L_b(\tau-\tau')} L'_w e^{-(i/\hbar)L_b\tau'} \rho_b(t_0)]. \quad (2.14)$$

If we explicit this expression, it reduces to

$$C_{\text{bath}}(\tau, \tau') = \sum_{\{n_{k_b}\}, \{n'_{k_b}\}, \{n''_{k_b}\}} L'_{w\{n_{k_b}\}\{n'_{k_b}\}\{n''_{k_b}\}} \times (e^{-(i/\hbar)L_b(\tau-\tau')})_{\{n'_{k_b}\}\{n''_{k_b}\}\{n_{k_b}\}} \times L'_{w\{n'_{k_b}\}\{n''_{k_b}\}\{n_{k_b}\}} \rho_b\{n_{k_b}\}\{n'_{k_b}\}\{n''_{k_b}\}(t_0) \quad (2.15)$$

and assuming, as usual, a Boltzmann distribution for the bath oscillators in the initial configuration, the bath correlation function simplifies to

$$C_{\text{bath}}(\tau, \tau') = \sum_k |\beta_k|^2 [(\bar{n}_{k_b} + 1) \cos \omega_{k_b}(\tau - \tau') + \bar{n}_{k_b} \times \cos \omega_{k_b}(\tau - \tau')] [w^{(1)}]^2 |e_1\rangle \langle e_1| + [w^{(2)}]^2 \times |e_2\rangle \langle e_2|, \quad (2.16)$$

where $\bar{n}_{k_b} = \sum_{n_{k_b}} n_{k_b} e^{-(\hbar \omega_{k_b}/kT)(n_{k_b} + 1/2)} / Z_{k_b}$ if Z_{k_b} stands for the canonical function of the bath oscillator k_b . Of course, other type of bath correlation functions can be introduced as well. As an example, we can mention a model which has been commonly used in the description of numerous physical processes as diverse as nonadiabatic transitions [24–29] and tunneling [30] or in the description of nonlinear optical responses [3,31,32]. This model, termed the Brownian oscillator model, has been quite often used and has proved to be useful in describing pure dephasing processes resulting from coupling between molecular systems and their surrounding baths [8].

While the description introduced here is convenient for the linear response, it cannot be applied straightforwardly to

high-order-mixing processes because the bath average process cannot be treated so crudely. Then, a more refined approach is required and will be introduced in the following.

III. DYNAMICAL EVOLUTION OF A FOUR-WAVE-MIXING PROCESS

As long as we are concerned with the evolution of dynamical systems which can be conveniently described by a finite set of states, their corresponding evolution Liouvillian can be expressed in terms of exponential arguments involving linear time dependence only. Then, the multiple time integrations required to evaluate the polarization can be performed by retaining the pulse overlaps. Even if the evaluation is tedious, in principle, it can be done. However, for system undergoing more intricate dynamics, as in the case of systems involving stochastic interactions or memory terms such as the one we are dealing with, such an approach cannot be applied and the additional impulsive limit approximation introduced by Mukamel [8] is required.

Photon-echo [3,5,6,11,33] and other related nonlinear optical processes [34,35] are accounted for by the third-order perturbation expansion of the density matrix with respect to the laser-molecule interaction $L'_v(t)$ obtained from Eq. (2.6). Then, for the three-pulse photon-echo process we want to discuss here, the general contribution to a third-order optical process $\sigma^{(3)}(t)$ takes the form

$$\begin{aligned} \sigma^{(3)}(t) = & \frac{i}{\hbar^3} \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 G(t - \tau_3) L'_v(\tau_3) \\ & \times G(\tau_3 - \tau_2) L'_v(\tau_2) G(\tau_2 - \tau_1) L'_v(\tau_1) \sigma(-\infty) \end{aligned} \quad (3.1)$$

and corresponds to the traditional photon-echo in its various forms. The set of pathways, contributing to the third-order density matrix element, is listed in Appendix A. They contribute to the evaluation of the third-order polarization induced by the three laser pulses participating in the photon-echo spectroscopy. Of course, according to the geometry of the experiment determined by the phase-matched conditions and energetic and temporal structures of the laser excitation, not all the pathways contribute significantly. Furthermore,

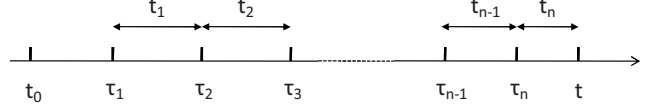


FIG. 1. Time ranges required in the definition of the reference Hamiltonians.

due to the presence of the product of the evolution Liouvillians $G(\tau_i - \tau_j)$, the bath average is more intricate than for the linear response and a more refined average procedure can be applied overcoming the crude well-known factorization approximation. In the following, we will take advantage of the impulsive limit, to perform the multiple time integrations. To this end, we first assume the initial conditions defined at time $t_0 \rightarrow -\infty$ with the molecular system in the ground state, so that $\rho(-\infty) = |g\rangle\langle g|$. The evaluation of $\rho^{(3)}(t)$ requires the change of variables

$$t_1 = \tau_2 - \tau_1, \quad t_2 = \tau_3 - \tau_2, \quad \text{and} \quad t_3 = t - \tau_3, \quad (3.2)$$

which is quite convenient for our purpose. It gives the perturbation expansion into the form

$$\begin{aligned} \sigma^{(3)}(t) = & \frac{i}{\hbar^3} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 G(t_3) L'_v(t - t_3) \\ & \times G(t_2) L'_v(t - t_3 - t_2) G(t_1) L'_v(t - t_3 - t_2 - t_1) \sigma(-\infty). \end{aligned} \quad (3.3)$$

Also, for the sake of simplicity, we factorize the time dependence of the interaction with the laser fields, to leave the Liouvillian with respect to the laser-system interaction into the form

$$L'_v(t) = \sum_p \mathcal{A}_p(t - T_p) [e^{-i\omega_p(t - T_p) + i\vec{k}_p \cdot \vec{r}} + \text{c.c.}] L'_{v(p)},$$

with

$$L'_{v(p)} = [-\vec{\mu} \cdot \vec{E}_p(\omega_p), \quad], \quad (3.4)$$

where c.c. stands for the complex-conjugate part. Then, the third-order contribution to the density matrix can be expressed as

$$\begin{aligned} \sigma^{(3)}(t) = & \frac{i}{\hbar^3} \sum_{j=p,q,r} \sum_{\eta_j=\pm 1} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{A}_p(t - T_p - t_3) \mathcal{A}_q(t - T_q - t_3 - t_2) \mathcal{A}_r(t - T_r - t_3 - t_2 - t_1) \\ & \times e^{-i\eta_p\omega_p(t-t_3) - i\eta_q\omega_q(t-t_3-t_2) - i\eta_r\omega_r(t-t_3-t_2-t_1) + i(\eta_p\vec{k}_p + \eta_q\vec{k}_q + \eta_r\vec{k}_r) \cdot \vec{r}} G(t_3) L'_{v(p)} G(t_2) L'_{v(q)} G(t_1) L'_{v(r)} \sigma(-\infty). \end{aligned} \quad (3.5)$$

In this expression, the symbol $\sum_j$ stands for the summation over the three electric fields of the laser beams and $\sum_{\eta_j}$ stands for the summation over their corresponding positive and negative Fourier frequency components. In the previous expressions, the indices η_j , where $j=p, q$, or r , stand for the particular combinations of fields that need to be considered for each given pathway in the Liouville space. Of course, in the framework of the rotating wave approximation only some of them will be required. In the following, we will explicitly evaluate these contributions.

The evaluation of a given $\vec{K}$ component of the third-order polarization contributions induced by the laser fields requires the determination of the matrix elements $\sigma_{e_1g}^{(3)}(t)$ and $\sigma_{e_2g}^{(3)}(t)$ can be expressed from the previous expression (3.5). It takes the form

$$\begin{aligned} \tilde{P}_K^{(3)}(t) = & \frac{i}{\hbar^3} \sum_{p,q,r} \sum_{\eta_j=\pm 1}^{j=p,q,r} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_q(t-T_q-t_3-t_2) \mathcal{A}_r(t-T_r-t_3-t_2-t_1) \\ & \times e^{-i\eta_p\omega_p(t-t_3)-i\eta_q\omega_q(t-t_3-t_2)-i\eta_r\omega_r(t-t_3-t_2-t_1)+i(\eta_p\vec{k}_p+\eta_q\vec{k}_q+\eta_r\vec{k}_r)\cdot\vec{r}} \text{Tr}[\vec{\mu}\mathbf{G}(t_3)\mathbf{L}'_{v(p)}\mathbf{G}(t_2)\mathbf{L}'_{v(q)}\mathbf{G}(t_1)\mathbf{L}'_{v(r)}\sigma(-\infty)], \end{aligned} \quad (3.6)$$

where only the combination of field components satisfying the phase-matched condition chosen in the experiment is retained. In Sec. IV, the polarization term will be evaluated in the particular case of the three-pulse photon-echo experiment and applied to the study of the role played by the presence of nonresonant neighboring levels on the photon-echo signal, of interest here.

IV. APPLICATION TO PHOTON-ECHO SPECTROSCOPY

Photon-echo spectroscopy refers to a large number of techniques according to the excitation structure, phase-matched directions, and detection conditions. They can be as diverse as two-pulse photon-echo and three-pulse photon-echo, stimulated photon-echo both, with homodyne or heterodyne detection, and even accumulated photon-echo [36–39]. For our purpose, we will consider a three-pulse photon-echo experiment. As an example, we can mention the three-pulse photon-echo technique that has been very effective as a probe of solvation dynamics [11] because of its high sensitivity for relatively small Stokes shifts such as in non-polar systems, and can be easily applied to the infrared region of the spectrum. Here, we will consider the phase-matched condition for photon-echo, say, $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$, with probing times T_a , T_b , and T_c . In the framework of the rotating wave approximation, we will first evaluate the contribution given by relation (3.6). Assuming the system to be unexcited electronically at the initial time, the contribution to the photon-echo signal results from expression (3.6), and we are left with the evaluation of the terms

$$\vec{\mu}_{e_jg} \langle \langle e_jg | \mathbf{G}(t_3) \mathbf{L}'_{v(p)} \mathbf{G}(t_2) \mathbf{L}'_{v(q)} \mathbf{G}(t_1) \mathbf{L}'_{v(r)} | gg \rangle \rangle, \quad j=1,2, \quad (4.1)$$

which gives rise to the various pathways described in Appendix A, where it is assumed that the model does not support

relaxation processes and, consequently, no decay rate participates in the dynamics, an assumption satisfied on this time scale. This implies that relaxations can only occur on a time scale much longer than the coherent processes contributing to the photon-echo signal, of interest here.

At first, we must evaluate the different matrix elements of the Green's function $\mathbf{G}(t)$ participating in the individual pathways. Once the contributions of the individual pathways are explicitly written, the bath average has to be performed. Because we require the evaluation of both vibronic and bath populations in the ground and the excited electronic configurations, the bath Hamiltonian will be different not only according to the type of pathway, but also according to the time evolution on a given pathway. Then, we require the introduction of a reference bath Hamiltonian for each individual pathway. Remember that the bath Hamiltonian corresponds to

$$\mathbf{H}_b = \begin{cases} \mathbf{H}_b^{(g)} & \text{for configuration } g \\ \mathbf{H}_b^{(g)} + \mathbf{W}^{(e_i)} & \text{for configuration } e_i \quad \forall i=1,2. \end{cases} \quad (4.2)$$

To evaluate the contribution associated to the pathways involving a population evolution in the ground configuration $|g\rangle$, the reference Hamiltonian can be chosen as $\mathbf{H}_b^{(g)}$ during the complete time evolution. However, for the contributions associated to all the other pathways, the system evolves in the ground configuration during the t_1 period and in one of the excited configurations during the t_2 period. Therefore, we have to define two different types of reference Hamiltonians, say

$$\begin{aligned} \mathbf{H}_\alpha &= \mathbf{H}_b^{(g)}, \\ \mathbf{H}_{\beta_i}(\tau) &= \begin{cases} \mathbf{H}_b^{(g)} & \text{if } 0 < \tau < t_1 \\ \mathbf{H}_b^{(e_i)} = \mathbf{H}_b^{(g)} + \mathbf{W}^{(e_i)} & \text{if } t_1 < \tau < t_1 + t_2 + t_3 \quad \forall i=1,2, \end{cases} \end{aligned} \quad (4.3)$$

according to the choice of the excited configuration or, equivalently, according to the reference Hamiltonians described previously by relation (4.3). The definition of the

time ranges can easily be understood remembering that the various t_j have been defined from the time ordering τ_j as shown in Fig. 1. For those pathways R involving the popu-

lation of state $|e_i\rangle$ only, $\mathbf{H}_{\beta_i}(\tau)$ will be the appropriate reference Hamiltonian, while for pathways R involving the ground-state population only, the Hamiltonian $\mathbf{H}_\alpha$ will be more convenient. Notice that the evolution bath operators associated to these reference Hamiltonians are

$$U_b(t) = e^{-(i/\hbar)\mathbf{H}_\alpha t} \quad \text{for } \mathbf{H}_\alpha,$$

$$U_b(t) = \exp_+ \left[-\frac{i}{\hbar} \int_0^t d\tau \mathbf{H}_{\beta_i}(\tau) \right] \quad \text{for } \mathbf{H}_{\beta_i}(\tau) \quad \forall i = 1, 2. \quad (4.4)$$

The first-order contribution requires the evaluation of $\mathbf{G}_{e_i g e_i g}(t_1) \mathbf{V}_{e_i g} \mathbf{p}_{gg}(t_0)$ and $-\mathbf{G}_{g e_i g e_i}(t_1) \mathbf{V}_{g e_i} \mathbf{p}_{gg}(t_0)$. On this time scale, both reference Hamiltonian are equivalent. For instance, with $\mathbf{H}_\alpha$ as a reference Hamiltonian, the first term gives

$$\begin{aligned} \mathbf{G}_{e_i g e_i g}(t_1) \mathbf{O} &= e^{-i\omega_{e_i g} t_1} (U_b(t_1))_{e_i e_i} \mathbf{O} (U_b^\dagger(t_1))_{gg} \\ &= e^{-i\omega_{e_i g} t_1} e^{-(i/\hbar)\mathbf{H}_\alpha t_1} \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) \right] \\ &\quad \times \mathbf{O} e^{(i/\hbar)\mathbf{H}_\alpha t_1} \\ &= e^{-i\omega_{e_i g} t_1} \mathbf{G}_{b(\alpha)}(t_1) \\ &\quad \times \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) \right] \mathbf{O}, \end{aligned} \quad (4.5)$$

where $\mathbf{G}_{b(\alpha)}(t_1)$ describes the evolution of the bath part only, $\mathbf{O}$ a given operator, and similarly

$$\begin{aligned} \mathbf{G}_{g e_i g e_i}(t_1) \mathbf{O} &= e^{-i\omega_{g e_i} t_1} (U_b(t_1))_{gg} \mathbf{O} (U_b^\dagger(t_1))_{e_i e_i} \\ &= e^{-i\omega_{g e_i} t_1} e^{-(i/\hbar)\mathbf{H}_\alpha t_1} \mathbf{O} \\ &\quad \times \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) \right] e^{(i/\hbar)\mathbf{H}_\alpha t_1} \\ &= e^{-i\omega_{g e_i} t_1} \mathbf{G}_{b(\alpha)}(t_1) \mathbf{O} \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) \right], \end{aligned} \quad (4.6)$$

where $\mathbf{W}_{\alpha(l)}^{(e_i)}(\tau)$ stands for

$$\mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) = e^{(i/\hbar)\mathbf{H}_\alpha \tau} \mathbf{W}^{(e_i)} e^{-(i/\hbar)\mathbf{H}_\alpha \tau}. \quad (4.7)$$

To the third-order perturbation, the coherence Green's function $\mathbf{G}_{e_i g e_i g}(t_3)$ appears in all the contributions. For the terms of R corresponding to pathways going through the ground-state population, its evaluation is done along the same line as in Eq. (4.5), and we have

$$\mathbf{G}_{e_i g e_i g}(t_3) \mathbf{O} = e^{-i\omega_{e_i g} t_3} \mathbf{G}_{b(\alpha)}(t_3) \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\alpha(l)}^{(e_i)}(\tau) \right] \mathbf{O}. \quad (4.8)$$

However, except for these terms evolving through ground-state populations and coherences only, all the other terms R will require $\mathbf{H}_{\beta_i}(\tau)$ or $\mathbf{H}_{\beta_j}(\tau)$ as reference Hamiltonians. Using $\mathbf{H}_{\beta_i}(\tau)$ as reference Hamiltonian, we have

$$\begin{aligned} \mathbf{G}_{e_i g e_i g}(t_3) \mathbf{O} &= e^{-i\omega_{e_i g} t_3} (U_b(t_3))_{e_i e_i} \mathbf{O} (U_b^\dagger(t_3))_{gg} \\ &= e^{-i\omega_{e_i g} t_3} \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{H}_{\beta_i}(\tau) \right] \\ &\quad \times \mathbf{O} \exp_- \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_i(l)}^{(e_i)}(\tau) \right] \\ &\quad \times \exp_- \left[\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{H}_{\beta_i}(\tau) \right] \\ &= e^{-i\omega_{e_i g} t_3} \mathbf{G}_{b(\beta_i)}(t_3) \mathbf{O} \exp_- \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_i(l)}^{(e_i)}(\tau) \right], \end{aligned} \quad (4.9)$$

where $\mathbf{G}_{b(\beta_i)}(t_3)$ stands for the evolution of the bath only in the excited configuration $|e_i\rangle$ and

$$\begin{aligned} \mathbf{G}_{g e_i g e_i}(t_3) \mathbf{O} &= e^{-i\omega_{g e_i} t_3} (U_b(t_3))_{gg} \mathbf{O} (U_b^\dagger(t_3))_{e_i e_i} \\ &= e^{-i\omega_{g e_i} t_3} \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{H}_{\beta_i}(\tau) \right] \\ &\quad \times \exp_+ \left[\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_i(l)}^{(e_i)}(\tau) \right] \\ &\quad \times \mathbf{O} \exp_- \left[\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{H}_{\beta_i}(\tau) \right] \\ &= e^{-i\omega_{g e_i} t_3} \mathbf{G}_{b(\beta_i)}(t_3) \exp_+ \left[\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_i(l)}^{(e_i)}(\tau) \right] \mathbf{O} \end{aligned} \quad (4.10)$$

on account of the notation

$$\begin{aligned} \mathbf{W}_{\beta_i(l)}^{(e_i)}(\tau) &= \exp_- \left[\frac{i}{\hbar} \int_0^\tau d\tau' \mathbf{H}_{\beta_i}(\tau') \right] \mathbf{W}^{(e_i)} \\ &\quad \times \exp_+ \left[-\frac{i}{\hbar} \int_0^\tau d\tau' \mathbf{H}_{\beta_i}(\tau') \right]. \end{aligned} \quad (4.11)$$

At this stage, we have all the required intermediate quantities to calculate the contributions to the photon-echo signal. This will be done in Sec. V.

V. DESCRIPTION OF THREE-PULSE PHOTON-ECHO SIGNAL

According to the previous evaluation of the third-order polarization given by Eq. (3.6) and using the rotating wave approximation, we can evaluate the contribution to the polarization in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$. It can be expressed into the form

$$\begin{aligned}
\tilde{P}_{\vec{k}_{PE}}^{(3)}(t) = & \frac{i}{\hbar^3} \sum_{p,r=b,c}^{r \neq p} \sum_{m=1}^2 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_a(t-T_a-t_3-t_2) \mathcal{A}_r(t-T_r-t_3-t_2-t_1) \\
& \times e^{-i\omega_p(t-t_3)+i\omega_a(t-t_3-t_2)-i\omega_r(t-t_3-t_2-t_1)+i(-\vec{k}_a+\vec{k}_b+\vec{k}_c)\cdot\vec{r}} \text{Tr}_b[\vec{\mu}_{ge_m} \langle e_m | \mathbf{G}(t_3) \mathbf{L}'_{v(p)} \mathbf{G}(t_2) \mathbf{L}'_{v(a)} \mathbf{G}(t_1) \mathbf{L}'_{v(r)} \rho_b(-\infty) | g \rangle] \\
& + \frac{i}{\hbar^3} \sum_{p,q=b,c}^{q \neq p} \sum_{m=1}^2 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_q(t-T_q-t_3-t_2) \mathcal{A}_a(t-T_a-t_3-t_2-t_1) \\
& \times e^{-i\omega_p(t-t_3)-i\omega_q(t-t_3-t_2)+i\omega_a(t-t_3-t_2-t_1)+i(-\vec{k}_a+\vec{k}_b+\vec{k}_c)\cdot\vec{r}} \text{Tr}_b[\vec{\mu}_{ge_m} \langle e_m | \mathbf{G}(t_3) \mathbf{L}'_{v(p)} \mathbf{G}(t_2) \mathbf{L}'_{v(q)} \mathbf{G}(t_1) \mathbf{L}'_{v(r)} \rho_b(-\infty) | g \rangle], \quad (5.1)
\end{aligned}$$

where the two contributions are the only ones with the component $-\vec{k}_a$ of the field $\vec{E}_a(t)$ participating in the phase-matched direction $\vec{k}_{PE}$ in the framework of the rotating wave approximation. For the first term, assuming a chronological p - a - r field ordering, the field $\vec{E}_a(t)$ participates in the second interaction, while for the second term with a chronological p - q - a field ordering, it participates in the first interaction. Of course, for each term, the other fields $\vec{E}_b(t)$ and $\vec{E}_c(t)$ contribute twice because any of their chronological ordering contribute to the same phase-matched direction. Introducing some simplifications and notations, we get

$$\begin{aligned}
\tilde{P}_{\vec{k}_{PE}}^{(3)}(t) = & \frac{i}{\hbar^3} \sum_{p,r=b,c}^{r \neq p} \sum_{m=1}^2 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \{ \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_a(t-T_a-t_3-t_2) \mathcal{A}_r(t-T_r-t_3-t_2-t_1) \\
& \times e^{-i\omega_p(t-t_3)+i\omega_a(t-t_3-t_2)-i\omega_r(t-t_3-t_2-t_1)+i(-\vec{k}_a+\vec{k}_b+\vec{k}_c)\cdot\vec{r}} \text{Tr}_b[\vec{\mu}_{ge_m} \langle e_m | \mathbf{G}(t_3) \mathbf{L}'_{v(p)} \mathbf{G}(t_2) \mathbf{L}'_{v(a)} \mathbf{G}(t_1) \mathbf{L}'_{v(r)} \rho_b(-\infty) | g \rangle] \\
& + \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_r(t-T_r-t_3-t_2) \mathcal{A}_a(t-T_a-t_3-t_2-t_1) e^{-i\omega_p(t-t_3)-i\omega_r(t-t_3-t_2)+i\omega_a(t-t_3-t_2-t_1)+i(-\vec{k}_a+\vec{k}_b+\vec{k}_c)\cdot\vec{r}} \\
& \times \text{Tr}_b[\vec{\mu}_{ge_m} \langle e_m | \mathbf{G}(t_3) \mathbf{L}'_{v(p)} \mathbf{G}(t_2) \mathbf{L}'_{v(r)} \mathbf{G}(t_1) \mathbf{L}'_{v(a)} \rho_b(-\infty) | g \rangle] \}. \quad (5.2)
\end{aligned}$$

To perform the time integrations, we require the explicit expression of the vibronic density matrix elements. Introducing the contributions of the various pathways given in Appendix A, the third-order polarization takes the form

$$\begin{aligned}
\tilde{P}_{\vec{k}_{PE}}^{(3)}(t) = & \frac{i}{\hbar^3} \sum_{p,r=b,c}^{r \neq p} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \{ \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_a(t-T_a-t_3-t_2) \mathcal{A}_r(t-T_r-t_3-t_2-t_1) \\
& \times e^{-i\omega_p(t-t_3)+i\omega_a(t-t_3-t_2)-i\omega_r(t-t_3-t_2-t_1)+i\vec{k}_{PE}\cdot\vec{r}} [R_{1\vec{k}_{PE}}^{(1,1,1)} + R_{1\vec{k}_{PE}}^{(2,2,1)} + R_{4\vec{k}_{PE}}^{(1,1,1)} + R_{4\vec{k}_{PE}}^{(2,1,1)} + R_{1\vec{k}_{PE}}^{(2,2,2)} + R_{1\vec{k}_{PE}}^{(1,1,2)} + R_{4\vec{k}_{PE}}^{(2,2,2)} + R_{4\vec{k}_{PE}}^{(1,2,2)}] \\
& + \mathcal{A}_p(t-T_p-t_3) \mathcal{A}_r(t-T_r-t_3-t_2) \mathcal{A}_a(t-T_a-t_3-t_2-t_1) e^{-i\omega_p(t-t_3)-i\omega_r(t-t_3-t_2)+i\omega_a(t-t_3-t_2-t_1)+i\vec{k}_{PE}\cdot\vec{r}} [R_{2\vec{k}_{PE}}^{(1,1,1)} + R_{2\vec{k}_{PE}}^{(1,2,1)} \\
& + R_{3\vec{k}_{PE}}^{(1,1,1)} + R_{3\vec{k}_{PE}}^{(2,1,1)} + R_{2\vec{k}_{PE}}^{(2,2,2)} + R_{2\vec{k}_{PE}}^{(2,1,2)} + R_{3\vec{k}_{PE}}^{(2,2,2)} + R_{3\vec{k}_{PE}}^{(1,2,2)}] \}. \quad (5.3)
\end{aligned}$$

Notice that the sum over m disappears in this last expression since it is explicitly involved in the various terms $R_{n\vec{k}_{PE}}^{(t,u,v)}$ for $n=1,4$ that need to be evaluated. For the sake of simplicity, we just calculate explicitly the first one as an example

$$\begin{aligned}
R_{1\vec{k}_{PE}}^{(1,1,1)} = & -\vec{\mu}_{ge_1} \vec{\mu}_{e_1g} \cdot \vec{E}_p \vec{\mu}_{ge_1} \cdot \vec{E}_a^* \vec{\mu}_{e_1g} \cdot \vec{E}_r e^{-i\omega_{e_1g}t_3} \\
& \times \text{Tr}_b \left\{ \mathbf{G}_{b(\beta_1)}(t_3) \mathbf{G}_{b(\beta_1)}(t_2) e^{-i\omega_{e_1g}t_1} \mathbf{G}_{b(\beta_1)}(t_1) \right. \\
& \times \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau) \right] \rho_{gg}(t_0) \\
& \left. \times \exp_- \left[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau) \right] \right\}. \quad (5.4)
\end{aligned}$$

Because the interaction operators with the laser beams are

independent of the bath variables, they can be factorized in front of the expression like scalar quantities. Also, we take advantage of the invariance of the trace over the bath states by the unitary transformation $\mathbf{G}_{b(\beta_1)}(t_3)$ and by circular permutation of $\exp[-\frac{i}{\hbar} \int_0^{t_3} d\tau \mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau)]$ to reject the bath density matrix to the right. Finally, applying the bath evolution Liouvillians $\mathbf{G}_{b(\beta_1)}(t_2)$ and $\mathbf{G}_{b(\beta_1)}(t_1)$ on the left, we get the expression given below. All the other terms are obtained similarly and are given by

$$\begin{aligned}
R_{1\vec{k}_{PE}}^{(1,1,1)} = & -\vec{\mu}_{ge_1} \vec{\mu}_{e_1g} \cdot \vec{E}_p \vec{\mu}_{ge_1} \cdot \vec{E}_a^* \vec{\mu}_{e_1g} \cdot \vec{E}_r e^{-i\omega_{e_1g}(t_1+t_3)} \\
& \times \left\langle \exp_- \left[-\frac{i}{\hbar} \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau) \right] \right. \\
& \left. \times \exp_+ \left[-\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau) \right] \right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{1\vec{k}_{PE}}^{(2,2,1)} = & -\vec{\mu}_{ge_1}\vec{\mu}_{e_2g}\cdot\vec{E}_p\vec{\mu}_{ge_2} \\
& \cdot\vec{E}_a^*\vec{\mu}_{e_1g}\cdot\vec{E}_re^{-i\omega_{e_1g}(t_1+t_3)}e^{-i\omega_{e_1e_2}t_2} \\
& \times\left\langle\exp_{-}\left[\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right. \\
& \times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right] \\
& \times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right] \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{4\vec{k}_{PE}}^{(1,1,1)} = & -\vec{\mu}_{ge_1}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{ge_1}\cdot\vec{E}_a^*\vec{\mu}_{e_1g}\cdot\vec{E}_re^{-i\omega_{e_1g}(t_1+t_3)} \\
& \times\left\langle\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{4\vec{k}_{PE}}^{(2,1,1)} = & -\vec{\mu}_{ge_2}\vec{\mu}_{e_2g}\cdot\vec{E}_p\vec{\mu}_{ge_1}\cdot\vec{E}_a^*\vec{\mu}_{e_1g}\cdot\vec{E}_re^{-i\omega_{e_1g}t_1-i\omega_{e_2g}t_3} \\
& \times\left\langle\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{1\vec{k}_{PE}}^{(2,2,2)} = & -\vec{\mu}_{ge_2}\vec{\mu}_{e_2g}\cdot\vec{E}_p\vec{\mu}_{ge_2}\cdot\vec{E}_a^*\vec{\mu}_{e_2g}\cdot\vec{E}_re^{-i\omega_{e_2g}(t_1+t_3)} \\
& \times\left\langle\exp_{-}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\beta_2(l)}^{(e_2)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\beta_2(l)}^{(e_2)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{1\vec{k}_{PE}}^{(1,1,2)} = & -\vec{\mu}_{ge_2}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{ge_1}\cdot\vec{E}_a^*\vec{\mu}_{e_2g}\cdot\vec{E}_re^{-i\omega_{e_2g}(t_1+t_3)}e^{-i\omega_{e_2e_1}t_2} \\
& \times\left\langle\exp_{-}\left[\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right. \\
& \times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right] \\
& \times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right] \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{4\vec{k}_{PE}}^{(2,2,2)} = & -\vec{\mu}_{ge_2}\vec{\mu}_{e_2g}\cdot\vec{E}_p\vec{\mu}_{ge_2}\cdot\vec{E}_a^*\vec{\mu}_{e_2g}\cdot\vec{E}_re^{-i\omega_{e_2g}(t_1+t_3)} \\
& \times\left\langle\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right\rangle_b, \\
R_{4\vec{k}_{PE}}^{(1,2,2)} = & -\vec{\mu}_{ge_1}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{ge_2}\cdot\vec{E}_a^*\vec{\mu}_{e_2g}\cdot\vec{E}_re^{-i\omega_{e_2g}t_1-i\omega_{e_1g}t_3} \\
& \times\left\langle\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right\rangle_b \quad (5.5)
\end{aligned}$$

for the contributions participating in the phase-matched direction $\vec{k}_{PE}=-\vec{k}_a+\vec{k}_b+\vec{k}_c$ when the field $\vec{E}_a$ participates in the second interaction, and

$$\begin{aligned}
R_{2\vec{k}_{PE}}^{(1,1,1)} = & -\vec{\mu}_{ge_1}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{e_1g}\cdot\vec{E}_r\vec{\mu}_{ge_1}\cdot\vec{E}_a^*e^{-i\omega_{ge_1}(t_1-t_3)} \\
& \times\left\langle\exp_{-}\left[\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau)\right]\right. \\
& \left.\times\exp_{-}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\beta_1(l)}^{(e_1)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{2\vec{k}_{PE}}^{(1,2,1)} = & -\vec{\mu}_{ge_2}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{e_2g}\cdot\vec{E}_r\vec{\mu}_{ge_1}\cdot\vec{E}_a^*e^{-i\omega_{ge_1}t_1-i\omega_{e_2g}t_3-i\omega_{e_2e_1}t_2} \\
& \times\left\langle\exp_{-}\left[\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right. \\
& \times\exp_{-}\left[\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right] \\
& \times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right] \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1}^{t_1+t_2}d\tau\mathbf{W}_{\alpha(l)}^{(e_2)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{3\vec{k}_{PE}}^{(1,1,1)} = & -\vec{\mu}_{ge_1}\vec{\mu}_{e_1g}\cdot\vec{E}_p\vec{\mu}_{e_1g}\cdot\vec{E}_r\vec{\mu}_{ge_1}\cdot\vec{E}_a^*e^{-i\omega_{ge_1}(t_1-t_3)} \\
& \times\left\langle\exp_{-}\left[\frac{i}{\hbar}\int_0^{t_1}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right. \\
& \left.\times\exp_{+}\left[-\frac{i}{\hbar}\int_{t_1+t_2}^{t_1+t_2+t_3}d\tau\mathbf{W}_{\alpha(l)}^{(e_1)}(\tau)\right]\right\rangle_b,
\end{aligned}$$

$$\begin{aligned}
R_{3k_{PE}}^{(2,1,1)} &= -\vec{\mu}_{ge_2} \vec{\mu}_{e_2g} \cdot \vec{E}_p \vec{\mu}_{e_1g} \cdot \vec{E}_r \vec{\mu}_{ge_1} \cdot \vec{E}_a^* e^{-i\omega_{ge_1}t_1 - i\omega_{e_2g}t_3} \\
&\quad \times \left\langle \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_1)}(\tau) \right] \right. \\
&\quad \left. \times \exp_+ \left[-\frac{i}{\hbar} \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(l)}^{(e_2)}(\tau) \right] \right\rangle_b, \\
R_{2k_{PE}}^{(2,2,2)} &= -\vec{\mu}_{ge_2} \vec{\mu}_{e_2g} \cdot \vec{E}_p \vec{\mu}_{e_2g} \cdot \vec{E}_r \vec{\mu}_{ge_2} \cdot \vec{E}_a^* e^{-i\omega_{ge_2}(t_1-t_3)} \\
&\quad \times \left\langle \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\beta_2(l)}^{(e_2)}(\tau) \right] \right. \\
&\quad \left. \times \exp_- \left[-\frac{i}{\hbar} \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\beta_2(l)}^{(e_2)}(\tau) \right] \right\rangle_b, \\
R_{2k_{PE}}^{(2,1,2)} &= -\vec{\mu}_{ge_1} \vec{\mu}_{e_2g} \cdot \vec{E}_p \vec{\mu}_{e_1g} \cdot \vec{E}_r \vec{\mu}_{ge_2} \cdot \vec{E}_a^* e^{-i\omega_{ge_2}t_1 - i\omega_{e_1g}t_3 - i\omega_{e_1e_2}t_2} \\
&\quad \times \left\langle \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_2)}(\tau) \right] \right. \\
&\quad \times \exp_- \left[\frac{i}{\hbar} \int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(l)}^{(e_2)}(\tau) \right] \\
&\quad \times \exp_+ \left[-\frac{i}{\hbar} \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(l)}^{(e_1)}(\tau) \right] \\
&\quad \left. \times \exp_+ \left[-\frac{i}{\hbar} \int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(l)}^{(e_1)}(\tau) \right] \right\rangle_b, \\
R_{3k_{PE}}^{(2,2,2)} &= -\vec{\mu}_{ge_2} \vec{\mu}_{e_2g} \cdot \vec{E}_p \vec{\mu}_{e_2g} \cdot \vec{E}_r \vec{\mu}_{ge_2} \cdot \vec{E}_a^* e^{-i\omega_{ge_2}(t_1-t_3)} \\
&\quad \times \left\langle \exp_- \left[\frac{i}{\hbar} \int_0^{t_1} d\tau \mathbf{W}_{\alpha(l)}^{(e_2)}(\tau) \right] \right. \\
&\quad \left. \times \exp_+ \left[-\frac{i}{\hbar} \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(l)}^{(e_2)}(\tau) \right] \right\rangle_b,
\end{aligned}
\tag{5.6}$$

for the terms contributing to the same phase-matched direction with the field $\vec{E}_a(t)$ acting on the first interaction. Also, the usual notation for the bath average $\langle \mathbf{Q} \rangle_b = \text{Tr}_b[\mathbf{Q}\rho]$ has been introduced. The reference Hamiltonian, required for the evaluation of each individual pathway, is indicated in Appendix A.

Now, we are left with the evaluation of the various bath correlation factors participating in the dynamical photon-echo process. In Sec. VI, we will take advantage of the impulse limit approximation, to avoid the complicated multiple time integrations and evaluate the various correlation factors associated to the different pathways.

VI. EVALUATION OF THE BATH CORRELATION FACTORS PARTICIPATING IN THE THREE-PULSE PHOTON-ECHO

The various bath correlation factors of the contributions to the three-pulse photon-echo signal can be evaluated from a second-order expansion with respect to the vibronic and bath interaction. To this end, we use the series expansion of the positive time-ordered exponential which is expressed by the following relation:

$$\exp_+ \left[\frac{i\epsilon}{\hbar} \int_{t_0}^t d\tau f(\tau) \right] = 1 + \sum_{n=1}^{\infty} \left(\frac{i\epsilon}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 f(\tau_n) f(\tau_{n-1}) \cdots f(\tau_1). \tag{6.1}$$

Of course, a similar expansion exists for the negative time-ordered exponential and corresponds to

$$\exp_- \left[\frac{i\epsilon'}{\hbar} \int_{t_0}^t d\tau f(\tau) \right] = 1 + \sum_{n=1}^{\infty} \left(\frac{i\epsilon'}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 f(\tau_1) f(\tau_2) \cdots f(\tau_n). \tag{6.2}$$

Then, up to the second order, the bath correlation factors involving two time-ordered exponential operators can be calculated into the form

$$\begin{aligned}
& \left\langle \exp_{+(-)} \left[\frac{i\epsilon_1}{\hbar} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau f_1(\tau) \right] \exp_{+(-)} \left[\frac{i\epsilon_2}{\hbar} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau f_2(\tau) \right] \right\rangle_b \\
&= \left\langle \left[1 + \frac{i\epsilon_1}{\hbar} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau f_1(\tau) - \frac{1}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_1}}^{\tau_2} d\tau_1 f_1(\tau_{2(1)}) f_1(\tau_{1(2)}) \right] \right. \\
&\quad \times \left. \left[1 + \frac{i\epsilon_2}{\hbar} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau f_2(\tau) - \frac{1}{\hbar^2} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_2 \int_{t_{\alpha_2}}^{\tau_2} d\tau_1 f_2(\tau_{2(1)}) f_2(\tau_{1(2)}) \right] \right\rangle_b \\
&= \left\langle 1 + \frac{i\epsilon_1}{\hbar} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau f_1(\tau) + \frac{i\epsilon_2}{\hbar} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau f_2(\tau) \right. \\
&\quad \left. - \frac{\epsilon_1 \epsilon_2}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau' f_1(\tau) f_2(\tau') - \frac{1}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_1}}^{\tau_2} d\tau_1 f_1(\tau_{2(1)}) f_1(\tau_{1(2)}) - \frac{1}{\hbar^2} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_2 \int_{t_{\alpha_2}}^{\tau_2} d\tau_1 f_2(\tau_{2(1)}) f_2(\tau_{1(2)}) \right\rangle_b, \tag{6.3}
\end{aligned}$$

and a second-order expansion for the fourth-order product can be obtained similarly,

$$\begin{aligned}
& \left\langle \exp_{+(-)} \left[\frac{i\epsilon_1}{\hbar} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau f_1(\tau) \right] \exp_{+(-)} \left[\frac{i\epsilon_2}{\hbar} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau f_2(\tau) \right] \exp_{+(-)} \left[\frac{i\epsilon_3}{\hbar} \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau f_3(\tau) \right] \exp_{+(-)} \left[\frac{i\epsilon_4}{\hbar} \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau f_4(\tau) \right] \right\rangle_b \\
&= \left\langle 1 + \frac{i\epsilon_1}{\hbar} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau f_1(\tau) + \frac{i\epsilon_2}{\hbar} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau f_2(\tau) + \frac{i\epsilon_3}{\hbar} \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau f_3(\tau) + \frac{i\epsilon_4}{\hbar} \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau f_4(\tau) - \frac{\epsilon_1 \epsilon_2}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_1 f_1(\tau_2) f_2(\tau_1) \right. \\
&\quad - \frac{\epsilon_1 \epsilon_3}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau_1 f_1(\tau_2) f_3(\tau_1) - \frac{\epsilon_1 \epsilon_4}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau_1 f_1(\tau_2) f_4(\tau_1) - \frac{\epsilon_2 \epsilon_3}{\hbar^2} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_2 \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau_1 f_2(\tau_2) f_3(\tau_1) \\
&\quad - \frac{\epsilon_2 \epsilon_4}{\hbar^2} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_2 \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau_1 f_2(\tau_2) f_4(\tau_1) - \frac{\epsilon_3 \epsilon_4}{\hbar^2} \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau_2 \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau_1 f_3(\tau_2) f_4(\tau_1) - \frac{1}{\hbar^2} \int_{t_{\alpha_1}}^{t_{\beta_1}} d\tau_2 \int_{t_{\alpha_1}}^{\tau_2} d\tau_1 f_1(\tau_{2(1)}) f_1(\tau_{1(2)}) \\
&\quad \left. - \frac{1}{\hbar^2} \int_{t_{\alpha_2}}^{t_{\beta_2}} d\tau_2 \int_{t_{\alpha_2}}^{\tau_2} d\tau_1 f_2(\tau_{2(1)}) f_2(\tau_{1(2)}) - \frac{1}{\hbar^2} \int_{t_{\alpha_3}}^{t_{\beta_3}} d\tau_2 \int_{t_{\alpha_3}}^{\tau_2} d\tau_1 f_3(\tau_{2(1)}) f_3(\tau_{1(2)}) - \frac{1}{\hbar^2} \int_{t_{\alpha_4}}^{t_{\beta_4}} d\tau_2 \int_{t_{\alpha_4}}^{\tau_2} d\tau_1 f_4(\tau_{2(1)}) f_4(\tau_{1(2)}) \right\rangle_b. \tag{6.4}
\end{aligned}$$

These expressions enable us to overcome the crude factorization approximation. In fact, we can generalize these expressions to a product of N time-ordered exponential operators to get

$$\begin{aligned}
& \left\langle \prod_{n=1}^N \exp_{+(-)} \left[\frac{i\epsilon_n}{\hbar} \int_{t_{\alpha_n}}^{t_{\beta_n}} d\tau f_n(\tau) \right] \right\rangle_b = \left\langle 1 + \sum_{n=1}^N \frac{i\epsilon_n}{\hbar} \int_{t_{\alpha_n}}^{t_{\beta_n}} d\tau f_n(\tau) - \sum_{n=1}^{N-1} \sum_{m=n+1}^N \frac{\epsilon_n \epsilon_m}{\hbar^2} \int_{t_{\alpha_n}}^{t_{\beta_n}} d\tau_2 \int_{t_{\alpha_m}}^{t_{\beta_m}} d\tau_1 f_n(\tau_2) f_m(\tau_1) \right. \\
&\quad \left. - \sum_{n=1}^N \frac{1}{\hbar^2} \int_{t_{\alpha_n}}^{t_{\beta_n}} d\tau_2 \int_{t_{\alpha_n}}^{\tau_2} d\tau_1 f_n(\tau_{2(1)}) f_n(\tau_{1(2)}) \right\rangle_b. \tag{6.5}
\end{aligned}$$

We assume that the first-order terms cancel because, in any case, the average value of the interaction can be involved in the zeroth-order energy by a simple energy-renormalization procedure. Then, we can evaluate the correlation factors of the two groups of contributions given by Eqs. (5.5) and (5.6). However, as previously mentioned, the first group of contributions given by Eq. (5.5) where the field $\vec{E}_a(t)$ participates in the second interaction does not participate in the photon-echo process due to our field-ordering prescription. The second group of contributions given by Eq. (5.5) contains only the ones with the field $\vec{E}_a(t)$ acting first as in the case of the experiment we are dealing with. Their corresponding correlation factors are given by the following expressions:

$$\begin{aligned}
& \left\langle e_-^{(i/\hbar) \int_0^{t_1} d\tau \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau)} e_-^{-(i/\hbar) \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau)} \right\rangle_{b, R_{2k_{PE}}^{(1,1,1)}} = \exp \left[-\frac{1}{\hbar^2} \left(-\int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau) \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau') \right. \right. \\
&\quad \left. \left. \times \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau') \mathbf{W}_{\beta_1(t)}^{(e_1)}(\tau) \rangle_b \right) \right]
\end{aligned}$$

$$\begin{aligned}
& \left\langle e_{-}^{(i\hbar)\int_0^{t_1} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} e_{-}^{(i\hbar)\int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau)} \right\rangle_{b, R_{2k_{PE}}^{(1,2,1)}} \\
&= \exp \left[-\frac{1}{\hbar^2} \left(\int_0^{t_1} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b - \int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b \right. \right. \\
&\quad - \int_0^{t_1} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b - \int_{t_1}^{t_1+t_2} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b \\
&\quad - \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b \\
&\quad + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \rangle_b + \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \rangle_b \\
&\quad \left. + \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \rangle_b \right) \Bigg] \\
&\left\langle e_{-}^{(i\hbar)\int_0^{t_1} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} \right\rangle_{b, R_{3k_{PE}}^{(1,1,1)}} = \exp \left[-\frac{1}{\hbar^2} \left(- \int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau) \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau') \right. \right. \\
&\quad \left. \left. \times \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau) \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau') \rangle_b \right) \right] \\
&\left\langle e_{-}^{(i\hbar)\int_0^{t_1} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau)} \right\rangle_{b, R_{3k_{PE}}^{(2,1,1)}} = \exp \left[-\frac{1}{\hbar^2} \left(- \int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau) \mathbf{W}_{\beta_1(I)}^{(e_2)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau') \right. \right. \\
&\quad \left. \left. \times \mathbf{W}_{\beta_1(I)}^{(e_1)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\beta_1(I)}^{(e_2)}(\tau) \mathbf{W}_{\beta_1(I)}^{(e_2)}(\tau') \rangle_b \right) \right] \\
&\left\langle e_{-}^{(i\hbar)\int_0^{t_1} d\tau \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau)} e_{-}^{-(i\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau)} \right\rangle_{b, R_{2k_{PE}}^{(2,2,2)}} = \exp \left[-\frac{1}{\hbar^2} \left(- \int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau) \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau') \right. \right. \\
&\quad \left. \left. \times \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau') \mathbf{W}_{\beta_2(I)}^{(e_2)}(\tau) \rangle_b \right) \right] \\
&\left\langle e_{-}^{(i\hbar)\int_0^{t_1} d\tau \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau)} e_{-}^{(i\hbar)\int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} e_{+}^{-(i\hbar)\int_{t_1}^{t_1+t_2} d\tau \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau)} \right\rangle_{b, R_{2k_{PE}}^{(2,1,2)}} \\
&= \exp \left[-\frac{1}{\hbar^2} \left(\int_0^{t_1} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \rangle_b - \int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b \right. \right. \\
&\quad - \int_0^{t_1} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b - \int_{t_1}^{t_1+t_2} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b \\
&\quad - \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1}^{t_1+t_2} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \rangle_b \\
&\quad + \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_2)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \rangle_b \\
&\quad \left. + \int_{t_1}^{t_1+t_2} d\tau \int_{t_1}^{\tau} d\tau' \langle \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau') \mathbf{W}_{\alpha(I)}^{(e_1)}(\tau) \rangle_b \right) \Bigg]
\end{aligned}$$

$$\begin{aligned}
\left\langle e_{-}^{(i/\hbar)\int_0^{t_1} d\tau W_{\alpha(l)}^{(e_2)}(\tau)} e_{+}^{-(i/\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau W_{\alpha(l)}^{(e_2)}(\tau)} \right\rangle_{b,R_{3k_{PE}}^{(2,2,2)}} &= \exp \left[-\frac{1}{\hbar^2} \left(-\int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle W_{\beta_1(l)}^{(e_2)}(\tau) W_{\beta_1(l)}^{(e_2)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle W_{\beta_1(l)}^{(e_2)}(\tau) W_{\beta_1(l)}^{(e_2)}(\tau') \rangle_b \right. \right. \\
&\quad \left. \left. \times W_{\beta_1(l)}^{(e_2)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle W_{\beta_1(l)}^{(e_2)}(\tau) W_{\beta_1(l)}^{(e_2)}(\tau') \rangle_b \right) \right] \\
\left\langle e_{-}^{(i/\hbar)\int_0^{t_1} d\tau W_{\alpha(l)}^{(e_2)}(\tau)} e_{+}^{-(i/\hbar)\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau W_{\alpha(l)}^{(e_1)}(\tau)} \right\rangle_{b,R_{3k_{PE}}^{(1,2,2)}} &= \exp \left[-\frac{1}{\hbar^2} \left(-\int_0^{t_1} d\tau \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau' \langle W_{\beta_1(l)}^{(e_2)}(\tau) W_{\beta_1(l)}^{(e_1)}(\tau') \rangle_b + \int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle W_{\beta_1(l)}^{(e_2)}(\tau) W_{\beta_1(l)}^{(e_1)}(\tau') \rangle_b \right. \right. \\
&\quad \left. \left. \times W_{\beta_1(l)}^{(e_2)}(\tau) \rangle_b + \int_{t_1+t_2}^{t_1+t_2+t_3} d\tau \int_{t_1+t_2}^{\tau} d\tau' \langle W_{\beta_1(l)}^{(e_1)}(\tau) W_{\beta_1(l)}^{(e_1)}(\tau') \rangle_b \right) \right]. \quad (6.6)
\end{aligned}$$

From relations (6.1)–(6.4), these quantities can be straightforwardly evaluated, once the expressions of the bath correlation functions are known. To evaluate the bath factors entering in the expressions of the contributions associated to the various pathways described in Eq. (6.6), we note that only two different types of integral arguments are involved. According to Appendix B, these arguments can be obtained straightforwardly from the generic functions $g_1(A, B, C, D; \lambda, i, j)$ and $g_2(A, B, C; \lambda, i, j)$. From their explicit evaluations, the various R quantities in Eq. (5.6) can readily be expressed in terms of these functions. As an example, we write down the first term $R_{2k_{PE}}^{(1,1,1)}$ as

$$R_{2k_{PE}}^{(1,1,1)} = -\vec{\mu}_{ge_1} \vec{\mu}_{e_1g} \cdot \vec{E}_p \vec{\mu}_{e_1g} \cdot \vec{E}_r \vec{\mu}_{ge_1} \cdot \vec{E}_a^* e^{-i\omega_{ge_1}(t_1-t_3)} e^{-(1/\hbar^2)[-g_1(0, t_1, t_1+t_2, t_1+t_2+t_3; \beta_1, 1, 1) + g_2(0, t_1, 0; \beta_1, 1, 1) + g_2(t_1+t_2, t_1+t_2+t_3, t_1+t_2; \beta_1, 1, 1)]}, \quad (6.7)$$

all the other terms being deduced similarly. Notice that the functions g_1 and g_2 are dependent on each one another in the simple case of a two-level system [8]. In our case, because not all the arguments of a given exponential depend on the same state, it is more convenient to straightforwardly evaluate them from the bath correlation functions which can be obtained from specific type of bath made of quantum or stochastic models. Notice that the baths can be described in terms of a set of continuous distribution of oscillators describing the acoustic or optical phonon modes of the surrounding medium. In the case of slow modulation limit, where the phonon dynamics is slow compared to the magnitude of the fluctuations, the bath generates an inhomogeneous broadening responsible for the dephasing. Although this type of bath has been used in a number of works [27,40–42], its generalization and extension to the simultaneous description of both homogeneous and inhomogeneous broadenings was formulated by Mukamel and co-workers [2,3,8].

Therefore, in addition to the phase factors which are important for the rephasing process, the bath correlation factors evaluated above govern the internal dynamics of the global vibronic and bath system.

VII. THREE-PULSE PHOTON-ECHO SIGNAL INTENSITY

In most of the problems where vibrational or electronic dephasings play an active role, the bath correlation function accounting for these processes usually has an intricate dependence, such as in the case of our concern. In such a situation, and for short enough laser pulses, the impulsive limit approximation [8] is quite convenient. Of course, when light

pulses do not overlap, the pulse ordering of the excitation determines the contributions that need to be considered in the description. This is mostly the case in the impulsive limit approximation. Here, the ordering of the pulses has to be respected because such an evaluation does not account for the balance of the contributions resulting from the various pulse overlaps. On account of these comments and assuming homodyne detection, we will express the intensity of the three-pulse photon-echo signal into the form

$$I_{3PPE} = \int_{-\infty}^{\infty} dt |P_{k_{PE}}^{(3)}(t)|^2, \quad (7.1)$$

where the polarization is obtained from relation (5.3) and reduces to

$$\begin{aligned}
\tilde{P}_{k_{PE}}^{(3)}(t) &= \frac{i}{\hbar^3} \sum_{p,r=b,c}^{r \neq p} \int_0^{\infty} dt_3 \int_0^{\infty} dt_2 \int_0^{\infty} dt_1 \\
&\quad \times \{ \mathcal{A}_p(t - T_p - t_3) \mathcal{A}_r(t - T_r - t_3 - t_2) \\
&\quad \times \mathcal{A}_a(t - T_a - t_3 - t_2 - t_1) \\
&\quad \times e^{-i\omega_p(t-t_3) - i\omega_r(t-t_3-t_2) + i\omega_a(t-t_3-t_2-t_1) + i\vec{k}_{PE} \cdot \vec{r}} \\
&\quad \times [R_{2k_{PE}}^{(1,1,1)} + R_{2k_{PE}}^{(1,2,1)} + R_{3k_{PE}}^{(1,1,1)} + R_{3k_{PE}}^{(2,1,1)} + R_{2k_{PE}}^{(2,2,2)} \\
&\quad + R_{2k_{PE}}^{(2,1,2)} + R_{3k_{PE}}^{(2,2,2)} + R_{3k_{PE}}^{(1,2,2)}] \}. \quad (7.2)
\end{aligned}$$

where only one chronological combination of fields participate, say field $\vec{E}_a(t)$ interacts first, next $\vec{E}_b(t)$, and finally $\vec{E}_c(t)$. Introducing the various contributions with respect to the different pathways given by Eq. (5.6) with their corre-

sponding bath correlation factors described in expressions (6.6), we can evaluate the signal intensity.

At this stage, if we introduce the impulsive limit approximation valid for short pulses, we can avoid the complicated multiple time integration by greatly simplifying our previous expression (7.2). Taking advantage of this restriction, we have

$$t_1 \sim T_q - T_r, \quad t_2 \sim T_p - T_q, \quad \text{and} \quad t_3 \sim t - T_p. \quad (7.3)$$

With well chronologically ordered nonoverlapping laser pulses, only the combination of fields $\vec{E}_a(t-T_a) \rightarrow \vec{E}_b(t-T_b) \rightarrow \vec{E}_c(t-T_c)$ is required to describe the three-pulse photon-echo experiment, and we necessarily have the conditions $t - T_c \geq 0$, $T_c - T_b \geq 0$, and $T_b - T_a \geq 0$, implying

$$\begin{aligned} \tilde{P}_{k_{PE}}^{(3)}(t) = & \frac{i}{\hbar^3} \mathcal{K} \sum_{p,r=b,c}^{r \neq p} e^{-i\omega_c T_c - i\omega_b T_b + i\omega_a T_a + i\vec{k}_{PE} \cdot \vec{r}} \\ & \times [R_{2k_{PE}}^{(1,1,1)} + R_{2k_{PE}}^{(1,2,1)} + R_{3k_{PE}}^{(1,1,1)} + R_{3k_{PE}}^{(2,1,1)} + R_{2k_{PE}}^{(2,2,2)} \\ & + R_{2k_{PE}}^{(2,1,2)} + R_{3k_{PE}}^{(2,2,2)} + R_{3k_{PE}}^{(1,2,2)}], \end{aligned} \quad (7.4)$$

where the notation

$$\begin{aligned} \mathcal{K} = & \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \mathcal{A}_c(t - T_c - t_3) \\ & \times \mathcal{A}_b(t - T_b - t_3 - t_2) \mathcal{A}_a(t - T_a - t_3 - t_2 - t_1) \end{aligned} \quad (7.5)$$

has been introduced. Now, we have all what we need to perform the numerical simulations to illustrate the influence of the bath and of the neighboring level on the three-pulse photon-echo signal. It will enable us to discuss the role of this perturbing level on the rephasing processes.

To perform the numerical simulations on the time dependence of the three-pulse photon-echo signal, the vibronic transition frequency has been chosen as $\omega_{e_1g} = 20\,000 \text{ cm}^{-1}$, while different values are considered for ω_{e_2g} , as indicated in the captions of the figures. The three laser fields are resonant with the first vibronic transition so that $\omega_{e_1g} = \omega_p \forall p = a, b, c$. Also, the probing times of the pulses are $T_a = 0$, $T_b = 1$, and $T_c = 3$. The dipole moments and field amplitudes, which are irrelevant multiplicative constants for our purpose, are all arbitrarily fixed as $\mu_{e_1g} = \mu_{g e_1} = 1 \forall i = 1, 2$ and $E_p = 1 \forall p = a, b, c$.

Finally, the physical parameters of the bath correlation functions are defined according to the different physical situations and characterization of different types of bath through the constants $\Delta_{ij}^{(\lambda)}$ and $\Lambda_{ij}^{(\lambda)}$. In the particular case shown in Fig. 2, the time dependence of the three-pulse photon-echo signal is analyzed for different energy gaps between the two excited vibronic levels. The simulation shows that the signal is quite sensitive to this energy mismatch. In the case of resonant levels, say $E_{e_1} - E_{e_2} = 0 \text{ cm}^{-1}$, we observe a monotonic increase in the photon-echo signal which cannot really be interpreted because the pulse shape is missing due to the impulse limit approximation used here, followed by a monotonic decrease driven by the inverse bath correlation time $\Lambda_{ij}^{(\lambda)}$ and its corresponding fluctuation amplitude $\Delta_{ij}^{(\lambda)}$. How-

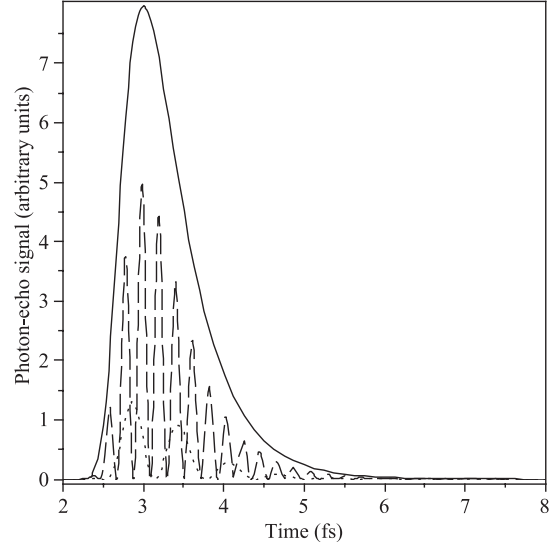


FIG. 2. Time dependence of the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$ for different energy gaps $E_{e_1} - E_{e_2} = 0 \text{ cm}^{-1}$ (solid line), 10 cm^{-1} (dashed line), and 30 cm^{-1} (long-dashed line). The values of the bath parameters have been chosen as $\Delta_{ii}^{(\lambda)} = 2 \text{ cm}^{-1}$ and $\Lambda_{ii}^{(\lambda)} = 4 \text{ cm}^{-1}$ for $i = 1, 2$ and $\forall \lambda$, while for the crossed bath correlation parameters we have $\Delta_{ij}^{(\lambda)} = 5 \text{ cm}^{-1}$ and $\Lambda_{ij}^{(\lambda)} = 12 \text{ cm}^{-1}$ for $i \neq j$ and $\forall \lambda$.

ever, when there is an energy mismatch, chosen here as $E_{e_1} - E_{e_2} = 10 \text{ cm}^{-1}$ (dashed line) and 30 cm^{-1} (long-dashed line), the contributions $R_{nk_{PE}}^{(i_1, i_2, i_3)}$ of the various pathways oscillating at different frequencies interfere and give rise to oscillations in the photon-echo signal, as we can see from Fig. 2. The exponential damping resulting from the dephasing induced by the bath is better represented by the logarithmic variation in the photon-echo signal shown in Fig. 3. Because of the particular values chosen here for $\Delta_{ij}^{(\lambda)}$ and

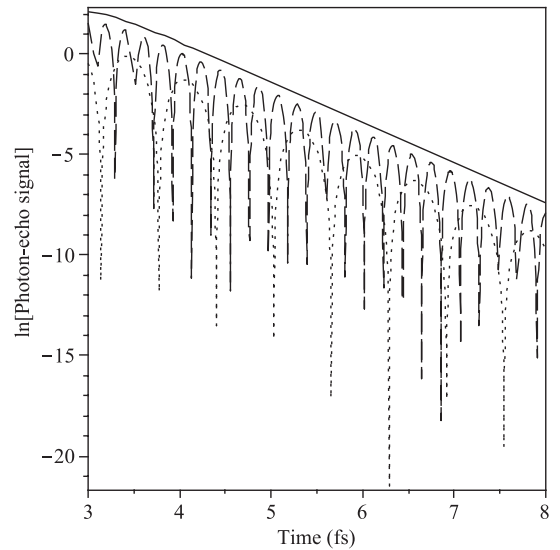


FIG. 3. Logarithmic variations in the time dependence shown in Fig. 2 for the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$ with the same energy mismatches.

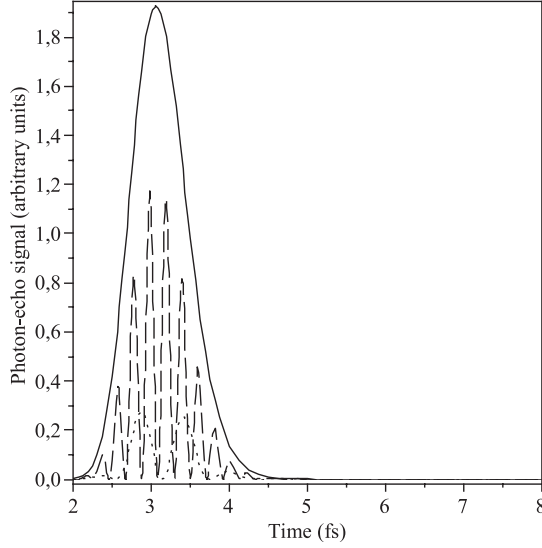


FIG. 4. Like in the previous Fig. 2, we show the time dependence of the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$ for the same three different energy gaps $E_{e_1} - E_{e_2} = 0$ cm^{-1} (solid line), 10 cm^{-1} (dashed line), and 30 cm^{-1} (long-dashed line) considered previously, but with longer crossed bath correlation times. Here, the corresponding values are $\Delta_{ij}^{(\lambda)} = 2$ cm^{-1} for $i, j = 1, 2$ and $\forall \lambda$, $\Lambda_{ii}^{(\lambda)} = 1$ cm^{-1} for $i = 1, 2$ and $\forall \lambda$, and $\Lambda_{ij}^{(\lambda)} = 2$ cm^{-1} for $i \neq j$ and $\forall \lambda$.

$\Lambda_{ij}^{(\lambda)}$, the time dependence is almost exponential because the bath correlation time $(\Lambda_{ii}^{(\lambda)})^{-1}$ is much shorter than its Markovian limit $(\Delta_{ij}^{(\lambda)^2} / \Lambda_{ij}^{(\lambda)})^{-1}$ and the individual constants $(\Delta_{ii}^{(\lambda)}, \Lambda_{ii}^{(\lambda)})$ give the dominant effect over the crossed constants $(\Delta_{ij}^{(\lambda)}, \Lambda_{ij}^{(\lambda)}, i \neq j)$. Of course, the occurrence of oscillations obtained for nonresonant vibronic levels generates the variations observed in the dashed and long-dashed curves. But, even for these curves, an exponential decay is recovered. Whereas, the previous simulations have been done for bath correlation times on the order of $\Delta_{ij}^{(\lambda)^2} / \Lambda_{ij}^{(\lambda)}$, if we decrease the fluctuation amplitudes of the crossed terms $\Delta_{ij}^{(\lambda)}$, with $i \neq j$, and increase their corresponding bath correlation times $\Lambda_{ij}^{(\lambda)}$, the duration of the photon-echo signal is shortened as shown in Fig. 4.

Moreover, the exponential character of the photon-echo decay is strongly modified due to the appearance of non-Markovian behavior of the bath and is better emphasized by the logarithmic representation of the signal, as done in Fig. 5. Next, by choosing a resonant situation with $E_{e_1} - E_{e_2} = 0$, we analyze the time dependence of the photon-echo signal for different values of the bath correlation time as sketched in Fig. 6. Again, for a reasonable range of the bath correlation times that is not too far from the Markovian limit, the time dependence of the photon-echo signal exhibits an exponential decay quite sensitive to the dephasing processes. It is interesting to note from Fig. 7 that for times longer than the bath correlation time, the time dependences are dominated by the decay constants associated to the Markovian limit $\Delta_{ij}^{(\lambda)^2} / \Lambda_{ij}^{(\lambda)}$.

Now, we come to the analysis of the integrated photon-echo signal for our non-Markovian three-level vibronic sys-

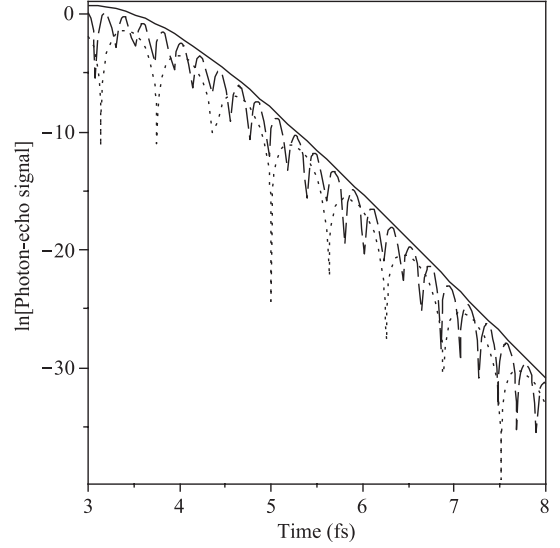


FIG. 5. Logarithmic variations in the time dependence shown in Fig. 4 for the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$ with the same energy mismatches.

tem. To this end, we analyze the dependence of the integrated photon-echo with the time of delay between the first and the second laser pulses. Of course, due to the complicated structure of the bath correlation factors, this integration can only be performed numerically.

Like in previous simulations, the detection is performed in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$. In the Figs. 8 and 9, we exhibit the variations in the integrated photon-echo signal with the delay time between the two first laser pulses for different types of baths. For resonant vibronic levels, we observe a monotonic decay of the signal with a com-

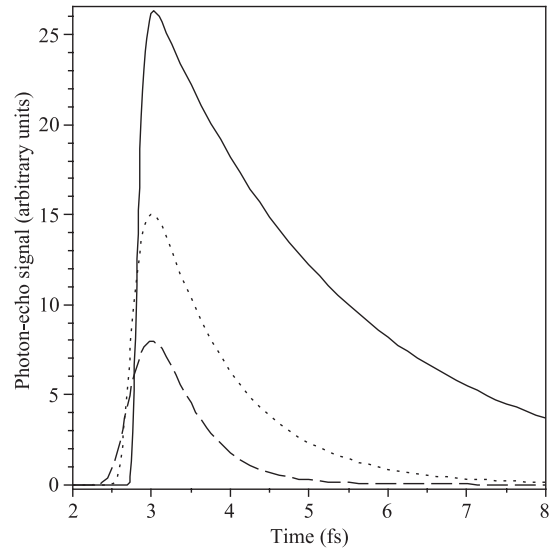


FIG. 6. Time dependence of the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$ with resonant vibronic levels $\omega_{e_{18}} = \omega_{e_{28}} = 20\,000$ cm^{-1} . The cases of different bath correlation times $\Lambda_{ij}^{(\lambda)} = 4$ cm^{-1} (long-dashed line), 8 cm^{-1} (dashed line), and 20 cm^{-1} (solid line) are considered with $\Delta_{ij}^{(\lambda)} = 2$ cm^{-1} $\forall i, j, \lambda$. Other parameters are the same as in previous figures.

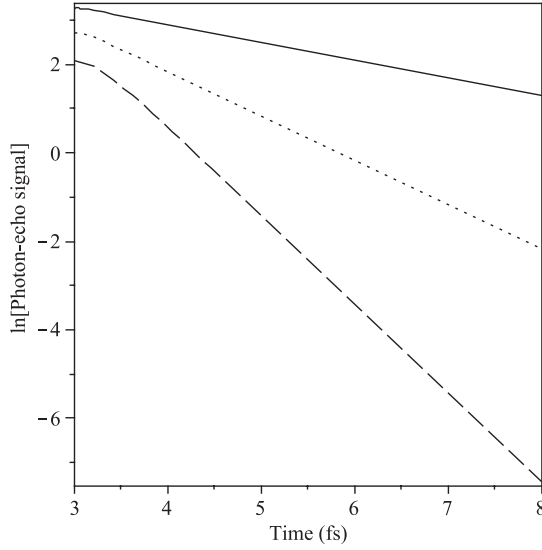


FIG. 7. Logarithmic variations in the time dependence shown in Fig. 6 for the three-pulse photon-echo signal in the phase-matched direction $\vec{k}_{PE}$ and resonant vibronic levels.

bination of exponentials, each one being characterized by the decay constants of the individual excited vibronic levels $|e_1\rangle$ and $|e_2\rangle$ plus the ones associated to the crossed terms resulting from pathways going through levels $|e_1\rangle$ and $|e_2\rangle$. This last contribution strongly depends on the bath correlation factors associated to each individual vibronic level, but also

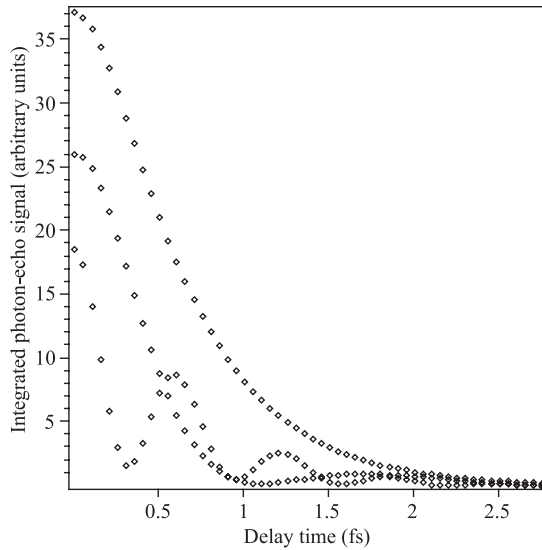


FIG. 8. Integrated three-pulse photon-echo signal as a function of the delay time between the two first laser pulses, $T_b - T_a$. The phase-matched direction is $\vec{k}_{PE} = -\vec{k}_a + \vec{k}_b + \vec{k}_c$. Three different cases of vibronic energy mismatches are considered, say $\omega_{e_{1g}} = 20\,000\text{ cm}^{-1}$ with $\omega_{e_{2g}} = 20\,000, 19\,997$, and $19\,990\text{ cm}^{-1}$. The bath fluctuation amplitudes and inverse bath correlation times for the individual vibronic states $i=1,2$ are $\Delta_{ii}^{(\lambda)} = 2\text{ cm}^{-1}$, $\Lambda_{ii}^{(\lambda)} = 4\text{ cm}^{-1}$, $\Delta_{ij}^{(\lambda)} = 5\text{ cm}^{-1}$ and $\Lambda_{ij}^{(\lambda)} = 12\text{ cm}^{-1}$ for the crossed bath constants $i \neq j$. Other parameters are the same as in previous figures. The three curves with decreasing initial amplitudes correspond to $\omega_{e_{1g}} - \omega_{e_{2g}} = 0, 3$, and 10 cm^{-1} , respectively.

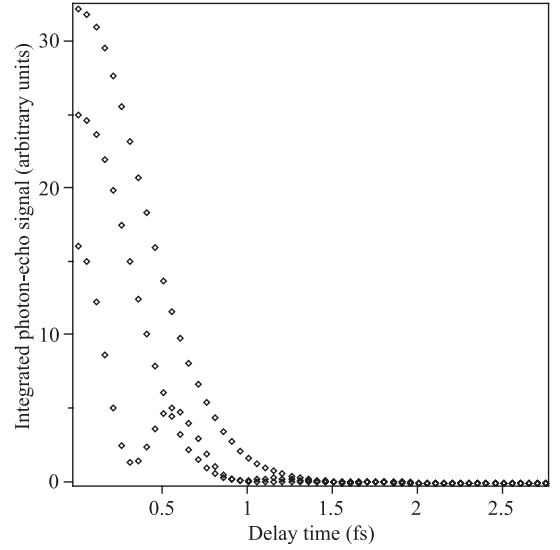


FIG. 9. Same variations as in Fig. 8 with different bath parameters. For the individual states $i=1,2$, we have $\Delta_{ii}^{(\lambda)} = 2\text{ cm}^{-1}$ and $\Lambda_{ii}^{(\lambda)} = 1\text{ cm}^{-1}$, while we have $\Delta_{ij}^{(\lambda)} = 2\text{ cm}^{-1}$ and $\Lambda_{ij}^{(\lambda)} = 2\text{ cm}^{-1}$ for mixed states $i \neq j$. Other parameters, as well as identification of the curves, are the same as in previous figures.

on the correlations existing between the subparts of the bath acting on the different vibronic levels. All the contributions are weighted by the overlapping of the spectral resonances and spectral distributions of the laser excitations. Of course, for a resonant excitation and isoenergetic vibronic levels, $\omega_{e_{1g}} - \omega_{e_{2g}} = 0\text{ cm}^{-1}$, the overlapping is maximum and gives the larger amplitude for the signal. The second and third curves exhibit interferences resulting from the coherent combination of the signal emitted by the individual vibronic levels. For near-resonant excitation, as in the case of the second curve obtained for an energy mismatch of $\omega_{e_{1g}} - \omega_{e_{2g}} = 3\text{ cm}^{-1}$, the weight of each contribution is comparable and the coherent combination gives the larger interferences with minima quite close from zero. However, for larger values of the energy mismatch, the individual contributions are weighted differently and the oscillations start to smooth down. Subsequently, the minima do not cancel anymore as can be seen from Figs. 8 and 9. Of course, the oscillation period is strictly related to the energy mismatch of the vibronic levels. To emphasize the influence of the non-Markovian baths, we show in Fig. 10 the delay time dependence of the photon-echo signal for two different energy mismatches, say $\omega_{e_{1g}} - \omega_{e_{2g}} = 0\text{ cm}^{-1}$ for the two top curves and $\omega_{e_{1g}} - \omega_{e_{2g}} = 3\text{ cm}^{-1}$ for the two lower curves. For each pair of curves the fluctuation amplitudes and correlation times have been chosen according to the values indicated in the figure captions. Notice that the non-Markovian effects of the baths are much more efficient when the energy mismatch is small.

It is interesting to note that this model involving either two independent or two correlated baths, according to the values of the bath parameters, can be applied to physical systems such as large dimers or even reaction centers where the spatial extension of the molecular system is large enough

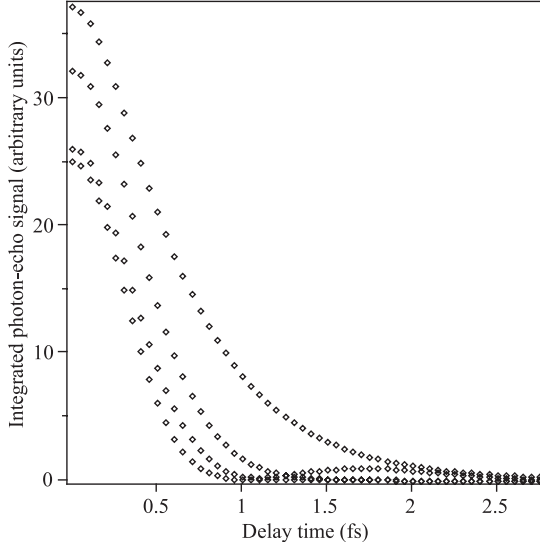


FIG. 10. We compare the delay time dependences of the photon-echo signal for two different types of baths and different vibronic energy mismatches. The two top curves correspond to $\omega_{e_1g} - \omega_{e_2g} = 0 \text{ cm}^{-1}$ with different bath fluctuation amplitudes and inverse correlation times, say $\Delta_{ii}^{(\lambda)} = 2 \text{ cm}^{-1}$, $\Lambda_{ii}^{(\lambda)} = 4 \text{ cm}^{-1}$, and $\Delta_{ij}^{(\lambda)} = 5 \text{ cm}^{-1}$, $\Lambda_{ij}^{(\lambda)} = 12 \text{ cm}^{-1}$ if $i \neq j$ for curve 1 from the top, while $\Delta_{ii}^{(\lambda)} = 2 \text{ cm}^{-1}$, $\Lambda_{ii}^{(\lambda)} = 1 \text{ cm}^{-1}$, and $\Delta_{ij}^{(\lambda)} = 2 \text{ cm}^{-1}$, $\Lambda_{ij}^{(\lambda)} = 2 \text{ cm}^{-1}$ if $i \neq j$ for curve 2 from the top. Curves 3 and 4 are deduced from curves 1 and 2 respectively, by changing the energy mismatch $\omega_{e_1g} - \omega_{e_2g}$ from 0 to 3 cm^{-1} .

to probe different local surroundings. Another situation could be the case where the molecular system and bath interactions could induce different kinds of thermalization processes, due to particular internal symmetries.

VIII. CONCLUSION

In this work, we have developed a detailed description of the dynamics underlying a three-pulse photon-echo process performed on a vibronic system coupled to non-Markovian baths. The peculiar role of a neighboring level coming into play due to the broadband excitation has been studied as well as the influence of the energy mismatch between the vibronic levels. An oscillating behavior has been observed not only on the time dependence of the photon-echo signal, but also on its delay time dependence. These interferences result from the summation of the contributions provided by the indi-

vidual vibronic levels, but also from contributions associated to pathways involving different vibronic levels. The influence of the non-Markovian effects on the photon-echo has been discussed and the role of possible correlations between the baths coupled to the different vibronic levels has been considered as well. The present study opens the way to more detailed investigations on two-dimensional spectroscopy developed in recent years [22,43] where the possibility of going beyond the impulse limit approximation can be considered, validating the evaluation of the required double Fourier transformation when the laser pulses overlap.

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APPENDIX A

We give in Table I the different pathways contributing to the third-order polarization without any restriction due to phase-matched conditions. Their corresponding contributions participate in the photon-echo signal.

APPENDIX B

We evaluate the formal expression valid for the various double time integrals of the bath correlation functions participating in the determination of the three-pulse photon-echo signal. For convenience, it is assumed that the correlation function itself can be described by the analytical expression

$$\langle \mathbf{W}_{\lambda(I)}^{(e_i)}(\tau) \mathbf{W}_{\lambda(I)}^{(e_j)}(\tau') \rangle_b = (\Delta_{ij}^{(\lambda)})^2 e^{-\Lambda_{ij}^{(\lambda)} |\tau - \tau'|}, \quad (\text{B1})$$

where $1/\Lambda_{ij}^{(\lambda)}$ and $\Delta_{ij}^{(\lambda)}$ stand for the bath correlation times and fluctuation amplitudes. For the first type of double time integral defined by the expression

$$g_1(A, B, C, D; \lambda, i, j) = (\Delta_{ij}^{(\lambda)})^2 \int_A^B d\tau \int_C^D d\tau' e^{-\Lambda_{ij}^{(\lambda)} |\tau - \tau'|}, \quad (\text{B2})$$

we obtain

$$g_1(A, B, C, D; \lambda, i, j) = \left\{ \mathcal{H}(A - D) \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{-\Lambda_{ij}^{(\lambda)}(B-D)} - e^{-\Lambda_{ij}^{(\lambda)}(B-C)} - e^{-\Lambda_{ij}^{(\lambda)}(A-D)} + e^{-\Lambda_{ij}^{(\lambda)}(A-C)}) + \mathcal{H}(D - A) \mathcal{H}(A - C) \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{-\Lambda_{ij}^{(\lambda)}(B-A)} - e^{-\Lambda_{ij}^{(\lambda)}(B-C)} - 1 + e^{-\Lambda_{ij}^{(\lambda)}(A-C)}) + \mathcal{H}(C - A) \mathcal{H}(D - B) \mathcal{H}(B - C) \left[-B + C + \frac{1}{\Lambda_{ij}^{(\lambda)}} (1 - e^{-\Lambda_{ij}^{(\lambda)}(B-C)}) \right] + \mathcal{H}(A - C) \mathcal{H}(D - B) \left[-B + A + \frac{1}{\Lambda_{ij}^{(\lambda)}} (1 - e^{-\Lambda_{ij}^{(\lambda)}(B-A)}) \right] + \mathcal{H}(D - A) \mathcal{H}(A - C) \mathcal{H}(B - D) \left[-D + A \right] \right\}$$

TABLE I. Pathways participating in the evaluation of $\vec{P}^{(3)}(t)$. The symbols $(\pm)$ indicate the signs of the wave vectors when the rotating wave approximation (RWA) is considered. Also, the reference Hamiltonians are indicated for each pathway.

	H_{ref}	$\vec{\mu}$	$G(t_3)$	$L'_{v[p]}$	$G(t_2)$	$L'_{v[q]}$	$G(t_1)$	$L'_{v[r]}$	$\rho(t_0)$
$R_1^{(1,1,1)}$	β_1	ge_1	e_1ge_1g	$e_1ge_1e_1^{(+)}$	$e_1e_1e_1e_1$	$e_1e_1e_1g^{(-)}$	e_1ge_1g	$e_1ggg^{(+)}$	gg
$R_1^{(2,2,1)}$	α	ge_1	e_1ge_1g	$e_1ge_1e_2^{(+)}$	$e_1e_2e_1e_2$	$e_1e_2e_1g^{(-)}$			
$R_4^{(1,1,1)}$	α	ge_1	e_1ge_1g	$e_1ggg^{(+)}$	$gggg$	$ggge_1g^{(-)}$			
$R_4^{(2,1,1)}$	α	ge_2	e_2ge_2g	$e_2ggg^{(+)}$					
$R_1^{(2,2,2)}$	β_2	ge_2	e_2ge_2g	$e_2ge_2e_2^{(+)}$	$e_2e_2e_2e_2$	$e_2e_2e_2g^{(-)}$	e_2ge_2g	$e_2ggg^{(+)}$	
$R_1^{(1,1,2)}$	α	ge_2	e_2ge_2g	$e_2ge_2e_1^{(+)}$	$e_2e_1e_2e_1$	$e_2e_1e_2g^{(-)}$			
$R_4^{(2,2,2)}$	α	ge_2	e_2ge_2g	$e_2ggg^{(+)}$	$gggg$	$ggge_2g^{(-)}$			
$R_4^{(1,2,2)}$	α	ge_1	e_1ge_1g	$e_1ggg^{(+)}$					
	H_{ref}	$\vec{\mu}$	$G(t_3)$	$L'_{v[p]}$	$G(t_2)$	$L'_{v[q]}$	$G(t_1)$	$L'_{v[r]}$	$\rho(t_0)$
$R_2^{(1,1,1)}$	β_1	ge_1	e_1ge_1g	$e_1ge_1e_1^{(+)}$	$e_1e_1e_1e_1$	$e_1e_1ge_1^{(+)}$	ge_1ge_1	$ge_1gg^{(-)}$	gg
$R_2^{(1,2,1)}$	α	ge_2	e_2ge_2g	$e_2ge_2e_1^{(+)}$	$e_2e_1e_2e_1$	$e_2e_1ge_1^{(+)}$			
$R_3^{(1,1,1)}$	α	ge_1	e_1ge_1g	$e_1ggg^{(+)}$	$gggg$	$ggge_1^{(+)}$			
$R_3^{(2,1,1)}$	α	ge_2	e_2ge_2g	$e_2ggg^{(+)}$					
$R_2^{(2,2,2)}$	β_2	ge_2	e_2ge_2g	$e_2ge_2e_2^{(+)}$	$e_2e_2e_2e_2$	$e_2e_2ge_2^{(+)}$	ge_2ge_2	$ge_2gg^{(-)}$	
$R_2^{(2,1,2)}$	α	ge_1	e_1ge_1g	$e_1ge_1e_2^{(+)}$	$e_1e_2e_1e_2$	$e_1e_2ge_2^{(+)}$			
$R_3^{(2,2,2)}$	α	ge_2	e_2ge_2g	$e_2ggg^{(+)}$	$gggg$	$ggge_2^{(+)}$			
$R_3^{(1,2,2)}$	α	ge_1	e_1ge_1g	$e_1ggg^{(+)}$					

$$\begin{aligned}
& + \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{-\Lambda_{ij}^{(\lambda)}(B-D)} - e^{-\Lambda_{ij}^{(\lambda)}(B-A)}) \Big] + \mathcal{H}(C-B) \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{\Lambda_{ij}^{(\lambda)}(B-D)} - e^{\Lambda_{ij}^{(\lambda)}(B-C)} - e^{\Lambda_{ij}^{(\lambda)}(A-D)} + e^{\Lambda_{ij}^{(\lambda)}(A-C)}) \\
& + \mathcal{H}(D-B) \mathcal{H}(B-C) \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{\Lambda_{ij}^{(\lambda)}(B-D)} - 1 - e^{\Lambda_{ij}^{(\lambda)}(A-D)} + e^{\Lambda_{ij}^{(\lambda)}(A-B)}) - \mathcal{H}(C-A) \mathcal{H}(D-B) \mathcal{H}(B-C) \\
& \times \left[B - C + \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{\Lambda_{ij}^{(\lambda)}(A-B)} - e^{\Lambda_{ij}^{(\lambda)}(A-C)}) \right] - \mathcal{H}(A-C) \mathcal{H}(D-B) \left[B - A + \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{\Lambda_{ij}^{(\lambda)}(A-B)} - 1) \right] \\
& - \mathcal{H}(D-A) \mathcal{H}(A-C) \mathcal{H}(B-D) \left[D - A + \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{\Lambda_{ij}^{(\lambda)}(A-D)} - 1) \right] \Big\} \frac{(\Delta_{ij}^{(\lambda)})^2}{\Lambda_{ij}^{(\lambda)}} \quad (B3)
\end{aligned}$$

if, as usual, $\mathcal{H}(E)$ stands for the Heaviside function. Next, the second type corresponding to

$$g_2(A, B, C; \lambda, i, j) = (\Delta_{ij}^{(\lambda)})^2 \int_A^B d\tau \int_C^\tau d\tau' e^{-\Lambda_{ij}^{(\lambda)}|\tau-\tau'|} \quad (B4)$$

is given by

$$g_2(A, B, C; \lambda, i, j) = \frac{(\Delta_{ij}^{(\lambda)})^2}{\Lambda_{ij}^{(\lambda)}} \left[B - A + \frac{1}{\Lambda_{ij}^{(\lambda)}} (e^{-\Lambda_{ij}^{(\lambda)}(B-C)} - e^{-\Lambda_{ij}^{(\lambda)}(A-C)}) \right]. \quad (B5)$$

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