Dynamics of Coupled Electron-Boson Systems with the Multiple Davydov D1 Ansatz and the Generalized Coherent State

Efficient orientational averaging of nonlinear optical signals in multi-chromophore systems

Maxim F. Gelin[1], Raffaele Borrelli[2], and Wolfgang Domcke[1]

[1]*Department of Chemistry, Technische Universität München, D-85747 Garching, Germany*

[2]*DISAFA, Università di Torino, I-10095 Grugliasco, Italy*

Abstract

The simulation of nonlinear optical signals measured in isotropic media requires averaging over the orientations of the chromophores. Herein, we discuss the evaluation of orientationally averaged four-wave-mixing, six-wave-mixing, etc., signals in terms of contracted transition dipole moment operators, which were introduced earlier for the orientational averaging of linear absorption signals. We demonstrate that the contracted transition dipole moment operators substantially facilitate the orientational averaging of nonlinear signals in multi-chromophore systems. We consider both the perturbative evaluation of signals (through nonlinear response functions) as well as the non-perturbative evaluation (through the numerical calculation of the nonlinear polarization of driven systems).

I. INTRODUCTION

The basic quantity required for the calculation of femtosecond four-wave-mixing (4WM) signals is the third order polarization $\boldsymbol{P}^{(3)}(t)$ [1–5]. In the perturbative formalism of femtosecond nonlinear optics, $\boldsymbol{P}^{(3)}(t)$ is expressed in terms of third-order dipole response functions [1]. The transition dipole moment vectors are defined in the molecular frame, the polarization vectors of the laser pulses are defined in the laboratory frame, and the 4WM signal has to be averaged over all possible orientations of the molecular frame with respect to the laboratory frame. In their seminal work, Andrews and Thirunamachandran showed how to carry out the orientational averaging for tensors of arbitrary rank N [6]. With this result, the orientational averaging of 4WM and higher-order NWM signals can straightforwardly be performed.

Herein, we address a technical issue which becomes relevant for the calculation of orientationally-averaged NWM signals in multi-chromophore systems: the scaling of the computational cost with the number of transition dipole moments involved. Let us consider an ensemble of multi-chromophore systems, such as J-aggregates or biological antenna complexes, in an isotropic medium. The Hamiltonian describing the interaction of the aggregate with the external fields of three laser pulses reads

$$H_F(t) = -\sum_{\alpha=1}^{3} (\boldsymbol{e}_\alpha \hat{\boldsymbol{\mu}}) \mathcal{E}_\alpha(t) \tag{1}$$

where $\boldsymbol{e}_\alpha$ is the unit vector of the linear polarization of pulse α, $\mathcal{E}_\alpha(t)$ is its scalar amplitude, and the parentheses indicate the scalar product of two vectors. The total transition dipole moment operator is defined as

$$\hat{\boldsymbol{\mu}} = \sum_{n_0 n_1} \boldsymbol{\mu}_{n_0 n_1} |n_0\rangle\langle n_1| + \sum_{n_1 n_2} \boldsymbol{\mu}_{n_1 n_2} |n_1\rangle\langle n_2| + \sum_{n_2 n_3} \boldsymbol{\mu}_{n_2 n_3} |n_2\rangle\langle n_3| + ... + H.c. \tag{2}$$

Here $n_0, n_1, n_2, n_3, ...$ represent the relevant levels of the ground, singly-excited, doubly-excited, triply-excited, etc., states of the aggregate while $\boldsymbol{\mu}_{n_0 n_1}$, $\boldsymbol{\mu}_{n_1 n_2}$, $\boldsymbol{\mu}_{n_2 n_3}$, etc., are the vectors of the corresponding transition dipole moment matrix elements. In short-hand notation, Eq. (2) is written as

$$\hat{\boldsymbol{\mu}} = \sum_n \boldsymbol{\mu}_n \hat{X}_n. \tag{3}$$

where the summation runs over all relevant transitions, the $\boldsymbol{\mu}_n$ are the vectors of the transition dipole moment matrix elements and the $\hat{X}_n$ are the transition operators. In the case

of 4WM signals, the expansion of Eq. (2) can be truncated after doubly-excited sates. In the case of 6WM signals, triply-excited states may contribute to the signal, and so forth. The challenge of a proliferation of possible transitions and corresponding transition dipole moments is thus aggravated for higher-order signals due to the contribution of multi-excited states.

In the perturbative formalism of nonlinear optics, the third-order polarization $\boldsymbol{P}^{(3)}(t)$ and a higher-order polarization $\boldsymbol{P}^{(N)}(t)$ can be represented as a sum over all optical pathways (that is, over all combinations of N allowed sequential transitions) [1–4]. The orientational averaging can be performed analytically for every specific pathway [6]. However, the evaluation of the total NWM signal may become computationally demanding for multi-chromophore systems, since the number of the pathways grows with the Nth power of the number of allowed transitions. Moreover, the summation over all optical pathways may represent a routine problem when the dipole response functions are given by simple analytical expressions (e.g., for few-level systems [1] or for separable Brownian oscillator models [1, 7]), but may become a major computational bottleneck when the response functions have to be evaluated by expensive numerical computations for realistic models of molecular systems. As an example of multi-chromophore system, the Fenna-Matthews-Olsen (FMO) complex may be considered, which contains transitions between the ground state, 7 singly-excited states and 21 doubly-excited sates. Ref. [8] gives an example of non-trivial response functions and their orientational averaging in the evaluation of 4WM signals of FMO. It has been demonstrated in Refs. [8, 9] that the concept of contracted transition dipole moment operators substantially facilitates orientational averaging of linear absorption spectra of multi-chromophore systems. Herein, we extend the method of Refs. [8, 9] towards orientational averaging of nonlinear optical signals in the perturbative formalism of nonlinear optics.

In the alternative non-perturbative formalism of nonlinear optics, all relevant laser fields are incorporated into the system Hamiltonian and $\boldsymbol{P}^{(3)}(t)$ or $\boldsymbol{P}^{(N)}(t)$ in a specific phase-matching direction is extracted from the numerical solution of a Schrödinger equation [10, 11] (for isolated system) or a master equation [12, 13] (for system coupled to an environment). While $\boldsymbol{P}^{(N)}(t)$ depends on the $(\boldsymbol{e}_\alpha \hat{\boldsymbol{\mu}})$ parametrically, this dependence is not given by analytic expressions. Herein, we show that the contracted dipole moments also simplify considerably the non-perturbative evaluation of orientationally-averaged signals of multi-chromophore

systems.

In the present work, we assume that molecular reorientation is slow compared to the time scale of the femtosecond experiment and its effect can be neglected. In Sections II and III, we consider in detail orientational averaging of 4WM signals evaluated by perturbative and non-perturbative methods, respectively. The generalization of these results to 6WM and higher-order signals is discussed in the Appendix.

II. PERTURBATIVE EVALUATION OF THE POLARIZATION

The 4WM signal is uniquely determined by the third-order phase-matched polarization $\boldsymbol{P}^{(3)}(t)$. If the signal is detected by the convolution of $\boldsymbol{P}^{(3)}(t)$ with a local oscillator field, the signal is

$$I \sim i \int dt\, \mathcal{E}_4(t)(\boldsymbol{P}^{(3)}(t)\boldsymbol{e}_4) \tag{4}$$

where $\boldsymbol{e}_4$ is the unit vector of polarization and $\mathcal{E}_4(t)$ is the scalar amplitude of the local oscillator field [5]. If $\boldsymbol{P}^{(3)}(t)$ is detected directly, for example via a spectrometer, then

$$I \sim (\boldsymbol{P}^{(3)}(t)\boldsymbol{e}_4) \tag{5}$$

where $\boldsymbol{e}_4$ is determined by the polarization filter. From the point of view of orientational averaging, we do not need to distinguish between Eqs. (4) and (5), because $(\boldsymbol{P}^{(3)}(t)\boldsymbol{e}_4)$ is the key object in both cases.

The fundamental quantity describing the 4WM signal is the four-time correlation function of the transition dipole moment operators [1, 14–16],

$$\Phi(\tau_4, \tau_3, \tau_2, \tau_1) = \langle (\boldsymbol{e}_1\hat{\boldsymbol{\mu}}(\tau_4))(\boldsymbol{e}_2\hat{\boldsymbol{\mu}}(\tau_3))(\boldsymbol{e}_3\hat{\boldsymbol{\mu}}(\tau_2))(\boldsymbol{e}_4\hat{\boldsymbol{\mu}}(\tau_1))\rangle\,. \tag{6}$$

Here the Heisenberg operators

$$\hat{\boldsymbol{\mu}}(\tau) = e^{iH\tau}\hat{\boldsymbol{\mu}}e^{-iH\tau} \tag{7}$$

evolve with the total field-free Hamiltonian H, and the angular brackets represent the trace over the vibrational and electronic degrees of freedom.

The description of the signal in terms of the response functions (6) is not suitable for the explicit performing of orientational averagings, because the $\boldsymbol{\mu}_n$ of Eq. (3) are hidden in the $\hat{\boldsymbol{\mu}}(\tau)$. We can make the dependence on the $\boldsymbol{\mu}_n$ explicit by introducing response functions

for all relevant optical pathways (pathway response functions, superscript p) contributing to the 4WM signal:

$$\Phi^{(p)}_{klmn}(\tau_4,\tau_3,\tau_2,\tau_1) = \left\langle \hat{X}_k(\tau_4)\hat{X}_l(\tau_3)\hat{X}_m(\tau_2)\hat{X}_n(\tau_1)\right\rangle, \tag{8}$$

$$\hat{X}_k(\tau) = e^{iH\tau}\hat{X}_k e^{-iH\tau}. \tag{9}$$

The signal can then be evaluated as

$$I = \sum_{klmn} (\boldsymbol{e}_1\boldsymbol{\mu}_k)(\boldsymbol{e}_2\boldsymbol{\mu}_l)(\boldsymbol{e}_3\boldsymbol{\mu}_m)(\boldsymbol{e}_4\boldsymbol{\mu}_n) I^{(p)}_{klmn} \tag{10}$$

where each rotationally isotropic contribution $I^{(p)}_{klmn}$ corresponds to a specific optical pathway and is expressed in terms of $\Phi^{(p)}_{klmn}$. This formalism is commonly used in the literature [1, 16]. The orientational averaging (henceforth denoted by an overbar) of the 4WM signal of Eq. (10) yields

$$\bar{I} = \sum_{klmn} C_{klmn} I^{(p)}_{klmn}, \tag{11}$$

where the coefficients

$$C_{klmn} \equiv \overline{(\boldsymbol{e}_1\boldsymbol{\mu}_k)(\boldsymbol{e}_2\boldsymbol{\mu}_l)(\boldsymbol{e}_3\boldsymbol{\mu}_m)(\boldsymbol{e}_4\boldsymbol{\mu}_n)} \tag{12}$$

have explicitly been given in Refs. [6, 17]. Evaluation of the signal via Eq. (11) requires a four-fold summation over all allowed transitions. For complex multi-chromophore systems, the evaluation of $\Phi^{(p)}_{klmn}$ for specific $klmn$ may require considerable numerical effort. In this case, the practical application of Eq. (11) is tedious. The optimal strategy of performing orientational averaging for such systems is formulated below.

Let us introduce an orthogonal molecular reference frame with the axes x, y, z specified by three mutually orthogonal unit vectors $\boldsymbol{d}_a$ ($a = x, y, z$) and decompose vectors of the matrix elements of the transition dipole moments as follows:

$$\boldsymbol{\mu}_n = \sum_{a=x,y,z} \mu_{na}\boldsymbol{d}_a, \tag{13}$$

$$\mu_{na} = (\boldsymbol{d}_a\boldsymbol{\mu}_n).$$

Usually, this kind of decomposition is performed individually for each $\boldsymbol{\mu}_k$, $\boldsymbol{\mu}_l$, $\boldsymbol{\mu}_m$ and $\boldsymbol{\mu}_n$ entering Eq. (10) [18–21]. This results in the sum-over-pathways formula for the 4WM signal. Following Refs. [8, 9], we rewrite the total transition dipole moment operator as

$$\hat{\boldsymbol{\mu}} = \sum_{a=x,y,z} \boldsymbol{d}_a\hat{Y}_a \tag{14}$$

where the $\hat{Y}_a$ are contracted dipole moment operators

$$\hat{Y}_a = \sum_n \mu_{na} \hat{X}_n. \tag{15}$$

The choice of the molecular frame unit vectors $\boldsymbol{d}_a$ depends on the structure of the molecule. If, for example, all $\boldsymbol{\mu}_n$ lie in one plane denoted as xy, only two vectors $\boldsymbol{d}_x$ and $\boldsymbol{d}_y$ are needed to fully characterize the total transition dipole moment.

With the definition (14) the system-field interaction Hamiltonian reads

$$H_F(t) = -\sum_{\alpha,a} (\boldsymbol{e}_\alpha \boldsymbol{d}_a) \mathcal{E}_\alpha(t) \hat{Y}_a. \tag{16}$$

Therefore, the 4WM signal (4) can be written as

$$I = \sum_{abcd} (\boldsymbol{e}_1 \boldsymbol{d}_a)(\boldsymbol{e}_2 \boldsymbol{d}_b)(\boldsymbol{e}_3 \boldsymbol{d}_c)(\boldsymbol{e}_4 \boldsymbol{d}_d) I^{(c)}_{abcd} \tag{17}$$

where the orientationally isotropic contributions $I^{(c)}_{abcd}$ can be evaluated in terms of the contracted (superscript c) response functions

$$\Phi^{(c)}_{abcd}(\tau_4, \tau_3, \tau_2, \tau_1) = \left\langle \hat{Y}_a(\tau_4) \hat{Y}_b(\tau_3) \hat{Y}_c(\tau_2) \hat{Y}_d(\tau_1) \right\rangle, \tag{18}$$

$$\hat{Y}_k(\tau) = e^{iH\tau} \hat{Y}_k e^{-iH\tau}. \tag{19}$$

The orientationally averaged 4WM signal becomes

$$\bar{I} = \sum_{abcd} C_{abcd} I^{(c)}_{abcd}, \tag{20}$$

where the C_{abcd} are given by Eq. (12) with the substitutions $\boldsymbol{\mu} \to \boldsymbol{d}$, $klmn \to abcd$.

The advantage of using Eq. (20) for multi-chromophore systems is seen immediately: the summation over each of the subscripts $abcd$ runs only over x, y, z, rather than over all transitions. Furthermore, the $\boldsymbol{d}$-vectors are orthonormal by construction,

$$(\boldsymbol{d}_a \boldsymbol{d}_b) = \delta_{ab}. \tag{21}$$

Therefore, only those C_{abcd} are nonzero in which two out of four indexes $abcd$ coincide with the remaining two. There are 21 nonzero C_{abcd} – as for any fourth-order tensor describing the third-order response in isotropic media [19]. This yields 21 nonzero contributions to the 4WM signal, irrespective of the number of transition dipole moments involved. Hence the

contracted transition dipole moment operators $\hat{Y}_a$ (Eq. (15)) and the contracted response functions $\Phi^{(c)}_{abcd}$ (Eq. (18)) are optimal from the point of view of orientational averaging of 4WM signals (Eq. (20)). On the other hand, the $\Phi^{(c)}_{abcd}$ are more difficult to evaluate than the traditional pathway response functions $\Phi^{(p)}_{klmn}$ (Eq. (8)), because the $\hat{Y}_a$ are linear combinations of many dipole moment operators $\hat{X}_k$. Hence, the practical advantage of the contracted description depends on the problem under study. If the evaluation of the $\Phi^{(p)}_{klmn}$ is inexpensive and if the number of dipole transitions is not too large, the evaluation of the signal via the pathway response functions may be the method of choice. If, on the other hand, the evaluation of the $\Phi^{(p)}_{klmn}$ for specific $klmn$ is numerically expensive, then the evaluation of the signal via the $\Phi^{(c)}_{abcd}$ is more efficient.

III. NON-PERTURBATIVE EVALUATION OF THE POLARIZATION

The contracted transition dipole moment operators (15) are also useful for the orientational averaging of the third-order polarization $\boldsymbol{P}^{(3)}(t)$ extracted from a non-perturbative calculation. Since no explicit dependence of the phase-matched polarization $\boldsymbol{P}^{(3)}(t)$ on $(\boldsymbol{e}_\alpha \boldsymbol{d}_a)$ is provided by non-perturbative methods, a different strategy has to be employed. Consider the system-field interaction Hamiltonian $H_F(t)$ as defined by Eq. (16). Assume, for the moment, that the $\boldsymbol{e}_\alpha$ are not the actual polarization unit vectors of the laser pulses $\mathcal{E}_\alpha(t)$, but free parameters. Let us perform a nonperturbative evaluation of the polarization $\boldsymbol{P}^{(3)}(t)$ with the choice

$$\boldsymbol{e}_1 = \boldsymbol{d}_A,\, \boldsymbol{e}_2 = \boldsymbol{d}_B,\, \boldsymbol{e}_3 = \boldsymbol{d}_C \tag{22}$$

$(A, B, C = x, y, z)$. Denote the so-obtained polarization as $\boldsymbol{P}^{(3)}_{ABC}(t)$ and calculate the 4WM signal (4) by setting

$$\boldsymbol{e}_4 = \boldsymbol{d}_D \tag{23}$$

$(D = x, y, z)$. This yields

$$I_{ABCD} = i \int dt\, \mathcal{E}_4(t) (\boldsymbol{P}^{(3)}_{ABC}(t) \boldsymbol{d}_D). \tag{24}$$

We can then state that

$$I_{ABCD} = I^{(c)}_{abcd}. \tag{25}$$

The proof of the statement (25) can be sketched as follows. The perturbative and non-perturbative methods are equivalent for weak pulses: they yield the same third-order po-

larization $\boldsymbol{P}^{(3)}(t)$ and the same 4WM signal I before orientational averaging. Therefore, the signal (24) is equal to the signal (17) provided the polarizations are chosen according to Eqs. (22) and (23). The substitution of Eqs. (22) and (23) into Eq. (17) yields, due to the orthogonality of the $\boldsymbol{d}$-vectors defined in Eq. (21), the r.h.s. of Eq. (25). Once all 21 components $I^{(c)}_{abcd}$ have been evaluated through a series of nonperturbative calculations of I_{ABCD}, the orientationally averaged 4WM signal is given by Eq. (20).

This scheme can also be applied in the perturbative calculations of $\boldsymbol{P}^{(3)}(t)$ when the response functions (6) are evaluated through the numerical solution of master equations [8, 22, 23]. Hein et al., for example, demonstrated that the evaluation of $\boldsymbol{P}^{(3)}(t)$ for ten different values of $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ yields reasonably accurate orientationally averaged two-dimensional (2D) spectra [8]. The present analysis shows that the evaluation of 21 polarizations $\boldsymbol{P}^{(3)}_{ABC}(t)$ is sufficient for performing the exact orientational averaging.

For pump-probe signals, $\mathcal{E}_1(t) = \mathcal{E}_2(t)$ and therefore $\boldsymbol{P}^{(3)}_{ABC}(t) = \boldsymbol{P}^{(3)}_{BAC}(t)$. In this case, only 15 polarizations need to be evaluated. An approximate orientational averaging of the non-perturbatively evaluated pump-probe signal was performed in Ref. [24] by a Monte Carlo integration of the polarization over ten values of $\boldsymbol{e}_1$ and $\boldsymbol{e}_3$. Using the methods of the present work, this approximate numerical integration can be avoided.

IV. CONCLUSION

We introduced contracted transition dipole moment operators $\hat{Y}_a$ for facilitating the orientational averaging of nonlinear optical signals of multi-chromophore systems. The description in terms of the $\hat{Y}_a$ has significant advantage over the standard description in terms of the transition dipole moment operators $\hat{X}_k$. The use of the $\hat{X}_k$ requires the orientational averaging for *each* combination of dipole transitions contributing to the NWM signal. Hence the numerical effort of the evaluation of the signal scales as the number of allowed transitions to the power N. The use of the $\hat{Y}_a$ renders orientational averaging independent of the number dipole transitions involved.

The contracted description is optimal from the point of view of the orientational averaging. Exact orientational averaging of a 4WM signal requires the evaluation of 21 response functions (in the perturbative method) or the evaluation of $\boldsymbol{P}^{(3)}(t)$ for 21 specific orientations of the unit vectors of the of polarization of the laser fields (in the non-perturbative

method). For pump-probe signals, this number reduces to 15. Exact orientational averaging of 6WM and 8WM signals requires the evaluation of 183 and 1641 contributions, respectively. The use of the contracted operators $\hat{Y}_a$ drastically reduces the numerical effort of performing orientational averagings for multi-chromophore systems – notably if the evaluation of the response functions and/or phase-matched polarizations requires extensive numerical simulations.

The results of the present work are of purely geometrical character and are equally applicable to nonlinear UV/Vis and IR spectroscopy. Various kinds of anisotropy parameters [17, 25] can also efficiently be evaluated by this method. If necessary, the present analysis can be generalized towards accounting for the effects of molecular reorientation along the lines developed in Refs. [17–21, 26, 27].

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Appendix A: 6WM and higher order signals

In this Appendix, we demonstrate how the contracted transition dipole moment operators can be used for the evaluation of the orientational averaging of 6WM signals in the perturbative and non-perturbative formalisms. The consideration of 6WM signals requires a straightforward generalization of the methods developed in this work for 4WM signals. Higher-order signals can be treated analogously. Orientational averaging of the 6WM signal for a chromophore with a single transition dipole moment has been considered in detail in Ref. [27].

1. Perturbative method

The 6WM signal is uniquely determined by the fifth-order phase-matched polarization $\boldsymbol{P}^{(5)}(t)$. In terms of contracted transition dipole moments operators (15), it can be evaluated

as

$$I = \sum_{abcdef} (\boldsymbol{e}_1\boldsymbol{d}_a)(\boldsymbol{e}_2\boldsymbol{d}_b)(\boldsymbol{e}_3\boldsymbol{d}_c)(\boldsymbol{e}_4\boldsymbol{d}_d)(\boldsymbol{e}_5\boldsymbol{d}_e)(\boldsymbol{e}_6\boldsymbol{d}_f) I^{(c)}_{abcdef} \tag{A1}$$

where the isotropic contributions $I^{(c)}_{abcdef}$ can be expressed in terms of the fifth-order contracted response functions

$$\Phi^{(c)}_{abcdef}(\tau_6, \tau_5, \tau_4, \tau_3, \tau_2, \tau_1) = \left\langle \hat{Y}_a(\tau_6)\hat{Y}_b(\tau_5)\hat{Y}_c(\tau_4)\hat{Y}_d(\tau_3)\hat{Y}_e(\tau_2)\hat{Y}_f(\tau_1) \right\rangle . \tag{A2}$$

The orientationally averaged 6WM signal is then given by

$$\bar{I} = \sum_{abcdef} C_{abcdef} I^{(c)}_{abcdef}, \tag{A3}$$

where the explicit expression for the coefficients C_{abcdef} has been given in Ref. [6]. The summation indexes $abcdef$ run over x, y, z, rather than over all allowed transitions. Due to the orthonormality of the $\boldsymbol{d}$-vectors (Eq. (21)), only those C_{abcdef} are nonzero for which three out of six indexes $abcdef$ coincide with the remaining three. Hence, there exist $6!/2!/2!/2! + 6!/4!/2! \times 6 + 3 = 183$ nonzero components of C_{abcdef}. Therefore, 183 components of $I^{(c)}_{abcdef}$ should be evaluated for the performing of exact orientational averaging of a general 6WM signal, irrespective of the number of optical transitions involved. The averaging of higher-order signals is performed absolutely analogously. For 8WM, for example, one has to evaluate $8!/2!/2!/4! \times 3 + 8!/4!/4! \times 3 + 8!/6!/2! \times 6 + 3 = 1641$ components of the seventh-order contracted response function. We were unable to determine a general expression for the number of nonzero components of the NWM signal. For large N, it can be estimated by the asymptotic formula $3^N/4$, which is quite accurate. For $N = 6$ it yields $3^6/4 = 182.25$ and for $N = 8$ one has $3^8/4 = 1640.2$.

2. Non-perturbative method

The fifth-order phase-matched polarization $\boldsymbol{P}^{(5)}(t)$, as well as a general $(N-1)$-order polarization $\boldsymbol{P}^{(N-1)}(t)$ can be evaluated nonperturbatively as detailed in Ref. [13]. Let us assume that the $\boldsymbol{e}_\alpha$ entering $\boldsymbol{P}^{(5)}(t)$ are not the actual polarization unit vectors of the laser pulses $\mathcal{E}_\alpha(t)$, but free parameters. Let us perform a nonperturbative evaluation of $\boldsymbol{P}^{(5)}(t)$ for

$$\boldsymbol{e}_1 = \boldsymbol{d}_A,\ \boldsymbol{e}_2 = \boldsymbol{d}_B,\ \boldsymbol{e}_3 = \boldsymbol{d}_C,\ \boldsymbol{e}_4 = \boldsymbol{d}_D,\ \boldsymbol{e}_5 = \boldsymbol{d}_E \tag{A4}$$

$(A, B, C, D, E = x, y, z)$. Denote the so-obtained polarization as $\boldsymbol{P}^{(5)}_{ABCDE}(t)$ and calculate the 6WM signal (A1) by setting

$$\boldsymbol{e}_6 = \boldsymbol{d}_F \tag{A5}$$

$(F = x, y, z)$. This yields

$$I_{ABCDEF} = i \int dt\, \mathcal{E}_6(t)(\boldsymbol{P}^{(5)}_{ABCDE}(t)\boldsymbol{d}_F). \tag{A6}$$

Then, we can state that

$$I_{ABCDEF} = I^{(c)}_{abcdef}. \tag{A7}$$

The proof of the statement (A7) is analogous to that of Eq. (25) and is not presented here. Once all 183 components of $I^{(c)}_{abcdef}$ have been evaluated through a series of nonperturbative calculations of I_{ABCDEF}, the orientational averaging of the 6WM signal is carried out by Eq. (A3). The analysis is analogous for higher-order signals.

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