Intrinsic Pulse-Width Dependence of Third-Order Nonlinear Optical Susceptibility in the Femtosecond Regime

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We demonstrate that the second-order coupling of local polarizations contributes significantly to the third-order nonlinear optical susceptibility $\chi^{(3)}$ through cascaded processes, as much as does direct third-order coupling. Temporal analysis of nonlinear polarization shows that $\chi^{(3)}$ depends intrinsically on pulse width if the pulse width is shorter than about 10 times the relaxation time of nonlinear polarization. Analysis of the pulse-width dependence of the third-order polarization in a femtosecond regime may differentiate the second-order local cascading process and the direct third-order process.

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As the field of second-order nonlinear optics matures, more attention is being focused on third-order nonlinear optical (NLO) processes, such as third-harmonic generation, optical soliton generation, two-photon absorption, and the nonlinear refractive index [1–3]. The third-order nonlinear susceptibility $\chi^{(3)}$ is an important parameter for the prediction and evaluation of those effects. However, it has been argued that $\chi^{(3)}$ cannot be regarded as an appropriate material constant characterizing third-order NLO properties, because values for $\chi^{(3)}$ have been often reported to vary wildly in magnitude, depending on illumination parameters, such as the light source pulse width [4,5]. In general, nonlinear susceptibility of the nth order $\chi^{(n)}$ ($n \geq 2$) of a medium does not have a single temporal dependence, because various constituents in the medium are responsible for NLO processes, such as valence and conduction electrons, nuclei, ionic groups, and molecules, all of which have different response times [4–9]. As sub-fs light pulses have become available recently [10], it is possible to differentiate the NLO processes arising from the various constituents.

In recent years, several authors have reported that even a single nonlinear constituent contributes to $\chi^{(3)}$ in two different ways [11–13]: a direct third-order coupling and locally cascaded second-order couplings. However, no study has yet been reported on the pulse-width dependence of these processes involving virtual states. In this Letter, we demonstrate that $\chi^{(3)}$ depends intrinsically on pulse width, even with a single nonlinear constituent, and the contributions of the second-order couplings and the third-order coupling to $\chi^{(3)}$ can be differentiated in femtosecond pulse-width regime. We present also that the second-order coupling of local polarizations that is entirely responsible for $\chi^{(2)}$ makes a significant contribution to $\chi^{(3)}$ as well, which enables us to resolve the long-standing question of whether, or how, $\chi^{(2)}$ and $\chi^{(3)}$ are related.

We deal with a system composed of a single type of charged particles, each of which is placed in an anharmonic potential with second- and third-order nonlinear terms. When a local electric field $\mathbf{F}(t)$ is applied to a particle, the equation of motion is represented as [12,14,15]

$$\ddot{x}_i + 2\gamma_{ii}\dot{x}_i + \Omega_i^2 x_i + a_{ijk}x_j x_k - b_{ijkl}x_j x_k x_l + \cdots = qF_i(t)/m, \quad (1)$$

where i, j, k, and l refer to the directions of the principal axes, and γ_{ii} and Ω_i denote a damping coefficient and a resonance frequency in the ith direction, respectively. a_{ijk} and b_{ijkl} represent the components of the second-order coupling tensor a and the third-order coupling tensor b, respectively. q is an electric charge of the particle and m is the particle mass.

Assuming the magnitude of the nonlinear terms in Eq. (1) is much smaller than that of the linear term, the solution can be obtained by using the Rayleigh-Schrödinger method of perturbation. As a result of nonlinear interactions, the total local field $\mathbf{F}(t)$ consists of a linear field $\mathbf{F}^{(1)}(t)$ and generated nonlinear fields. Thus, the solution and the local field can be written

$$x_i(t) = x_i^{(1)}(t) + \lambda x_i^{(2)}(t) + \lambda^2 x_i^{(3)}(t) + \cdots, \quad (2a)$$

$$F_i(t) = F_i^{(1)}(t) + \lambda F_i^{(2)}(t) + \lambda^2 F_i^{(3)}(t) + \cdots, \quad (2b)$$

where λ is an expansion parameter, which is to be set equal to one. The coefficients a_{ijk} and b_{ijkl} in Eq. (1) must be also replaced by λa_{ijk} and $\lambda^2 b_{ijkl}$. Using Eq. (2), the perturbative expansion in Eq. (1) leads to a set of equations for each order of λ and we obtain the third-order solution in the frequency domain as

$$x_i^{(3)}(\omega) = \frac{q^3}{2\pi m^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\frac{b_{ijkl}}{D_{ii}(\omega)} + \frac{2a_{ijh}a_{hkl}}{D_{ii}(\omega)D_{hh}(\omega-\omega_1)}\right]\frac{F_j^{(1)}(\omega_1)F_k^{(1)}(\omega_2)F_l^{(1)}(\omega-\omega_1-\omega_2)}{D_{jj}(\omega_1)D_{kk}(\omega_2)D_{ll}(\omega-\omega_1-\omega_2)}d\omega_1 d\omega_2 - \frac{2q^2}{\sqrt{2\pi}m^2}$$
$$\times\int_{-\infty}^{\infty}\frac{a_{ijk}F_j^{(1)}(\omega_1)F_k^{(2)}(\omega-\omega_1)}{D_{ii}(\omega)D_{jj}(\omega_1)D_{kk}(\omega-\omega_1)}d\omega_1 + \frac{qF_i^{(3)}(\omega)}{mD_{ii}(\omega)}, \quad (3)$$

where $D_{kk}(\omega) = \Omega_k^2 - \omega^2 - 2i\gamma_{kk}\omega$.

Equation (3) represents a comprehensive expression for the generation and propagation of the third-order local field $\mathbf{F}^{(3)}(t)$. The last term represents linear responses to $\mathbf{F}^{(3)}(t)$, while the second term represents a conventional $\chi^{(2)}\cdot\chi^{(2)}$ cascading process. These two terms did not appear in previous works [12,15,16], because only $\mathbf{F}^{(1)}(t)$ was considered as a driving force. The first term in Eq. (3) consists of two parts: the first for direct third-order nonlinear coupling [Fig. 1(a)] and the second for cascading of two second-order nonlinear couplings at the same local site [Fig. 1(b)]. The cascading process in the first term differentiates from the cascading process in the second term. The former takes place at the same local site, whereas the latter occurs over two different local sites [Fig. 1(c)]. The former is termed *local cascading* and the latter *nonlocal cascading* throughout this Letter.

The local polarization is given by the relation $\mathbf{P}_L = q\mathbf{x}/\upsilon$, where υ is the effective volume occupied by a single particle. The microscopic susceptibility $\chi_L^{(n)}$ is defined by

$$\chi_{L,ij_1\cdots j_n}^{(n)}(\omega;\omega_1,\ldots,\omega_n) = \frac{1}{\epsilon_0 n!}\frac{\partial^n P_{L,i}^{(p)}(\omega)}{\partial F_{j_1}^{(p_1)}(\omega_1)\cdots\partial F_{j_n}^{(p_n)}(\omega_n)}, \quad (4)$$

where ω_l's satisfy $\omega_1+\cdots+\omega_n=\omega$, and integers p and p_l's satisfy $p_1+\cdots+p_n=p\geq n$. Ignoring structural parameters for simplicity, macroscopic susceptibilities are related to microscopic susceptibilities by

$$\chi_{ii}^{(1)}(\omega) = L_{ii}(\omega)\chi_{L,ii}^{(1)}(\omega), \quad (5a)$$
$$\chi_{ij_1\cdots j_n}^{(n)}(\omega;\omega_1,\ldots,\omega_n) = L_{ii}(\omega)L_{j_1j_1}(\omega_1)\cdots L_{j_nj_n}(\omega_n)\times\chi_{L,ij_1\cdots j_n}^{(n)}(\omega;\omega_1,\ldots,\omega_n), \quad (5b)$$

where $\mathsf{L}(\omega)$ is the local field factor [15,16]. Then the second- and third-order nonlinear susceptibilities are expressed as

$$\chi_{ijk}^{(2)}(\omega;\omega_1,\omega_2) = -\frac{\epsilon_0^2 m\upsilon^2}{\sqrt{2\pi}q^3}a_{ijk}\chi_{ii}^{(1)}(\omega)\chi_{jj}^{(1)}(\omega_1)\chi_{kk}^{(1)}(\omega_2), \quad (6)$$

$$\chi_{ijkl}^{(3)}(\omega;\omega_1,\omega_2,\omega_3) = \chi_{ijkl}^{(3):3}(\omega;\omega_1,\omega_2,\omega_3) + \chi_{ijkl}^{(3):2\times2}(\omega;\omega_1,\omega_2,\omega_3), \quad (7)$$

with

$$\chi_{ijkl}^{(3):3}(\omega;\omega_1,\omega_2,\omega_3) = \frac{\epsilon_0^3 m\upsilon^3}{2\pi q^4}b_{ijkl}\chi_{ii}^{(1)}(\omega)\chi_{jj}^{(1)}(\omega_1)\times\chi_{kk}^{(1)}(\omega_2)\chi_{ll}^{(1)}(\omega_3), \quad (8a)$$
$$\chi_{ijkl}^{(3):2\times2}(\omega;\omega_1,\omega_2,\omega_3) = \frac{\epsilon_0^4 m^2\upsilon^4}{3\pi q^6}\chi_{ii}^{(1)}(\omega)\chi_{jj}^{(1)}(\omega_1)\times\chi_{kk}^{(1)}(\omega_2)\chi_{ll}^{(1)}(\omega_3)\times\sum_{(jkl)}a_{ijh}a_{hkl}\chi_{L,hh}^{(1)}(\omega-\omega_j), \quad (8b)$$

where (jkl) represents cyclic permutations of the indices, and ω_j indicates the frequency related to the linear susceptibility component $\chi_{jj}^{(1)}$. Because the second term of Eq. (3) is described by $\chi^{(2)}$, the term associated with the nonlocal cascading is left out in $\chi^{(3)}$ though it contributes to effective third-order nonlinear susceptibility.

The third-order susceptibility $\chi^{(3)}$ consists of two parts, $\chi^{(3):3}$ and $\chi^{(3):2\times2}$, which represent the third-order direct and second-order local cascading processes, respectively. It should be noted that the second-order coupling coefficient a_{ijk} that is responsible for $\chi^{(2)}$ also contributes, in part, to $\chi^{(3)}$. The coefficient a_{ijk} contributes to $\chi^{(3)}$ even in a material with inversion symmetry, because the product $\mathsf{a}\cdot\mathsf{a}$ in Eq. (8b) follows the same symmetry rule for fourth-rank tensors as b. This implies that a material consisting of molecules with large first-order molecular hyperpolarizability β can have large $\chi^{(3)}$ even in a centrosymmetric structure, where $\chi^{(2)}$ vanishes, because a is proportional to β.

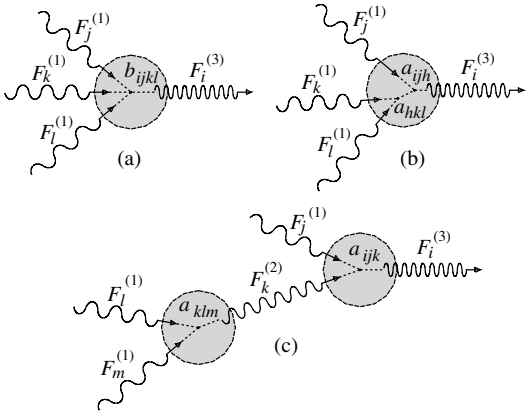

FIG. 1. Schematics of three different processes for third-order NLO effects: (a) a direct third-order coupling process, (b) a local cascading process, and (c) a nonlocal cascading process. Shaded circles, dotted lines, and junctions of the dotted lines indicate effective regions of nonlinear couplings, local electric polarization fields, and nonlinear couplings, respectively.

Bassani and Lucarini suggested that the contribution of $\chi^{(3):2\times2}$ to $\chi^{(3)}$ is much smaller than that of $\chi^{(3):3}$ because the former goes to zero much faster than the latter [12]. However, our estimation shows that the magnitude of the two contributions to $\chi^{(3)}$ may be comparable. Using the reported $\chi^{(2)}$ and $\chi^{(3)}$ values for $KNbO_3$ [17] and assuming $\mathsf{L}(\omega)$ to be of the order of 1, the magnitudes of the coefficients Ω^2, a, and b are calculated to be in the range of 2×10^{31}–4×10^{31} in units of s^{-2}, $Å^{-1}s^{-2}$, and $Å^{-2}s^{-2}$, respectively. Using the coefficients, $\chi^{(3):3}_{3333}$ and $\chi^{(3):2\times2}_{3333}$ are estimated to be $\sim13\times10^{-22}\ m^2/V^2$ and $\sim24\times10^{-22}\ m^2/V^2$, respectively, for third-harmonic generation at 2.1 μm. This indicates that the contribution of the second-order local cascading process $\chi^{(3):2\times2}$ could be more significant than that of the direct third-order process $\chi^{(3):3}$, which is contrary to the suggestion made previously [12]. It has long been speculated that a material with large $\chi^{(2)}$ may also have large $\chi^{(3)}$. The present study shows clearly how $\chi^{(2)}$ and $\chi^{(3)}$ are related through the second-order coupling a and resolves the issue.

The contribution of the local cascading, $\chi^{(3):2\times2}$ given by Eq. (8b), can be rewritten as

$$\chi^{(3):2\times2}_{ijkl}(\omega;\omega_1,\omega_2,\omega_3) = -\frac{2\epsilon_0^2 m v^2}{3\sqrt{2\pi}q^3}\sum_{(jkl)} a_{ijh}\chi^{(1)}_{ii}(\omega)\chi^{(1)}_{jj}(\omega_j) \times\frac{\chi^{(2)}_{hkl}(\omega-\omega_j)}{L_{hh}(\omega-\omega_j)}. \quad (8b')$$

Multiplying Eqs. (8a) and (8b′) by the electric field and taking an inverse Fourier transform, the corresponding polarization can be expressed with respect to time as

$$P_i^{(3):3}(t) = \epsilon_0\int_0^\infty d\tau\chi^{(1)}_{ii}(\tau) \times\left[\frac{m v^3 b_{ijkl}}{q^4}P_j^{(1)}(t-\tau)P_k^{(1)}(t-\tau)P_l^{(1)}(t-\tau)\right], \quad (9a)$$

$$P_i^{(3):2\times2}(t) = \epsilon_0\int_0^\infty d\tau\chi^{(1)}_{ii}(\tau) \times\left[-\frac{2m v^2 a_{ijk}}{q^3}P_j^{(1)}(t-\tau)P^{(2)}_{L,h}(t-\tau)\right]. \quad (9b)$$

It should be noted that the local second-order polarization $\mathbf{P}^{(2)}_L$ is included in $\mathbf{P}^{(3):2\times2}$, because it couples with another linear polarization through the local cascading process to establish a third-order polarization $\mathbf{P}^{(3)}$ before emitting a second-order field [Fig. 1(b)]. If the terms in square brackets in Eqs. (9a) and (9b) are defined as effective electric fields $\mathbf{E}^{(3):3}_{\rm eff}$ and $\mathbf{E}^{(3):2\times2}_{\rm eff}$, respectively, $\mathbf{P}^{(3):3}(t)$ and $\mathbf{P}^{(3):2\times2}(t)$ can be interpreted as linear responses to the effective electric fields. In addition, Eq. (9) informs us that the nonlinear couplings take place cumulatively while all the polarization components remain in existence. In view of the findings of quantum mechanics, it can be understood that a nonlinear coupling occurs at a certain time to convert superposed states of an induced dipole into a coupled state, and the coupling probability is proportional to the product of the relevant polarization components at that time.

With respect to time, $\chi^{(1)}(\tau)$ represents a linear relaxation property of a medium in a relevant frequency region. Supposing that a component of third-order polarization is established at a time $t-\tau$ from three polarization fields at a local site, which were induced at respective times τ_1, τ_2, and τ_3, the temporal buildup procedures of $\mathbf{P}^{(3):3}(t)$ for direct third-order process and $\mathbf{P}^{(3):2\times2}(t)$ for second-order local cascading process are depicted Fig. 2, where only the magnitudes of $\mathbf{P}^{(n)}$'s are shown and all the coefficients in Eq. (9) are normalized to unity for convenience. Since the nonlinear polarizations are regarded as a linear response to the effective fields $\mathbf{E}^{(3):3}_{\rm eff}$ and $\mathbf{E}^{(3):2\times2}_{\rm eff}$, their relaxation is also described by $\chi^{(1)}(\tau)$. If the characteristic relaxation time of $\chi^{(1)}(\tau)$ in the transparent optical frequency region is denoted by $\bar\tau$ ($\sim\gamma^{-1}$), the average response times for the third-order direct and second-order local cascading processes are estimated to be $2\bar\tau$ and $3\bar\tau$, respectively (Fig. 2). Figure 3 shows temporal responses of $\mathbf{P}^{(3):3}(t)$ and $\mathbf{P}^{(3):2\times2}(t)$ for applied electric fields of square pulses with various pulse widths $\tau_{\rm PW}$ of an order of $\bar\tau$, which were calculated with Eq. (9). As the pulse width of the applied electric field increases to $10\bar\tau$, both $\mathbf{P}^{(3):3}(t)$ and $\mathbf{P}^{(3):2\times2}(t)$ reach saturation, which, in turn, leads to the saturation of $\chi^{(3)}$. However, for a pulse width of shorter than $10\bar\tau$, it is clear that $\chi^{(3)}$ depends on the pulse width of a light source, for both $\mathbf{P}^{(3):3}(t)$ and $\mathbf{P}^{(3):2\times2}(t)$ depend on pulse width. When the pulse width is less than $2\bar\tau$, $\mathbf{P}^{(3):3}(t)$ reaches its peak much

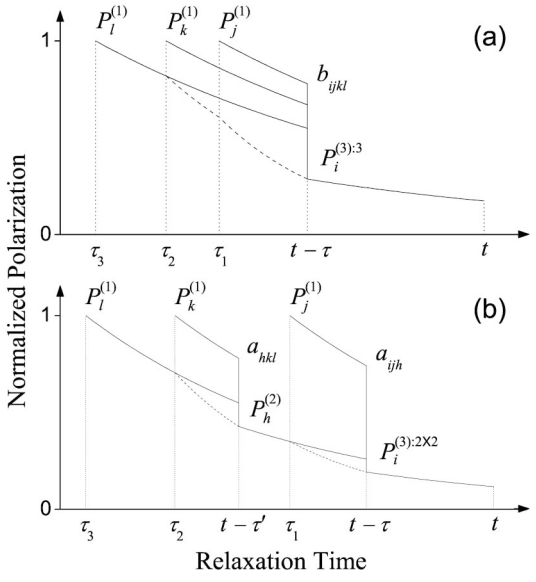

FIG. 2. Formation and relaxation of third-order nonlinear polarizations arising from (a) a direct coupling process and (b) a local cascading process. Solid and dashed curves indicate the linear relaxation described by $\chi^{(1)}(\tau)$ and the products of polarization components, respectively.

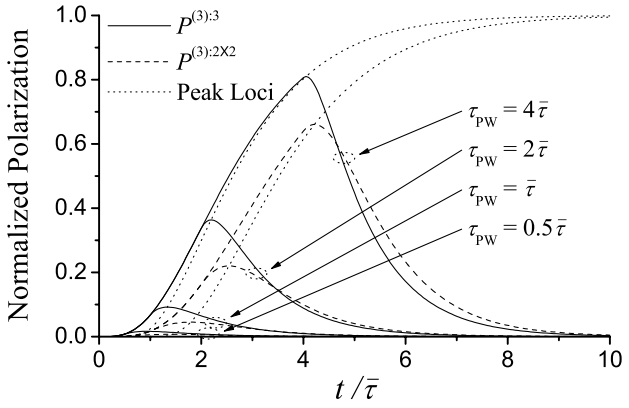

FIG. 3. Normalized third-order nonlinear polarizations for the applied electric fields of square pulses with various pulse widths τ_{PW}.

earlier than $\mathbf{P}^{(3):2\times2}(t)$, which reflects the faster response of the direct third-order process. We treat here only square pulses as a driving field. However, if a pulse shape other than square is employed, the overall shape of the temporal response curves may differ slightly, but the differentiation between the temporal responses of the direct and local cascading processes would exhibit similar features to that for square pulses. One can go further to examine the dependence of spectral profile if the dispersion of linear relaxation is taken into account, which is beyond the discussion of this work.

The pulse-width dependence applies to third-order nonlinear processes, due not only to electrons, but also to other types of nonlinear constituents, such as nuclei and ionic groups, all of which have different relaxation times. Therefore, one has to consider the pulse-width dependence of $\chi^{(3)}$, when $\chi^{(3)}$ is measured or used with pulses of shorter than $10\bar{\tau}$ of each nonlinear constituent. As noticed in Fig. 3, the peak positions of the two nonlinear polarizations $\mathbf{P}^{(3):3}(t)$ and $\mathbf{P}^{(3):2\times2}(t)$ are distinguishable at times of less than $5\bar{\tau}$. Hence, the amount of contribution of the direct third-order process and the second-order local cascading process to $\chi^{(3)}$ can be worked out separately, by measuring $\chi^{(3)}$ as a function of time. However, since polarizations due to electrons have a relaxation time of sub-fs, which corresponds to one period of a soft x-ray wave, it is impossible to differentiate between the two processes in the optical wavelength region. Meanwhile, the contribution of the two processes caused by nuclei, ionic groups, and molecules could be distinguished experimentally in the optical wavelength region, since the relaxation times of their polarizations are of an order of 100 fs or higher.

In summary, we have studied the temporal behavior of third-order nonlinear polarizations, using the Rayleigh-Schrödinger method of perturbation. Three distinct nonlinear processes lead to third-order NLO effects: a direct third-order process and a second-order local cascading process, both of which are responsible for $\chi^{(3)}$, and a second-order nonlocal cascading process, which is the $\chi^{(2)} \cdot \chi^{(2)}$ process. We have shown that both direct third-order polarizations and second-order local cascaded polarizations depend on pulse width, which leads to the conclusion that $\chi^{(3)}$ depends intrinsically on the pulse width of a light source even with a single nonlinear constituent, and, therefore, when $\chi^{(3)}$ is used as a material constant, pulse width should be specified. The direct third-order process and the second-order local cascading process may be differentiated experimentally using a pulse width of femtosecond.

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